CEEC-TAC3

BOOK OF ABSTRACTS

Editors:
Andrei Rotaru
Romana Cerc Korošec

3rd Central and Eastern European Conference on Thermal Analysis and Calorimetry
25-28 August 2015
Ljubljana, Slovenia

Book of abstracts of the 3rd Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC3)

3rd Central and Eastern European Conference on Thermal Analysis and Calorimetry:
25-28 August 2015
University of Ljubljana
Ljubljana
Slovenia

Editors:
Andrei Rotaru, Romana Cerc Korošec

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3rd Central and Eastern European Conference on Thermal Analysis and Calorimetry

CEEC-TAC3

25-28 August 2015 – Ljubljana, Slovenia

organized by the:
Central and Eastern European Committee for Thermal Analysis and Calorimetry (CEEC-TAC)

with the great support of the:
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&
University of Craiova (UC)
&
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Dear participants at CEEC-TAC3 Conference,

Let us express our great pleasure to welcome you here in Ljubljana; we thank very much to all 302 of you (this time from 41 countries on 5 continents) for joining us!

The first meeting of the Central and East European Conference on Thermal Analysis and Calorimetry took place at Craiova, Romania, in September 2011. Even though the original idea was to interconnect researchers working in the wide field of thermal analysis and calorimetry from the Central and Eastern European countries, even from the mere beginning the scientists all over the world contributed to this event. Following the latter, the second CEEC TAC conference was in Vilnius, Lithuania, two years ago. Again, Vilnius University hosted more than 300 participants from 35 different countries.

During the third CEEC-TAC conference in Ljubljana this year, 6 Plenary, 18 Invited and 3 Technical lecturers will bring attractive and detailed insights to various specific aspects in the field of thermal analysis and calorimetry. Beside the fundamental studies concerning the kinetic analysis and mechanisms of chemical reactions, which can be studied with different thermal techniques, thermal analysis is also an indispensable tool in the field of material and life sciences. With the aid of other measuring techniques it offers to compose a complex picture from separate puzzles, each representing one of these techniques. Therefore, the 84 oral presentations (divided in 4 sessions) give us a glimpse into the progress of the field itself, technical and measurement development, as well as new trans-disciplinary ideas. The poster sessions (3, of 85 works each) will also represent an adequate scientific forum, suitable for less formal discussions, which might in some cases bear even more fruition.

We would like to express our thanks to the people who contributed and supported the organization of this event, especially to the members of the Honorary Committee, Scientific Committee, International Organizing Committee, National Associations for Thermal Analysis and Calorimetry from the Central and Eastern European Countries, Executive Organizing Committee, University of Ljubljana, University of Craiova and INFLPR Bucharest. We are very grateful to the Faculty of Chemistry and Chemical Technology to provide a stimulating venue for the conference! We acknowledge the great support of our sponsors: TA INSTRUMENTS (Diamond Sponsor); METTLER TOLEDO and NETZSCH (Platinum Sponsors); SETARAM, LINSEIS and DSC CONSUMABLES (Gold Sponsors). A special acknowledgement has to be addressed to the *Journal of Thermal analysis and Calorimetry*, where one of its volumes is dedicated to the full research papers of our conference, presented as oral or poster contribution.

Ljubljana is the capital of Slovenia, a small country that lies in the heart of Europe, where the Alps meet the Mediterranean and the Pannonian Plain meets the Karst. It is a lively industrial, commercial, administrative, and cultural centre with a population of 300,000 people, of which 54,000 are students. Ljubljana has preserved evidence of all the five millennia of its history, including the remains of the Roman city of Emona and the old city centre with its medieval castle and beautiful buildings with Baroque façades and decorative portals. In the second half of the 20th century, it was the world famous architect Jože Plečnik that put a personal stamp on his native city, and the so called Plečnik's Ljubljana ranks among the 20th century's most prominent total works of art. Ljubljana's appearance was further shaped by Plečnik's pupils and a whole new wave of renowned young Slovenian architects. One year ago, the capital of Slovenia was awarded the coveted title of European Green Capital for 2016.

We hope that you will enjoy the city during your stay at the conference, and that you will leave Ljubljana with the same good feelings and memories as after attending our previous two conferences.

We expect that this conference will give you novel scientific and practical knowledge, and enrich you with a variety of new contacts.

Loking forward to seeing you in the very next future at forthcoming thermal analysis and calorimetry conferences, and hopefully in 2017 for CEEC-TAC4!

Romana Cerc Korošec and Andrei Rotaru
Co-chairs of CEEC-TAC3

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Sergey Vyazovkin (University of Alabama, USA)

Award Plenary Lecturess

Distinguished TA&C Researcher in Central & Eastern Europe
Henry Piekarski (University of Lodz, Poland)

Outstanding Young TA&C Researcher in Central & Eastern Europe
Jiri Kucerik (University Koblenz-Landau, Germany)

Invited lectures

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General Information

The 3rd Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC3) has gathered **302 registered participants** from **41 countries** and of **5 continents**, presenting a total number of **366 scientific works**. Of those, 4 are Plenary Lectures (**PL**), 2 Award Plenary Lectures (**APL**), 18 Invited Lectures (**IL**), 3 Technical Lectures (**TL**), 4 Parallel Sessions of Oral Presentations – 84 contributions (**OP**) & 3 Sessions of Poster Presentation - 255 contributions (**PS**). Each session of oral presentations comprises of 21 works, while each session of poster presentations includes 85 works.

An important task of CEEC-TAC is the initiation of 2 distinctive directions that our conference shall follow in the future, with 2 Workshops (**WS**) introducing the subjects.

For all these contributions, the University of Ljubljana has offered a number of 4 lecturing rooms and its inner and outer spaces.

Tuesday, 25th of August		Wednesday, 26th of August					Thursday, 27th of August			Friday, 28th of August				
9:00-17:00	Short Summer School on TA&C *Sponsored by TA Instruments*	9:00-9:30	IL01		IL02		9:00-9:30	IL09	IL10	9:00-9:30	IL13		IL14	
		9:30-10:00	IL03		IL04		9:30-10:00	IL11	IL12	9:30-10:00	IL15		IL16	
		10:00-10:20	OP1.01	OP2.01	OP3.01	OP4.01	10:00-11:00	Poster session 1		10:00-10:20	OP1.12	OP2.12	OP3.12	OP4.12
		10:20-10:40	OP1.02	OP2.02	OP3.02	OP4.02				10:20-10:40	OP1.13	OP2.13	OP3.13	OP4.13
		10:40-11:00	OP1.03	OP2.03	OP3.03	OP4.03				10:40-11:00	OP1.14	OP2.14	OP3.14	OP4.14
		11:00-11:20	Coffee break *Sponsored by TA Instruments*				11:00-11:20	Coffee break *Sponsored by TA Instruments*		11:00-11:20	Coffee break *Sponsored by TA Instruments*			
		11:20-11:30	CEEC-TAC3 Info				11:20-11:30	ESTAC12 Info		11:20-11:30	CEEC-TAC4 Info			
		11:30-12:30	Konstantin Gavrichev PL2 *Sponsored by TA Instruments*				11:30-12:30	Christoph Schick PL3 *Sponsored by Mettler-Toledo*		11:30-12:30	Sergey Vyazovkin PL4 *Sponsored by Netzsch*			
14:30-17:30	Registration of participants at CEEC-TAC3 (FKKT)	12:30-14:00	Lunch *Sponsored by TA Instruments*				12:30-14:00	Lunch *Sponsored by Mettler-Toledo*		12:30-14:00	Lunch *Sponsored by Netzsch*			
		14:00-15:00	Henryk Piekarski APL1 *Sponsored by TA Instruments*				14:00-15:00	Poster session 2		14:00-14:50	WS1 WS2 *Sponsored by Netzsch*			
		15:00-15:30	TL1: TA Instruments				15:00-15:20	TL2: Mettler-Toledo		14:50-15:10	TL3: Netzsch			
		15:30-16:00	IL05		IL06		15:20-16:20	Jiri Kucerik APL2 *Sponsored by Mettler-Toledo*		15:10-15:40	IL17		IL18	
		16:00-16:30	IL07		IL08					15:40-16:00	OP1.15	OP2.15	OP3.15	OP4.15
		16:30-16:50	Coffee break *Sponsored by TA Instruments*							16:00-16:20	OP1.16	OP2.16	OP3.16	OP4.16
		16:50-17:10	OP1.04	OP2.04	OP3.04	OP4.04	16:20-17:20	Poster session 3		16:20-16:40	OP1.17	OP2.17	OP3.17	OP4.17
		17:10-17:30	OP1.05	OP2.05	OP3.05	OP4.05				16:40-17:00	OP1.18	OP2.18	OP3.18	OP4.18
18:00-19:00	Opening Ceremony	17:30-17:50	OP1.06	OP2.06	OP3.06	OP4.06				17:00-17:20	OP1.19	OP2.19	OP3.19	OP4.19
		17:50-18:10	OP1.07	OP2.07	OP3.07	OP4.07	17:20-18:30	Afternoon break		17:20-17:40	OP1.20	OP2.20	OP3.20	OP4.20
		18:10-18:30	OP1.08	OP2.08	OP3.08	OP4.08				17:40-18:00	OP1.21	OP2.21	OP3.21	OP4.21
19:00-20:00	Jaroslav Sestak PL1 (CEEC-TAC Honour) *Sponsored by CEEC-TAC*	18:30-18:50	OP1.09	OP2.09	OP3.09	OP4.09	18:30	Busses leave for the Conference dinner		18:00	Closing Ceremony & Farwell			
		18:50-19:10	OP1.10	OP2.10	OP3.10	OP4.10								
		19:10-19:30	OP1.11	OP2.11	OP3.11	OP4.11								
20:00-22:00	Welcome Cocktail	19:30	CEEC-TAC Assembly				20:30-24:00	Conference Dinner						

FKKT Room A (ground floor)
FKKT Room B (1st floor)
FKKT Room P1 (1st floor)
FKKT Room P2 (1st floor)
FKKT Room P22 (1st floor)
City Center (18:30), FKKT Parking (18:45), Hotel Sheraton (19:00)
FKKT Poster and Coffee break area
Welcome Cocktail and Lunch FKKT Restaurant
Conference Dinner Panorama Restaurant in Bled

FKKT Faculty of Chemistry and Chemical Technology (New Building), Vecna pot 113, Ljubljana, Slovenia

Program of CEEC-TAC3

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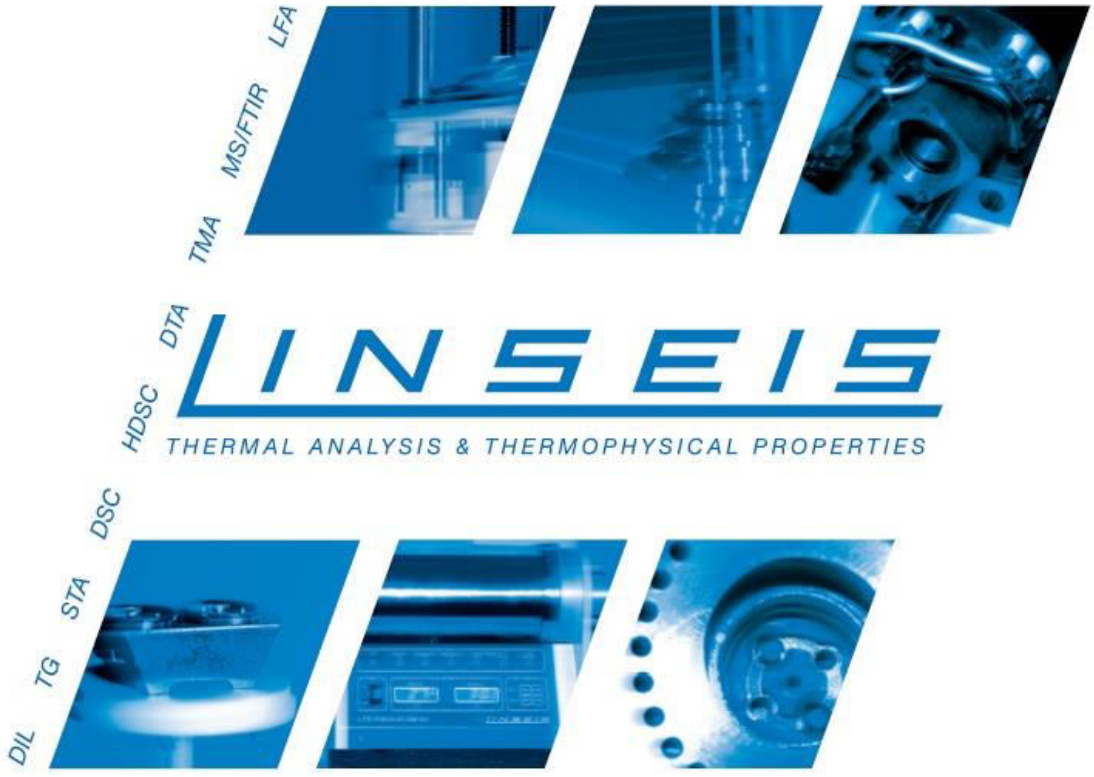

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Plenary Lectures

Idiosyncrasy of nano-structured systems: Thermodynamic (*top-down*) and quantum (*bottom-up*) prospects

Jaroslav ŠESTAK
New Technology - Research Center in the Westbohemian Region, West Bohemian University,
Universitní 8, CZ-30114 Pilsen; Czech Republic,
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The issue is a continuation of the GEFTA 2010 and CEEC-TAC 2011 lectures now directed to the new-fangled degree of freedom – *dimension,* instead the habit of paired h*eat-temperature*. Involved nanostructured systems have a rich history beginning with a colloidal solution (heterogeneous mixture) where a particle size of substances is intermediate between a true solution and a suspension, i.e., between 1-1000 nm (even smoke from a fire is a good example). Imperative status has a colloidal gold as a suspension (or colloid) of submicron sized particles of gold in a fluid (water) or glass providing an intense red color (for particles <100 nm) or blue purple (for larger particles). J. Herschel invented in 1842 a photographic process called chrysotype that used colloidal gold to record images on paper. Some properties of inherent nanoparticles were investigated using the term micro-clusters (which term was used for the first time in 1661 by English chemist R. Boyle) and associated with Alchemist process of multiplied division. Modern description came with the paper introducing the term 'microcluster' as a new phase of matter and book showing that they cannot be formed fully accidentally but the atoms are combined according some 'magic numbers' (e.g. Fibonacci following the calcium clusters series 561, 923, 1415, 2057, etc). The particle is in order of size ($\sqrt[3]{N}\, d$) where N is the number of atoms and d is their diameter showing that for d~2-3 A is N~2-10 nm. There exists a model metal clusters information describing systems up to 80 atoms. The number of atoms of a nanoparticle can be derived from the Loschmidt number giving 2.6×10^{19} atoms in a cubic cm of a substance so that about 10^4 atoms are contained in nanoparticle cube with a side of 100 nm. It associates with a notion of the so-cooled Planck's mass that amounts 2.17×10^{5}g of which specifies the boundary of the quantum world.

In a crystallographic view spheres of a given radius or regular tetrahedral with a given edge can be assumed as the most closely packed in space, i.e., crowded so that the ratio between the filled part of the space and the unfilled part would be as large as possible. Using polyhedra the whole space could be filled by appropriate packing of the congruent specimens of these polyhedra starting e.g. from a cube, adge, a, (surface/volume: $A/V \cong 6/a$), terehedron, via penta-, hexa-, hepta-, nona-, deca-, dodeca-, icosa-, triaconta-, hexaconta-, enneaconta-, up to an infinite faceted ultimate sphere of radius, r, ($A/V \cong 2/r$). Abatement of the restrictions of a regular symmetry in nanoworld leads to the appearance of icosahedral packing with unusual pentagonal symmetry (i.e. quasiparticles) Another important process of covering a space with polyhedra is the so called stellation, following the historical Kepler constructions (year 1611) of the first two other stellar polyhedron from dodecahedron. This multiplication process of self-repetition yields the specificity of a self-similar system which shows statistically the same properties at many scales and which is well known as sourced on the Koch curves (i.e. snowflakes), further defining the **self-similarity dimension** in the sphere of fractals expressing thus the complexity of an object and giving the intermediary to chaos (supposing both ways from the top to bottom and vice versa). Similarly assumed clustering is close to the real pattern of a structure evolution from disorder (chaos), local ordering up to periodic structures sometimes including structural code or even inorganic gene and became close to the topic of chemistry beyond the molecule and special associated behavior in terms of superatoms exhibiting the quantum properties of nanoclusters (i.e. *quantum nature* of nanostes).

Nanoworld *thermodynamic* groundwork unfolds from a single phase division into α and β separated by interface the curvature of which request the higher pressure on the concave side with respect to the surrounding, p, i.e., $p_\alpha > p_\beta = p$ (Young-Laplace effect). It can happen by splitting up

(division, cleavage) or nucleation, as well as by elastic deformation (strain) of already existing surface due to the impact if isotropic or nonisotropis stress, $dw_{surf} = \gamma\, dA$, where the scalar parameter γ (defined as a specific surface energy) is always positive (due to the stability criteria) and is independent on the surface, A. Performed work, $dw_{surf} = f\, dA_{elast} = f\, A\, d\varepsilon$, causes elastic deformation (*strain* ε) of the original surface assuming $d\varepsilon = dA/A$. Unite specific surface work is called surface stress, f, and possesses generally tensor denomination but for isotropous environment become scalar following $w_{surf} = f\, A_{elast}$. As a result we can say that any nano-system possesses its size as an extra degree of freedom, equilibrium of which requires a modification of traditional macroscopic thermodynamics.

Everything factually originates from the Kelvin historical relation, $p/p_\infty = 2V\gamma/(RTr)$, and the related equation for temperatures, $T/T_\infty = 2V\gamma/(\Delta H\, r)$. In the other words it means that if we want to create any equilibrium modification for a variation of curvature upon the change of external conditions (T, p) we have to change either pressure (from $p_{\beta\infty}$ to $p_{\beta r}$ under constant T_∞) or temperature (from T_∞ to T_r under constant$_\infty$) so that the change in the difference of bulk chemical potentials $\Delta\mu$ is compensated by negative $2\gamma V_{\alpha m}(1/r)$. Certainly there exists further particularizing models such as liquid skin melting (LSM) assuming that melting starts on the particle surface creating thus a thing surface layer of the thickness δ (an adjustable parameter) so that $T/T_\infty = 1-(2V\gamma/(\Delta H(r-\delta))$ eventually including the shape dependability $T/T_\infty = 1-(A/V\Delta H)(\gamma_{sol} - \gamma_{liq})$ where for a sphere A/V equals 3/r. Another impact relates to the particle volume contraction ΔV due to the internal over-pressure which often results to the internal phase transition. Also the mixing enthalpy ΔH_{mix} (and Gibbs energy ΔG) depends on the particle size and the atomic distribution of which may vary from the flat to curved surface owing to the cause of curvature yielding thus a surface interface segregation. There are yet unsolved specifics of melting due to the characteristic of the interface, such as coherent (with a small elastic deformation due to the small differences of atomic arrangements) and incoherent (with a large elastic deformation due to the significant differences in atomic arrangements). On the temperature dependence of melting for nanoparticles of indium in the matrix of alumina prepared through different techniques it was experimentally observed opposite temperature behavior of particles obtained by extreme melt-fast-quenching (firmly built-in the matrices thus having little volume flexibility) and those loosely integrated particle (produced by intensive ball milling having thus more space within the matrices) exhibiting classically assumed decrease of melting temperature upon the diminishing particle diameter (d). Correspondingly, it is necessary to consider the effect of the particle-matrix interaction in the case of polymeric nano-composites wherein nano-objects (often nano-fibres) are continuously surrounded by rigid solid phase often as a core-shell structure, the interior being covered with a thin surface layer of another material (filament surface chemically ached, oxidized, etc). It associates similar effect as rapidly changed temperature when observing real shapes *kinetic phase diagrams* (temperature shifts) providing a new space for novel thermophysical studies including impact of eccentricity of heat transfer, heat capacities or phase relations in nano-dimensional space.

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Phase transitions in $LnAO_4$ (A=P, V, Nb) and its influence on thermodynamic properties

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Inorganic compounds with the common formula $LnAO_4$ (A=P, V, Nb) is very stable in a weak acids and insoluble in the water and have a high melting point. They are widely used in practice as the thermal barrier materials, components of active media of solid lasers, luminescent materials and in many other applications. Very important also the application RE orthophosphates for the selective trapping of actinide element compounds from the mixture of nuclear waste composition. $LnAO_4$ compounds can be used in the wide temperature range and from this point of view information about phase transitions is very important not only for understanding of operating range of materials and for the influence of phase transition on thermodynamic properties also.

The review of available literature and obtained in IGIC results of calorimetric studies of $LnAO_4$ compounds will be given will be reported.

The main features of thermodynamic properties of lanthanides compounds are due to properties of REE elements. Among them are the magnetic phase transition from antiferromagnetic to paramagnetic state and Jahn-Teller structural transition which proceeds at a very low temperatures. Significant effect on the thermodynamic properties (especially on the entropy) of these compounds has also the Schottky anomaly inherent in all lanthanides except for lanthanum, gadolinium and lutetium.

Structural phase transition observed in $LnPO_4$ at high temperatures may lead to significant changes in the volume of the crystal and even to his destruction. From this point of view, the information on its parameters is very important. On the example of terbium orthophosphate the possibility of thermodynamic evaluation of stability ranges for tetragonal and monoclinic modifications will be presented.

Special features of calorimetric study of a second order structural phase transition in orthoniobates of lanthanides will be considered.

DSC study of thermal behavior of crystal hydrates of “light” lanthanide orthophosphates revealed not only the processes of dehydration but also the exothermic effect connected with the structural phase transition, which temperature depends on the size of crystal particles.

Fast scanning chip calorimetry – a modern calorimetric method for investigation of phase transitions

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Many materials are created or used far from thermodynamic equilibrium. Knowledge about the phase transitions on fast cooling is therefore required. Calorimetry is a powerful tool in this respect and it takes a special place among other methods. In addition to its simplicity and universality, the energy characteristics (heat capacity Cp and its integral over temperature -enthalpy H), measured via calorimetry, have a clear physical meaning even though sometimes interpretation may be difficult. Fast scanning calorimetry, especially on cooling, allows for the in situ investigation of structure formation, which is of particular interest in a wide range of materials like polymers, metals, and pharmaceuticals to name a few. Free standing silicon nitride membranes are commonly used as low addenda heat capacity fast scanning calorimetric sensors. The gauges consist of a film-thermopile and a film-heater which are both located in the central part of the membrane. At non adiabatic conditions controlled fast cooling up to 10^6 K/s is possible as well as fast heating at the same high rates [1, 2].

In addition to fast linear scanning the calorimeters allow also high frequency AC calorimetric investigations of the glass transition [3, 4].

The calorimeters were used in combination with conventional DSCs, including Calvet type DSCs, to study solidification of polymers on cooling, isothermal crystallization after fast quenches, and the frequency dependence of the glass transition in a wide frequency range. As an example, crystallization of PCL and nucleated PCL and PCL based nanocomposites were investigated with ms time resolution. [5-7]

The calorimeter was also used for studying thermal melting of beta sheeted silk proteins, which was possible only by depression of degradation using heating rates higher than 1000 K/s. [8]

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Isoconversional kinetics: Old misconceptions and new advances

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Over the past decade isoconversional (or model-free) methods have become the major tool in studying the kinetics of thermally stimulated processes [1]. Despite its wide and frequent use, the isoconversional kinetics has been associated recurrently with some misconceptions. Examples include alleged inability of estimating the preexponential factors and reaction models and supposed absence of a physical meaning of variable activation energy. The talk discusses some of the common misconceptions and links them to superficial understanding of isoconversional kinetics. The talk further focuses on the newest applications of isoconversional kinetics in the area of phase transitions. It discusses the meaning of variable and negative activation energies found for a variety of the phase transitions whose kinetics is driven by processes of nucleation. The examples discussed involve crystallization of polymer melts, gelation of polymer solutions, solid-solid phase transitions, polymer melting.

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Award Plenary Lecture1

Distinguished TA&C Researcher in Central and Eastern Europe

How does calorimetry help to see invisible?

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Calorimetry has been the most important experimental techniques used in our laboratory for many years. The calorimetric studies have been focused on measurements of dissolution and mixing effects in electrolytes and non-electrolytes solutions in water, non-aqueous and mixed solvents. In recent time a special attention has been devoted to the heterogenic mixtures and the systems that mimic natural biological ones. The observed behavior and properties of the examined solutions are connected with characteristic changes of thermodynamic functions. When appropriate model is applied for analysis of these data it is possible to obtain wide information about the phenomena that occur in the solution and to perceive in this way the hidden world of molecular structure and interactions.

The presentation contains information about the thermochemical properties of some three component liquid systems containing an electrolyte and binary solvent. Then some examples of application of different methods and models for analysis of results of calorimetric studies carried out in our laboratory are given. In particular the model of enthalpic interaction coefficients as well as the Covington's model of preferential solvation are presented and discussed. On the base of the results of calorimetric investigations of electrolyte solutions in the mixtures of water, methanol, *N,N*-dimethylformamide and acetonitrile with numerous organic cosolvents it is shown how and to what extent the properties of the systems examined are modified by the cosolvent added and how much the properties of the cosolvent are revealed in the mixtures with the solvents mentioned above.

Another part of the lecture is devoted to application of the differential scanning calorimetry for examination of heat capacities of aqueous solutions of surfactants and solvosurfactants and some methods of analysis of the obtained data are presented. It is shown how changes in the specific, apparent and partial molar heat capacities enables determination of the boundary between the region, within which the molecules of amphiphile occur in the form of monomers, and the area, in which the first large aggregates or micelles appear. The examination of the temperature dependence of differential heat flow makes it possible to determine the temperature of phase transition and the boundary between mono- and diphase systems. Finally, the two-point scaling model worked out in our laboratory that appeared to be very useful for the description of partial molar heat capacity function for micellar and microheterogenic systems is discussed. It confirmed the existence an interval of molalities around the critical molality where a variety of structural forms could occur and, moreover, it seems to give possibility to predict the shape of micelles formed.

Award Plenary Lecture 2

Outstanding Young TA&C Researcher in Central and Eastern Europe

Soil-water conundrum and thermal analysis

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Methods of thermal analysis have frequently been used in soil science [1, 2]. Although, their applications have brought some interesting results, the findings were not always original and convincing, because the whole potential of thermal analysis has not been completely exploited. In this contribution we would like to summarize the results, which demonstrate that one of the key parameters in soil analysis is (often ignored) equilibrated soil moisture.

In the first part, we focus on the application of differential scanning calorimetry (DSC), which revealed that moisture condensed in soils forms small clusters (nanodroplets) bridging the soil organic matter segments [3]. Their size and dynamics depend on the spatial distribution of polar groups [4] or presence of cations [5]. The formation of nanodroplets is connected with physicochemical aging of soil organic matter [6]. Our results indicate that in organic soils, equilibrated for two weeks, nanodroplets can represent around 60% of total water content.

Equilibrium water content and non-disturbed water nanodroplets appeared a crucial factor in soil analysis using thermogravimetry. It was shown that soil moisture content and evaporation dynamics are linked to soil microorganisms activity and thereby to the soil microbiological stability [7]. This connection enables prediction of amount of carbon dioxide released by some soils during several weeks [8]. Furthermore, mutual correlation between mass losses revealed a connection between soil moisture, content of soil carbon and clay minerals. This connection enables the modelling of total soil organic carbon irrespective the carbon protection mechanism as well as rapid soil assessment.

In the third part we will present evolved gas analysis results that can help to understand the mechanistic reason of obtained correlations [9]. It will be shown that water evaporation probably triggers the process of soil organic matter degradation, in particular of N-containing organic molecules.

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Invited Lectures

Thermal (kinetic) stability of inclusion compounds, based on porous metal–organic frameworks. Dependence on the guest and framework properties

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Metal–organic coordination polymer frameworks (MOFs) are crystalline compounds consisting of metal ions coordinated by bridging organic ligands, which form three-dimensional structures. MOFs provide flexibility in choosing various combinations of linkers and metal, have different pore size, shape, structure, and functionality. MOFs have received intense attention for their potential applications in catalysis, gas storage, molecular recognition, high-capacity adsorbents, nonlinear optics, magnetics and bio-medical imaging.

The standard process of the MOF production begins from the synthesis of the inclusion compound; the molecules of the used organic solvent are trapped in the channels and cages of the metal–organic polymer structure. These primary included guest molecules are excluded further by the evacuation and/or by the heating; this process is called the framework activation. The thermal stability of the primary inclusion compounds (i.e. the ease of the guest molecules removal) can be connected both with the structure of the empty frameworks, and with the guest molecules size. So we investigated the correlation between the thermal (kinetic) stability of the inclusion compounds and the properties of framework and guest molecules.

Studied compounds: $[Mn(HCOO)_2]\cdot 0.33$(tetrahydrofuran), $[Mn(HCOO)_2]\cdot 0.33$(dioxane); $[Li_2(H_2btc)]\cdot$(dioxane) (H_4btc = 1,2,4,5–benzenetetracarboxylic acid);
$[Zn_4(dmf)(ur)_2(ndc)_4]\cdot 6$(benzene), $[Zn_4(dmf)(ur)_2(ndc)_4]\cdot 5$(toluene) (dmf =dimethylformamide; ur = hexamethylentetramin, ndc^{2-} = 2,6–naphtalenedicarboxylate);
$[Li(H_2tatab)]\cdot 0.6$(benzene), $[Li(H_2tatab)]\cdot 0.6$(toluene) ($H_3tatab = C_{24}H_{17}N_6O_6$);
$[Zn_2(bdc)_2(dabco)]\cdot 3.5$(benzene), $[Zn_2(bdc)_2(dabco)]\cdot 3.5$(toluene) ($bdc^{2-}$ = terephthalate anion, dabco = 1,4–diazabicyclo[2.2.2]octane).

The thermogravimetric data were processed with the computer program Netzsch Thermokinetics 2.

The difference in the kinetic stability in the compared inclusion compounds is connected both with the geometry of pores (size of the cages, channels and interconnecting windows), and with a degree of the frameworks flexibility. The high flexibility of the framework structure can result from the long, manifold and multi–dentate ligands (e.g. H_2tatab^-). The easiness of the guest removal (through rather narrow channels, caves and windows) is connected with guest molecules kinetic diameters and can depend on a possible molecular conformation (of 1,4–dioxane and cyclohexane) under heating.

In the kinetic stability it exhibits in the different reaction zones (different topochemical equations), in activation energy (E) and pre–exponential factor (A) values. The entropy factor (A) is very significant.

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Physico-chemical strategies for molecular imaging in biomedicine

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Valuable applications of molecular imaging involve the non-invasive and quantitative detection of biomolecules in vivo by means of target-specific probing of biological and cellular diseases and other associated processes, like real-time assessment of drug-therapy. Thus, molecular imaging is believed to play a pivotal role in the personalized treatments and patient stratification. A good quality of the images obtained by contrast media (CM) largely depends on the concentration and efficiency of the molecular species that, for example, can be achieved in the bloodstream. Therefore, an intensive physico-chemical investigation is necessary behind the single formulation, no matter whether the technique used is magnetic.

As a first example, the relevant properties of the class of Iodinated-CM such as Iomeprol and Iopamidol, will be illustrated. The high percentage of iodine atoms per molecule (close to 50% in weight) make Iomeprol and Iopamidol very efficient as contrast media. Furthermore, their solutions display low-osmolarity and low-viscosity up to high concentrations in water. In order to investigate the reasons of such properties, a physico-chemical characterization of their solutions was carried out using NMR, calorimetry, and molecular dynamic simulations revealing the presence of soluble aggregates whose size depends on concentration. While several conformational polymorphs have been identified in the solid state, solution properties are dominated by irregular clustering of inter-converting conformers, responsible for the observed low osmolarity; this makes them suitable for being injected in high doses while sensibly reducing disadvantages such as pain in arteriography, dilatation of blood vessels with a pressure fall and viscosity changes of the blood.

Another example is provided by particular use of sugars in the interpretation of the role of glassy and glassy-nanocristalline material properties for molecular imaging (sensitivity enhancement by dynamic nuclear polarization, DNP). The general system investigated is a mixture of molecules to be hyperpolarized, radicals, and a glass former. It is believed that a glassy state is necessary in order to have a large polarization and that the radical must be homogeneously dispersed in the amorphous matrix. The aim of the research has been to investigate how the changes in the matrix structure affect the magnetic transport properties (DNP) of imaging agents used in Nuclear Magnetic Resonance. In particular, the effect of nanostructure heterogeneities of the glass matrix (in terms of size and fraction of crystals) on the hyperpolarization efficiency and NMR signals have been studied.

Energetic homogeneity of thermally stabilized metal and oxide surfaces, new oscillation theory of catalysis (OTCAT), and universalization of catalytic mechanisms

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It is proved that thermally stabilized crystalline metals and oxides are homogeneous relative to the chemisorption and catalytic activity of their surface centres [1–3], and the sources of erroneous notions on surface heterogeneity are revealed and specified [2, 4]. Surface homogeneity is a fundamental feature of thermally stabilized crystalline bodies. This conclusion follows from chemisorption heats measured in the period of several decades by about 40 author groups for about 20 gas/metal-oxide and 45 gas/metal systems at films, powders, and supported substrates and is confirmed by a number of works performed by other techniques, a number of systems being studied in several works.

Then, three principal discoveries that were made in the latter half of the 20th century in the field of heterogeneous catalysis and chemisorptions, among which (1) surfaces homogeneity; (2) island nature of chemisorptions [5–7]; (3) vast excess, at any fixed ambient conditions, of the frequency of acts of chemisorption at free surface centers over the frequency of the catalytic acts at the same quantity of such surface centers [8], were generalized, the new phenomenological oscillation theory of catalysis (OTCAT) was formulated [9, 10] and the new method of deduction of kinetic equations of catalytic processes was proposed [10] on its basis.

This method was successfully used [9–12] to deduce kinetic equations for 7 randomly chosen industrial catalytic reactions which proceed at more than ten metal and oxide catalysts.

Catalyst is a solid capable of forming at its surface an island chemadphase or a set of island chemadphases that are under equilibrium with the source substances and products; the rate of a reaction is determined by the rate of its rate-determining step. Thus, production of any substance is, in essence, one-step process; other surface reactions are rapid and equilibrium.

All this material will be generalized in the lecture.

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Global thermodynamic analysis of biomolecular folding and binding based on DSC and ITC data

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Folding/unfolding and binding/dissociation of biological macromolecules in solutions can be characterized thermodynamically, yielding information on the stability of various conformations and on the interactions that hold them together. The relevant thermodynamic parameters are usually obtained by employing spectroscopic and/or calorimetric techniques and fitting an appropriate model to the experimental data. We will present here the global approach of simultaneously fitting the model to all available data obtained from different, predominantly DSC and ITC experiments [1-7]. Specific examples of DNA and protein unfolding and ligand binding to them will be shown to demonstrate that the global fitting is essential for the appropriate selection and critical evaluation of the proposed model mechanism, for predicting the behavior of the system at various conditions and for determination of the corresponding driving forces.

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Thermal stability of 1D oxide nanostructures

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The discovery of the carbon nanotubes (CNT) in 1991 have stimulated numerous theoretical and experimental studies aimed to searching for and preparing analogues of such materials based on inorganic compounds. Since than many nanotubes and related quasi-one-dimensional nanostructures of inorganic compounds were synthesized: layered d-metal dichalcogenides (MX_2, where M = Mo, W; Ta; X= S, Se), other type of chalcogenides as InS, ZnS, Bi_2S_3, TiS_2, $TiSe_2$, CdS, CdSe, Ag_2S, boron nitride (BN), boron carbide (BC_x) and boron carbonitride ($B_xC_yN_z$), semiconducting materials, such as SiGe, InGe/GaAs, InGaAs/GaAs, SiGe/Si and InGeAs/GaAs, nanotubes of metals as: Co, Sb, Se, Bi, or p-, d-, f-metal (Al, Si**,** Ge, Ti, ZnO, Nb, Ta, Zr, V, Mo, Dy, Tb) oxide nanotubes.

The presentation is dedicated to state of art of synthesis, structure, morphology and thermal properties of oxides nanotubes/nanobars. Among the potential application of multifunctional nanomaterials with one-dimensional structure, domain as biochemistry (bioseparation, biointeraction), catalysis, nanotechnology (optical sensors), were previously mentioned. For applications as catalyst or sensors the thermal properties of the 1D oxide nanostructures are of great interest.

Own experimental results concerning synthesis of SiO_2 [1] and titanate nanotubes [2] and ZnO [3] based nanotubes/ nanobars by wet chemical methods will be presented and their thermal stability will be discussed. The SiO_2 tubes were prepared by sol-gel method in the presence of templating agent while titanate and ZnO based nanobars/nanotubes were synthesized by hydrothermal methods. Microwave assisted hydrothermal method was also approached in the case of titanate nanotubes. The obtained results have established that the thermal stability of the resulted oxide nanostructures strongly depend on type of precursors used and on the method of preparation.

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Thermodynamics and kinetics of chemical processes involving solids

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Thermodynamics is a phenomenological theory most generally describing states of the system in which the system can remain unchanged for infinite time or change in finite time. Thermodynamics of reversible processes describes states of the system through quantities named state functions which depend among others on state parameters. Transformation of the system from one state to another usually brings about changes of primary state functions, i.e. energy (enthalpy) and entropy, reflecting natural tendencies towards organization and dissipation of matter and energy, respectively. The state functions, which combine both of the above mentioned quantities, namely free energy or Gibbs free energy, determine whether the system is in an equilibrium state or is it able to undergo spontaneous or forced transformations. Thermodynamics of irreversible processes is based on the phenomenon of creation of entropy in such processes. It describes pathways of transformation of a system from one state to another in category of thermodynamic forces and fluxes. The quantity named entropy source, defined as a sum of products of thermodynamic forces and conjugated with them thermodynamic fluxes, determines conditions for non-stationary and stationary states in which chemical or physical processes occur. On the other hand, relations between thermodynamic fluxes and forces enable global description of system changes investigated in time. Chemical kinetics is a fragment of this global description, which concerns chemical processes.

The presentation will touch on fundamental issues of thermodynamics and kinetics of processes involving solids. Also, it will outline the possibilities of use of experimental and computational methods in determining values of thermodynamic and kinetic characteristics for chemical processes. The problems mentioned above will be illustrated by results of earlier and recent (also not yet published) author's [1,3] studies and investigations by other researchers [2,4]. Thermal decomposition of calcium oxalate monohydrate and the products of its dissociation – anhydrous calcium oxalate and calcium carbonate [2-4] will be discussed as well. The presentation will also comprise issues connected with thermal decomposition of hydrochlorides of amines and organic nitrogen bases [1]. These compounds were selected because they can be considered as model ones for investigation of thermodynamics and kinetics of the thermal decomposition of systems involving solids.

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Experimental investigation and thermodynamic calculations of some gallium-based ternary systems

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The results of experimental investigation and thermodynamic calculations of some gallium-based ternary alloys (Ga-Bi-Sn, Ga-Au-Sb, Ga-Sn-Zn, Ga-In-Sb, Ga-Sb-Sn, Ga-Bi-Ni, Ga-Ag-Zn, etc.) are presented in this paper.

Selected alloys in mentioned systems were experimentally examined using thermal analysis (DTA, DSC), microscopy (LOM, SEM-EDX) and calorimetric investigations (Oelsen calorimetry), while calculation of thermodynamic properties was done applying different predicting models (Toop, Muggianu, general solution model).

Experimentally obtained results were compared with the results of thermodynamic calculation of phase equilibria based on calculation of phase diagram (CALPHAD) method and literature data.

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Thermal behaviour of tungstates, tungsten oxides and tungsten bronzes

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In this lecture, it is shown through various examples how useful thermal analysis has been for studying the formation, structure and applications of tungstates, tungsten oxides and tungsten bronzes. These are all basic materials in tungsten metal production for lamp and hardmetal industry and they are also widely used in gas sensors, chromogenic (electro, photo-, thermo- and gasochromic) devices and catalysts. Particularly hexagonal (h-) WO_3 and hexagonal ammonium tungsten bronze, $(NH_4)_xWO_3$ have come into the focus of our interest, because they have several unique features. While h-WO_3 has an open-tunnel structure, $(NH_4)_xWO_3$ has ion exchange property and mixed (e^- and p^+) conductivity.

We studied the formation of $(NH_4)_xWO_3$, where (as in tungsten production) a complex tungstate salt, i.e. ammonium paratungstate, is decomposed thermally. Several thermal events were explored and explained by the parallel use of TG/DTA-MS and TG-FTIR (as well as by XRD, FTIR, Raman, UV-Vis, SEM-EDX, TEM-ED, XPS, NMR). Among others a model was set up on the formation of $(NH_4)_xWO_3$, and based on this, nanosize $(NH_4)_xWO_3$ was prepared in pure form.

Evolved gas analysis turned out to be a unique tool for characterizing the structure of $(NH_4)_xWO_3$. It was found that NH_3 – originating from the NH_4^+ content of $(NH_4)_xWO_3$ – was released thermally in three different steps. This was explained by that NH_4^+ ions could be situated at three different positions in $(NH_4)_xWO_3$. Up to now, detection of these different ion positions in tungsten bronzes has not been in the reach of other analytical methods. Evolved gas analysis was essential also, when the ion exchange reaction of $(NH_4)_xWO_3$ with K^+ ion was studied. Since the different NH_4^+ positions could be analyzed with this technique, it could be determined, where K^+ ions were built into the crystalline structure.

Thermal analysis was also a powerful tool, when the formation, structure and application of h-WO_3 were studied. As nanosize h-WO_3 was prepared by annealing $(NH_4)_xWO_3$, it was found that residual NH_4^+ ions were vital for stabilizing the structure of h-WO_3: when NH_4^+ ions were completely released, the structure collapsed and transformed into monoclinic (m-) WO_3. By adjusting the heating parameters of $(NH_4)_xWO_3$, the composition of h-WO_3 and m-WO_3 could be controlled in a wide range. Gas sensor and photocatalytic tests showed that composition had a major impact on the applications of h- and m-WO_3.

Finally, WO_3 nanofibers were obtained by electrospinning aqueous polyvinylpyrrolidone (PVP) and ammonium metatungstate (AMT). By thermal analysis, the optimal heating conditions were investigated for electrospun organic/inorganic composite fibers in order to get ceramic nanofibers in appropriate quality (crystal structure, composition, morphology) and to avoid their disintegration. On the WO_3 nanofibers 1.5 nm TiO_2 nanofilms were deposited by atomic layer deposition (ALD), and the WO_3/TiO_2 core/shell nanocomposite fibers were active photocatalysts using visible light.

Experimental investigation of the ternary Ge-Sb-X (X=Ag, In, Bi) systems

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The Ge-Sb–based systems have attracted considerable attention over the last few decades [1-4] due to their potential application as a new type of memory that is based on crystalline-to-amorphous state phase transition, i.e., phase-change material (PCM). In order to be considered as a potential PCM, alloys should possess good thermal stability and fast crystallization ability and be devoid of segregation of phases after the record/erase cycle. Consequently, there are only a limited number of PCMs that have any practical applications [5]. Ge-based alloys have wide industrial applications and can be found in optical discs, DVDs, Blue-Ray discs, and flash memory devices [6] as well as in different optical and electronic devices, transistors, optical cables, semiconductors, integrated circuits, etc. [7-9].

The aim of this study is the experimental and computational investigation of phase transitions and microstructures of alloys in the ternary Ge-Sb-X (X= Ag, In, Bi) system. Selected alloys of the three ternary system were prepared and studied using a combination of different experimental techniques (DTA, SEM-EDS and XRD). Experimentally obtained results were compared with predicted phase equilibria.

Also on a large number of alloys from three investigated systems are additionally studied Vickers micro hardness test, Brinell hardness test and electrical conductivity.

The obtained results presented in this study should contribute to further development of this application area, especially considering that the literature data related to this systems are scarce or no exist.

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Full-Temperature Range Crystallization Rates of Polyamides by FSC as Key to Processing

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For industrial research, Fast Scanning Calorimetry (FSC) is an increasingly important tool because it is able to provide crucial information on crystallization and melting behavior under conditions where metastability and reorganization occur frequently. Especially determination of overall crystallization rates as function of temperature in the range from Tg to Tm provides useful information for starting up and optimization of processing, because a perfect match with cooling and heating ramps as in practice is possible. Examples of crystallinity development by way of isothermal crystallization at various temperatures for different times are given for a variety of polyamides – PA6; PA66; P410; PA46; ForTii – by applying a selected number of thermal histories. In addition, different grades of PA6 have been studied to determine the influence on crystallization behavior of added nucleants; of chain defects by copolymerization and of retardation by compounding. Two methodologies have been applied.

Firstly by direct crystallization during isothermal stays at various temperatures, and determining the development of crystallinity by exothermic peak integration. In his way assessment of the crystallizability is made quickly. Secondly by crystallization in the same way and subsequent heating and resulting integration of the peak(s). In this way sometimes even better results are obtained but at the cost of much more time. The whole experimental set up relies on a striking advantage of the Flash DSC, namely its capability to operate at such high scan rates that crystallization does not occur at very fast cooling neither during heating. Thus, the polyamides can be studied across the whole range from Tg to Tm by approaching an isothermal measuring temperature without crystallization. This has been done with two very different procedures: coming from the hot side meaning coming directly from the melt; or coming from the cold side by adding a preceding stay in the vitrified, glassy state. The last procedure give rise to increased nucleation which speeds up the overall crystallization. For all polyamides the reciprocal isothermal crystallization rates show a bell-shaped curve ranging from Tg to Tm, which is usually double peaked. In a number of cases, e.g. coming from the cold side; for low molar mass PA6; and for nucleated PA6 the double peaks vanish and one single-peaked bell-shaped curve results.

Kinetic Deconvolution of Thermoanalytical Curves of Solid-State Reactions

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Many technologically important solid-state processes, such as in materials synthesis, combustion of biomass, CO_2 capture by solid absorbent, degradation of energetic materials, consist of a number of chemical processes that occur consecutively and concurrently. Kinetic understanding of each component process is necessary for controlling the overall process to achieve the best performance of the reactions and solid products. Although thermoanalytical techniques are powerful tool of tracking the solid-state processes, the experimentally resolved data are the trace of the overall process. The rigorous solution for those complex reactions is not always possible because of various interactions of many heterogeneous processes [1]. In such situation, a kinetically meaningful deconvolution of those component processes is the key to the success of the empirical kinetic analysis.

When assuming the overlapping chemical processes that are independent each other, the overall rate behavior can be expressed by a cumulative equation [2,3]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \sum_{i=1}^{N} c_i A_i \exp\left(-\frac{E_{\mathrm{a},i}}{RT}\right) f_i(\alpha_i) \quad \text{with} \quad \sum_{i=1}^{N} c_i = 1 \quad \text{and} \quad \sum_{i=1}^{N} c_i \alpha_i = \alpha \,, \tag{1}$$

where N is the number of component processes. The parameters c_i, A_i, $E_{\mathrm{a},i}$, α_i, and $f_i(\alpha_i)$ are the contribution ratio to the overall reaction rate, Arrhenius preexponential factor, apparent activation energy, fractional reaction, and kinetic model function, respectively, of each process i. After determined the initial values for all of the kinetic parameters on the basis of any available kinetic information, an optimization is run to minimize residuals when fitting the calculated overall rate behavior to that resolved experimentally. As the result, the overall kinetic process is empirically separated into each component process with optimizing the kinetic parameters.

Because of the primary assumption of independency of the component processes, results of the empirical kinetic deconvolution have different meanings for each reaction. The practical usefulness of the empirical kinetic deconvolution is discussed by reviewing the applications to different types of partially overlapping solid-state processes [4-10].

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Temperature modulated X-ray scattering applied to a study on the heat capacity and the structure of semi-crystalline polymers

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Temperature modulation method is known well as a technique for calorimetry such as ac calorimetry (acc), temperature modulated differential scanning calorimetry (TM-DSC). However, application of the temperature modulation technique has not been limited to the calorimetry. Various types of experiments has been reported[1] such as measurement of thermal diffusion coefficient, kinetic study utilizing dependence on the modulation frequency, combination with other experiments, and so on. In the author's laboratory an instrument for simultaneous experiment of acc and X-ray scattering has been developed aiming to study time dependence of the structure and the heat capacity of semi-crystalline polymers during isothermal annealing just blow the melting temperature. The semi-crystalline polymers are thermodynamically metastable and their states are sensitive to the thermal history. Simultaneous measurement has an advantage to measure the structure and the heat capacity with exactly the same thermal history.

The sample cell for X-ray scattering equipped with the heater and the temperature sensor for acc was set in the BL40B2 beam line of SPring8 synchrotron radiation facility. Both the small angle X-ray scattering (SAXS) and the wide angle X-ray diffraction (WAXD) were measured. In this work polyethylene and poly(ethylene oxide) were investigated. The heat capacity decreased monotonically with time in agreement with the results from the TM-DSC. It is known well that structure of the semi-crystalline polymers changes irreversibly during isothermal annealing. In our experiment increase in the crystallinity and improvement in the crystalline order have been observed. These were the thermodynamic stabilization processes of the metastable materials and induced the heat capacity decrease.

However, the experimental results showed that the heat capacity decrease could not be attributed only to the irreversible change in the crystallinity and the crystalline order. The decrease in the heat capacity continued after the irreversible structure changes observed with X-ray experiments has almost finished. This implied that there was the excess heat capacity independent of the irreversible process. We investigated the origin of the excess heat capacity paying attention to the structure change synchronizing with the temperature modulation. X-ray measurement was made at the interval of 15s with exposure time of 1s, and the temperature modulation period was longer than 100s. Therefore the time resolving experiment could be carried out successfully. It was found that there were two types of the structure change synchronizing the temperature modulation. The author would like to show the usefulness of the temperature modulation technique in studies of material properties not only in the calorimetry but also in structure analysis and other properties.

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Thermal degradation and crystallization kinetics

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Kinetic analysis of solid-state transformations is usually based on a single-step kinetic equation

$$d\alpha/dt = A\exp(-E/RT)f(\alpha)$$

where A (the preexponential factor) and E (the activation energy) are the Arrhenius parameters, R is the gas constant, α is the extent of conversion from the amorphous (liquid or solid) to crystalline phase and $f(\alpha)$ is the reaction model related to the mechanism. In nowdays for the calculation of the Activation Energy and the pre-exponential factor isoconversional methods have been used. Isoconversional methods are frequently called "model-free" methods. The most common differential isoconversional method is that of Friedman. Integral isoconversional methods differ in approximations of the temperature integral. The most known among them are the Ozawa, and/or Flynn and Wall equation and the Kissinger–Akahira–Sunose equation. Further increase in the accuracy can be accomplished by using numerical integration. An example of such approach is integral isoconversional methods developed by Vyazovkin. Also, because of its easy use the Kissinger method has been applied for determining the activation energies more extensively than any other multiple-heating rate method.

The thermal degradation of polymers has been studied quite extensively using thermogravimetric measurements. For the kinetic description, most of the times single rate heating data and model-fitting methods have been used. Since the thermal degradation of the polymers is a very complex reaction, the choice of a reliable model or a combination of kinetic models is very important. The advantages or the disadvantages of using a single heating rate or multiple heating rates data for the determination of the kinetic triplet have been investigated. Also, the activation energy has been calculated with the isoconversional and model-fitting methods. The reaction model was determined with the model-fitting method. The limits of all these procedures were investigated with experimental data of the thermal degradation of the poly(ethylene adipate) (PEAd)

For the study of crystallization kinetics, firstly the activation energy and the pre-exponential factor were calculated. For the determination of the reaction mechanism the model fitting methods are used. For three kinetic models (Bna, Cn, An) the quality of the mathematical fitting depending on the regression coefficient R, is at an accepted level. The value of the activation energy is 120 kJ/mol. The best fit is taken using the expanded Prout –Tompkins equation. In order to increase the quality of the fitting two mechanisms have been used obeying the Avrami model. The fitting results obtained by this model are very satisfactory. The activation energy is 122.9 and 143.5kJ/mol and the values of the reaction order are 4 and 1.1 for the first and the second mechanisms respectively.

Flash DSC – powerful tool for detection of hidden defects of injection moulded parts

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With increasing production and use of conventional plastic materials there is also increased risk of disposal of waste at landfills or marine environments.[1,2] Good alternative are bioplastics, materials that are bio-based and/or bio-degradable and do not affect the environment to such extent as conventional plastics.

Injection moulding is standard process for the fabrication of jars with thicker walls. After aging of the jars the surface crack can form. This effect may appear due to wrong cooling parameters of injection moulding.

In this work, fast differential scanning calorimetry or Flash DSC was used to examine the effect of different ageing temperatures of 2 and 4 mm thick injection moulded jars. Jars were put into oven and aged for four days at different temperatures (25, 40 and 60 °C). Samples were than taken from the surface and analysed with Flash DSC with 600 s long cold crystallization period between 80 and 140 °C. [3]

The aging temperature of 60 °C for the time period of 4 days raised the crystallinity of the surface. Above 120 °C, the rapid decrease of crystallinity at all aging temperatures was observed. The aging temperature of 60 °C for 4 days showed almost constant degree of crystallinity between 80 and 120 °C for the surface samples.

To confirm the results obtained by Flash DSC, the rise of crystallinity was monitored also by DMA, TGA and ATR FT-IR and Flash DSC measurements were performed with the jars injection moulded with different cavity temperatures.

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Thermal analysis of oxy-combustion of Estonian oil shale: Kinetics of process stages

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Oxy-fuel (OF) combustion is one of the promising carbon capture and storage technologies. In this technique, a mixture of oxygen and recycled flue gas is used instead of air as the oxidizer. The flue gas consisting mainly of CO_2 and H_2O is after desulfurization and removal of water ready for sequestration.

OF combustion of coal and lignite has been demonstrated already on the level of demo-plants (e.g. CIUDEN, Spain) but studies of oxy-combustion of oil shale (OS) are still developing. Knowledge about the effect of OF atmosphere on the reactivity of OS during different stages of combustion is needed for evaluating possibilities of application of OF combustion to OS.

In this research non-isothermal and isothermal thermal analysis methods combined with evolved gas analysis were used to characterize and compare the specifics of pyrolysis, oxidation and char oxidation of Estonian OS under air and oxy-combustion conditions using Ar, CO_2, O_2 and their mixtures. The changes in activation energy (E_A, kJ mol^{-1}) were calculated using the AKTS Advanced Thermokinetics software [1] enabling to obtain apparent conversion-dependent activation energies for different combustion stages.

The results of non-isothermal TA experiments showed that pyrolysis behavior is very similar in Ar and CO_2 until the end of decomposition of organic part of OS. The role of char carbon – CO_2 reaction is minor during oxidation stage but can increase at temperatures above 650–700°C. The emissions of CO_2 from mineral part of OS can be diminished as decomposition of calcite takes place at higher temperatures in OF combustion. However, the presence of inorganic minerals, like pyrite and sulfates can increase SO_2 emissions, especially, at higher temperatures and low O_2 concentrations.

The E_A values of OS oxidation in the range of conversion level α = 0.1–0.9 were 120–100 kJ mol^{-1} in Ar/21%O_2 and 35–45 kJ mol^{-1} in CO_2/30%O_2, being lower for the final stage of oxidation. However, the calculated conversion predictions indicate that oxidation under OF combustion conditions can last somewhat longer as compared to air combustion. In comparison, activation energies of OS char oxidation were 110–200 kJ mol^{-1} in Ar/21%O_2 and 90–125 kJ mol^{-1} in CO_2/30%O_2. The final stage of char oxidation in Ar/O_2 proceeded with higher activation energies than in CO_2/O_2 that can be related to the increasing role of reactions in the mineral part of OS.

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Structural and thermodynamic properties of azepine derivatives – A combined experimental and computational study

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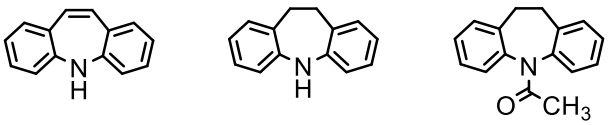
The azepine derivatives, namely the dibenzo[*b,f*]azepine and its 10,11-dihydro related molecules (structural formulae presented in Fig. 1) are well known templates for central nervous system active drugs. The availability of thermodynamic data for these compounds is very scarce in the literature [1], despite its inherent importance. One of our goals is to provide thermochemical values that will be the basic platform for a reliable database aiming to predict the energetic behaviour of related compounds. In this lecture, the experimental and computational studies for the determination of the gas-phase standard molar enthalpies of formation, at T = 298.15 K, of three dibenzo[*b,f*]azepine derivatives (Fig. 1) will be presented. The experimental thermodynamic studies were performed by mass-loss Knudsen effusion and static bomb combustion calorimetry, aiming the determination of the vapour pressures at different temperatures and of the massic energy of combustion, respectively. These parameters were used to derive the enthalpies of sublimation and formation (crystalline and gaseous phases) of the compounds at T = 298.15 K. A computational study was also performed using the composite G3(MP2)//B3LYP method, based on the Gaussian-*N* theory. This approach enabled the structural optimization of the molecules, as well as the computation of its vibrational frequencies and energies at 0 K, and its absolute enthalpies at 298.15 K. Additionally, the calculated values of the absolute enthalpies of selected auxiliary compounds used in hypothetical reactions allowed the estimation of the gas-phase standard molar enthalpy of formation, at 298.15 K, which are in good agreement with those obtained experimentally. Other issues were also addressed for as the frontier orbitals, electrostatic potential energy maps and other gas-phase thermodynamic properties for ionic/radical species.

The results obtained for the enthalpies of formation and the energetic costs associated with the structural changes between the three compounds will be discussed.



(a) (b) (c)

Figure 1. Structural formulae for 5*H*-dibenzo[*b,f*]azepine (a), 10,11-dihydro-5*H*-dibenzo[*b,f*]azepine (b) and 5-acetyl-10,11-dihydrodibenzo[*b,f*]azepine (c).

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Glass transition kinetics versus TA&C researchers

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Sadly, during the last years a new strong trend occurs in the field of glass transition kinetics, associated with application of simple Kissinger-type kinetic equations for the evaluation of the (apparent) activation energy of this phenomenon. Argumentation in the sense that the linearity of these equations automatically ensures their applicability or that their usage is already widely accepted in the scientific community often occurs in the literature. The Kissinger-type equations can be, indeed, applied to a variety of kinetic processes, i.e. diffusion as well as boundary reaction-controlled, surface as well as volume-located, processes with any possible dimensionality, single as well as complex overlapping processes, as well as processes such as decomposition, crystallization, degradation, etc. [1, 2]. Nevertheless, in all these cases, purely thermally activated processes are in fact being considered. In the case of glass transition kinetics, the physicochemical background is much more complicated. Structural relaxation shows very complex behavior, including hysteresis and various memory effects, which the Kissinger-type equations do not take into account.

In the first part of the present contribution it will be demonstrated (based on the theoretical simulations reflecting the true glass transition kinetics) that the Kissinger-type equations cannot correctly determine the activation energy for the glass transition phenomenon. In the second part current methodologies for description of enthalpy relaxation dynamics in amorphous materials will be critically reviewed. Advantages and disadvantages of particular methodologies will be demonstrated; explanations of possible data-distortive effects involving thermal gradients, improperly designed temperature programs, or incorrectly applied subtraction of the thermokinetic background will be suggested. In addition, two novel recently developed methodologies [3, 4] for evaluation of relaxation parameters, applicable even for extremely distorted differential scanning calorimetry data, will be presented. Lastly, an easy-to-follow guide for precise and reliable evaluation of glass transition kinetics will be introduced.

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Thermal behavior and pyrolytic decomposition kinetics of polymeric mixtures from waste packaging plastics

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Pyrolysis is commonly regarded as a valuable alternative to traditional mechanical recycling, as it brings the following advantages: on one hand, it is a low-cost technology, suitable to overcome the main issues connected to plastics contamination and composition heterogeneity [1, 2]; on the other hand, the plastic waste materials are processed back to produce basic petrochemicals that can be used as feedstock for the synthesis of new products [3]. This investigation deals with the thermal behaviour study and pyrolytic kinetic analysis applied to four waste thermoplastic polymers, namely polypropylene (PP), polyethylene film (PE), polyethylene terephthalate (PET), polystyrene (PS), and three synthetic mixtures thereof with different compositions representing commingled post-consumer plastics waste (CPCPW), residual from material recovery facilities. Pyrolysis thermogravimetry (TG) experiments were conducted under a nitrogen atmosphere at several constant heating rates in the temperature range 25 – 600 °C. Thermal decomposition of all single polymers and of one synthetic mixture, enriched in PP, occurred in one single step, while the other two mixtures underwent a more complex decomposition accompanied by two consecutive and partially overlapping mass loss steps. Further experiments on binary systems composed by PS/PP, PET/PP and PE/PP at different compositions showed that the TG/DTG curve profiles of these mixtures and therefore their thermal behaviour depend on their composition and on the decomposition temperatures of single polymers. Kinetic analysis of multi-step decomposition required a deconvolution to resolve the overlapped DTG peaks. Thereafter, the computation of activation energy E_a was performed according to the integral isoconversional method, developed by Vyazovkin [4]. The application of this last method allows to provide more accurate E_a values (as a function of □) than those commonly obtained using other integral isoconversional methods, like KAS and OFW methods. The results confirmed what already indicated by the decomposition temperatures: some interaction occurred during pyrolysis of plastic mixtures, especially when similar content of polymers structurally different are mixed together. Finally, this study ascertained that, for polymer mixtures which differ in nature, it is not possible to accurately foresee temperatures and activation energies by simply calculating the weighted averages of the corresponding properties of the single components.

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Technical Lectures

Multiple Dynamic Mechanical Analyzers (DMA) used for different types of samples, including Biomaterials, Tissue, Heart Valves, Stents, Polymers, Composites, Metals, and Ceramics.

Daniël F. ROEDOLF
TA Instruments – Waters LCC

Dynamic Mechanical Analysis measures the mechanical properties of materials as a function of time, temperature, and frequency. TA Instruments offers now more than six different Dynamic Mechanical Analyzers that incorporate unique technologies to provide the ultimate in performance, versatility, and ease-of-use. The combination of these technologies sets TA Instruments DMA's apart from competitive instruments that use conventional stepper motors, LVDT strain measurement devices, and mechanical springs.

The new RSA-G2 is the most advanced platform for mechanical analysis of solids. The separate motor and transducer technology of the RSA-G2 ensures the purest and most accurate mechanical data through independent control of deformation and measurement of stress. It is capable of performing many additional experiments including, iso-strain, iso-force, fatigue, multiwave and arbitrary waveform.

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The Discovery Hybrid Rheometer and ARES-G2 Rheometer, with DMA mode, adds a new dimension for testing of solid and soft-solid materials. Now in addition to the most sensitive and accurate rotational shear measurements, these two rheometers can deliver accurate linear dynamic mechanical analysis data in all of the key solids testing geometries: film tension, free and clamped bending, and compression. This unique capability is enabled by the DHR's patented magnetic bearing and active Force Rebalance Transducer (FRT). These unique design features of these rheometers allow for controlled amplitude linear oscillatory deformation, a capability that is not possible with instruments that employ air bearings or passive normal force measurements.

In addition, all above mentioned DMA's or rheometers can all be used as a DETA, or Dielectric Thermal Analyzer, for stand-alone or simultaneous measurements.

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All these DMA systems are used every day in the world's largest and most prestigious companies, academic institutions, and governmental laboratories.

Innovative technology, versatile modularity and Swiss quality for a broad range of Thermal Analysis applications

Matthias WAGNER
Mettler-Toledo AG, Business Unit Analytical, Sonnenbergstrasse 74, CH-8603 Schwerzenbach, Switzerland

Mettler-Toledo has been active in the field of thermal analysis for more than 50 years. The first thermal analyser that was introduced to the market from Mettler-Toledo was the TA 1 in 1964. Since then Mettler-Toledo has continuously introduced new types of thermal analysis instruments and has constantly improved existing instruments.

Over the years, Mettler-Toledo has launched Differential Scanning Calorimetry (DSC), Thermal Mechanical Analysis (TMA), different Dynamic Mechanical Analysis (DMA) instruments, Flash DSC (FDSC), Thermal Optical Analysis (Hot Stage), Melting Point (MP) and Dropping Point (DP) instruments. Additionally many accessories and options such as interfaces to hyphenated techniques like mass spectrometers (MS), Fourier Transform Infrared Spectrometers (FTIR) and GC/MS have been introduced.

For all of these techniques and instruments innovative technology, versatile modularity and Swiss quality are the prime properties.

Most recently Mettler-Toledo has introduced a new product range consisting of new DSCs, a new TGA, a new STA (TGA/DSC) and a new High Pressure DSC (HP DSC). All new instruments have a new touch screen terminal with optimized graphical user interface for convenient One Click user operation. Except the HP DSC the instruments are equipped with integrated gas supply units most of them with mass flow controllers (MFC).

The new approach to the dilatometry measurements with redefined instrumentation DIL 402 Expedis, new experience and the application examples

Hilary SMOGÓR
Netzsch Instrumenty Sp. z o.o. Kraków, Poland

Redefined Dilatometry - DIL 402 *Expedis, Classic* – The new dilatometry instruments line, in those cases major simplification begins with preparation of the measurement by using method-based test routines predefined by the operator. The *MultiTouch* feature places the sample into the optimum position using a unique, tail-like motion. The initial sample length is then automatically determined at a predefined contact force. The furnace closing is made smooth by cushioning which guarantees stable sample positioning. Exchanging the furnace is simple and requires no detailed experience. Only a few clicks are needed to start the measurement.

The new, pioneering *NanoEye* displacement system features perfect linearity and maximum resolution over a measuring range which was impossible to realize until now. The heart of the *NanoEye* is an opto-electrical sensor able to encode a position and convert it into a digital signal. Using a linear encoder has the advantage that resolution, accuracy and linearity remain stable over the entire measurement and temperature range. NanoEye is maintenance-free.

Oral Presentations 1

Theory & Methods, Kinetics & Catalysis, Fuels & Biofuels and Applied Thermal Engineering

Temperature functions in thermoanalytical kinetics

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Solid state processes are extensively studied by thermoanalytical methods. Mechanisms of these processes are very often unknown or too complicated to be characterised by a simple kinetic model. They tend to occur in multiple steps that have different rates. The global rate of such a process is very often described by a single-step general rate equation [1]

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

Eq. (1) substitutes the set of kinetic equations describing the global multi-step process by a sole single-step like equation where the global rate is formally expressed as a product of two functions independent of each other, the first one, $k(T)$, depending solely on temperature T and the other one, $f(\alpha)$, depending solely on the conversion, α.

The temperature function is mostly expressed by the Arrhenius equation

$$kT = Ae^{-\frac{E}{RT}} \quad (2)$$

where A is the preexponential factor, E is the activation energy, T is the absolute temperature and R stands for the gas constant. In [1] it has been discussed that the kinetic parameters are apparent quantities without a mechanistic interpretation. Since the temperature function is just a mathematical tool enabling to describe the kinetic hypersurface [2], there is no reason to be confined to the Arrhenius relationship; Berthelot-Hood and Harcourt-Esson temperature functions describe the experimental data so well as the Arrhenius function [3]:

$$kT = Ae^{DT} \quad (3)$$

$$k(T) = AT^m \quad (4)$$

The reason for the equivalence of the Arrhenius and non-Arrhenian temperature functions in the temperature range of measurements is the linear relationship between T, ln$T$ and 1/T. It has been demonstrated that the non-Arrhenian temperature functions provide much more reasonable extrapolation of thermooxidative stabilities of materials; the Arrhenius function tends to overestimate the stabilities [4,5].

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The validity of non-isothermal model-free predictions methods for assessment of conversion vs. time curves for decomposition of calcium carbonate under quasi-isothermal conditions

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The model-free methods [1, 2] have been applied to non-isothermal data corresponding to decomposition of calcium carbonate for evaluation of the dependence of activation energy on the conversion degree. It is shown that activation energy is practically constant in the range of conversion degree $0.03 \le \alpha \le 0.65$, and exhibits a slow decreasing in the range $0.65 < \alpha \le 0.95$. The model-free prediction methods suggested by Vyazovkin [3] and Roduit et al. [4] have been used to evaluate the conversion vs. time curves for decomposition of calcium carbonate under some quasi-isothermal conditions. The predicted conversion vs. time curves were compared with the experimental ones, as well as with those calculated using the decomposition mechanism and corresponding kinetic parameters obtained by Thermokinetics software package [5]. The errors of predictions performed by model-free and model-based procedures have been evaluated and discussed.

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Thermal decomposition and phase transition behaviours of NH_4NO_3/NH_4ClO_4 mixtures prepared by different procedure

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A solid rocket propellant consists chiefly of ammonium perchlorate (AP, NH_4ClO_4), aluminum, and some binder like hydroxyl-terminated polybutadiene (HTPB). The HCl released from the combustion of AP during rocket launches have harmful effects on the environment [1]. The release of the harmful combustion gases can be reduced by addition of ammonium nitrate (AN, NH_4NO_3), an affordable oxidizer containing only oxygen, hydrogen, and nitrogen. Based on this, we focused on adding AN into rocket propellants and investigating their properties. In this fundamental study on AN/AP-based rocket propellants, we prepared particles comprising AN and AP using three different techniques: spray drying, evaporation drying, and powder blending, and investigated their thermal decomposition and phase transition behaviors by thermogravimetry/differential thermal analysis (TG/DTA) and X-ray diffractometry (XRD).

In the TG/DTA curve, an exothermic peak corresponding to mass loss was observed in the range 230–280 °C regardless of the mixing method. The exothermic peak may result from the reaction between AP and AN because it is only observed in the curves of AN/AP and not in those of individual AN and AP. On the other hand, the melting behavior observed in the lower temperature region changed depending on the mixing procedure. In the case of evaporation-dried and powder-blended AN/AP, an endothermic peak derived from melting of AN was observed at ~150 °C. However, in spray-dried AN/AP, this peak was significantly smaller, and in some cases, the peak was not observed. In addition, when XRD was conducted at 140 °C, just before the melting point, the obtained diffraction pattern of the spray-dried AN/AP was different from those of the other samples; for example, the peaks derived from AN disappeared. Therefore, in the case of well-mixed AN/AP, such as the spray-dried sample, the crystal structure is changed, which may influence its melting behavior.

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Thermal behaviour of ammonium dinitramide and amine nitrate mixtures

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Energetic materials are now evaluated not only with regard to their performance but also their current or potential environmental and health impacts. Ammonium dinitramide (ADN) is one of the promising high energetic solid oxidizers, and its properties were studied extensively in the world [1-3]. We have been trying to use ADN as energetic ionic liquid propellants (EILPs). Our past studies showed that the mixture of ADN (melting point =93 °C), methylamine nitrate (MMAN) (melting point =110 °C), urea (melting point =133 °C) forms ionic liquid and it can exist as stable liquid even below room temperature. Especially, MMAN can significantly decrease melting point of ADN [4, 5].

This presentation focused on thermal behaviour of the mixtures of ammonium dinitramide and amine nitrates. The melting point and exothermal behaviour during constant rate heating was measured using differential scanning calorimetry (DSC). Some mixtures showed lower melting point and generated high energy. We combined thermal analysis with spectrometry to analyse thermal behaviour and evolved gases of ADN/amine nitrate during heating simultaneously. From these results, decomposition mechanism of ADN/amine nitrate mixtures was examined.

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The effect of amino acids on phase transition of ammonium nitrate

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Ammonium nitrate (AN) has been used as an oxidizer in energetic compositions like gas-generating agents and is a promising compound as propellants and gas generators because it has high oxygen balance (+20.0 %) and is halogen-free, smokeless when it decomposes and cost-effective. On the other hand, solid state phase transition causes volume change of AN crystal. Cracking in AN compositions was caused by the volume change leads to unwanted burning behavior of the compositions [1]. Some organic compounds as additives have studied for the phase stabilizer of AN. Several compounds having carbonyl, amino and imino groups have stabilization ability to AN because of forming intermolecular interaction between the chemicals and AN [2]. However, the stabilization mechanism of functional groups have not investigated in detail. In this study, we selected amino acids as additives because it has carbonyl and amino groups and simple structure. The purpose of this study is to obtain better understanding of effects of amino acids on the solid state phase transition of AN. We mixed AN with some amino acids in equimolar ratio. The influences of amino acids on solid-state phase transition of AN was studied using differential scanning calorimetry (DSC) and in-situ Raman spectrometry. Composition analysis was conducted using X-ray powder diffraction (XRD). DSC and Raman spectrometry results indicated that L-glycine and L-alanine inhibited solid state phase transition of AN. It is considered that AN reacted with these amino acids to form amino acids nitrate salts and formed clusters with the amino acids by interaction between these molecules from the XRD results.

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Crystal growth kinetics in Se-Te bulk glasses

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Selenium based chalcogenide glasses and thin films have been intensively studied during past few decades because of their commercial applications in photovoltaic materials, photoreceptors, etc. [1,2]. The properties of pure selenium can be significantly improved by alloying with other elements such as tellurium. The selenium-tellurium alloys form completely miscible system in liquid and solid state. The Se-Te mixtures exhibit numerous advantages in comparison with pure selenium (greater hardness, higher conductivity and photosensitivity) [1,2].

Very important processes taking place in amorphous materials are nucleation and crystallization. Knowledge of nucleation and crystallization kinetics can either help to prevent the crystallization to obtain stable glass or, on the other hand, is the essential fundament of considered technology (e.g. Phase Change Materials, optical recording). Crystal growth can be studied directly using microscopic techniques [3] or indirectly using different experimental techniques of thermal analysis (differential scanning calorimetry [4], thermomechanical analysis [5], measurement of electrical properties [6], and so on). Combination of results found by different thermoanalytical techniques with microscopic measurements can then provide better understanding of a crystallization process taking place in amorphous materials.

In the contribution the crystal growth in Se-Te bulk glasses followed by optical microscopy will be combined with thermal and thermomechanical properties of the studied materials (heat capacity data, viscosity) to describe and predict the crystal growth behaviour by conventional crystal growth models.

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Effect of heat transfer and thermodynamic equilibrium on experimental curves obtained by methods of thermal analysis

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TA methods investigate behavior of a sample exposed to an environment which temperature is changed by a controlled manner. The change of environmental temperature T_E (or reference temperature T_R) generally initiates processes tending to reach the state of sample which is the most stable at the present sample temperature T_S. Therefore the process inside sample is controlled by heat transfer between the sample and its environment as well as by the driving force tending to reach stable thermodynamic equilibrium.

There are three tasks for which the TA is used: a) identification of sample, b) study of equilibrium behavior of sample (including temperature dependence of equilibrium properties and calorimetry) c) study of kinetic behavior of sample. The procedures used for description of kinetic behavior do not respect the influence of heat transfer as well as the influence of equilibrium behavior. Evaluation methods proposed by e.g. Kissinger [1] or Piloyan [2] are then based on false assumptions. Also application of Arrhenius equation on decomposition reactions is incorrect since values of activation energy E_A and frequency factor Z in kinetic equation

$$d\alpha/dt = F(\alpha, T) = k(T).f(\alpha) = f(\alpha).Z.\exp(E_A/RT)$$

(in the case of decomposition reactions e.g. $CaCO_3 \rightarrow CaO + CO_2$) simulate the behavior which is factually determined by the equilibrium temperature of decomposition. The other general mistake of so called non-isothermal kinetics based on the above mentioned kinetic equation is using the wrong substitution T_E (or T_R) = T instead of the correct substitution T_S=T.

Our attempts of a correct approach to evaluate TA curves have been published from 1970s [3-5] up to the recent times [6-9] and substantial concepts of this heretic theory would be presented at the oral presentation at the CEEC-TAC3 conference.

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Liquidus and solidus temperatures and latent heats of melting of real steel grades

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The paper deals with the study of liquidus and solidus temperatures [1] and latent heats of melting [2] of real steel grades. Three real steel grades were investigated; liquidus and solidus temperatures and values of latent heats of melting were obtained. Liquidus and solidus temperatures and latent heats of melting were obtained using DSC method (Differential Scanning Calorimetry). Setaram MHTC (Multi High Temperature Calorimeter) Line 96 was used for all measurements. Temperatures of solidus and liquidus and latent heats were also computed using Thermo-Calc [3] with TCFE7 database. Comparison and discussion of experimental and computed data was performed.

All investigated quantities are very important for thermodynamic and kinetic modelling. These data are also valuable for many SWs used for technological processes modelling. The obtained data can serve for the addition and enhancement of many thermodynamic databases.

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Thermal Conductivity Measurements on Pyrex® Using the Heat Flow Meter with Instrumentation Kit - A comparison to Laser Flash Analysis and Literature

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The Heat Flow Meter technique is a well-known and accepted method to determine the thermal conductivity of insulating materials like EPS, rock-wool or glass-fiber boards. But also building materials like concrete or mortar with a higher thermal conductivity can be investigated with the HFM when the additional instrumentation kit is used which extends the thermal conductivity range up to 2 W/(m·K).

The interface thermal resistance between a specimen made of insulating material and the HFM plates is usually negligible compared to the thermal resistance of the specimen. For materials with a higher thermal conductivity this assumption is no longer valid. Although the specimen´s surface is very flat and plan-parallel, there always remain some small air gaps at the interface. These lead to significant differences between the plates´ and the specimen´s surface temperatures, and an inhomogeneous heat flow through the sample.

To avoid these negative impacts on measurements of stiff materials of higher thermal conductivity, the instrumentation kit is necessary. It consists of two additional thermocouples and two interface layers. The interface layers improve the thermal contact between the plates and the specimen, while the additional thermocouples are in direct contact to the specimen´s surface and therefore measure the exact surface temperature.

Pyrex® - a borosilicate glass - is a well-known thermal conductivity reference material since the 1960´s with a thermal conductivity about 1.14 W/(m·K) at 23°C [1]. HFM measurements with the instrumentation kit at room temperature on three different Pyrex specimens show an average thermal conductivity of 1.15 W/(m·K) with a standard deviation of 1.7%. The average values of measurements from 10 to 65 °C show a maximum difference compared to LFA results of 1.5% and compared to literature values of 1.8%. The good agreement with the LFA results and literature values proves the reliability of the HFM measurements with the instrumentation kit. A comparison to a measurement without the instrumentation kit at room temperature demonstrates additionally the need for the instrumentation kit: The result of 0.53 W/(m·K) is significantly lower than the expected value, due to the thermal contact resistance and the incorrect surface temperature measurement without the instrumentation kit.

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About the use of *IDENTIFY,* a thermoanalytical database

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Comparing analytical data and measurement results with values being already published in literature is a common approach to state quality, develop new materials or characterize materials behaviour in general. Since thermoanalytical measurement results are usually strongly influenced by measurement conditions such as the heating rate, crucible type and material, atmosphere, gas flow rate and sample mass, to mention only a few, it was always difficult to create libraries or data bases for comparison of results in the field of thermal analysis.

Nevertheless, already in 1976, G. Liptay published the "Atlas of Thermoanalytical Curves" containing more than 400 organic and inorganic compounds within 5 printed Volumes [1]. The authors present two results per sample, a smaller sample mass investigated with a low heating rate and a higher sample mass measured at a higher heating rate.

Furthermore, between 1991 and 1994, H. Möhler et al. published a three-volume anthology on thermal analysis of polymers [2].

All these approaches have been very helpful for numerous researchers, and they still are, in order to find appropriate measurement conditions or to receive suggestions for an adequate interpretation of the data observed. However, they all suffer from being printed documents and for this reason being not available for a software library comparison to currently measured data.

"*Identify*" is a newly developed part of the NETZSCH *Proteus*® measurement and evaluation software [3]. It allows for an online comparison of currently measured DSC data with a thermoanalytical library. As it is known for other analytical techniques such as FT-IR or MS, "*Identify"* delivers a relative value as a measure for similarity of measured data compared with library data. The library can be edited and customized to the application field of the user and can therefore be trained to recognize customer-specific reference materials, pure samples or mixtures.

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Thermokinetic analysis of spent ion exchange resins for the optimization of carbonization reactor condition

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Commercial nuclear industries utilize ion exchange resins to clean their process and process water. Over time, these resins have to be regenerated or replaced. When this happens, the spent ion exchange resins have to be disposed of. Owing to the high disposal cost and the shortage of available land, developing a process to reduce the volume of spent resin prior to disposal is an attractive goal from an economical perspective [1]. Several processes for reducing volume of spent resins are under development. Carbonization is a promising safe approach for volume reduction of spent resins without releasing radiocarbon (^{14}C) and semi-volatile radioactive elements such as cesium.

A detailed kinetic analysis of the complicated reactions involved in thermal decomposition of mixed waste is required to establish an optimum thermal treatment condition [2]. Optimum condition provides a substantial organics destruction without volatilization of hazardous inorganics. This study investigated an optimum carbonation condition based on the results of non-isothermal TG analyses of both typical cation and anion exchange resins. Three thermal decomposition reaction steps for both resins were established based on TG/DTG data and evolved gas analyses using FTIR/MS. Moisture were removed in the first reaction steps of both resins. In the 2nd thermal decomposition step of each resin, thermal dissociation of functional groups and carbonization of remaining polystyrene divinylbenzene copolymer occur simultaneously. The 2nd reaction steps start at about 200 °C for both spent resins. The starting temperature of the 3rd reaction step, which involves gasification of radiocarbon (^{14}C) and volatilization of semi-volatile cesium, could not be clearly identified in the DTG data. A model-free kinetic analysis of each reaction step was performed to model the progress of each reaction step as a function of temperature and time. Modelling of the progress of each reaction step helped us to determine the optimum operating condition that limits gasification of radioactive elements but provide substantial carbonization performance. A screw conveyor reactor was selected as the most appropriate reactor type for carbonization of spent resin. Its optimum operating temperature and residence time were also determined based on the results of kinetic analysis.

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Analysis of metastable materials at high heating rates

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Metastable materials can be polymers, metallic glasses, polymorphous organic substances and chemically instable liquids. These materials are not in equilibrium; their Gibbs free energy is not at a stable minimal value. When studying specimens of these types of materials, care needs to be taken not to allow the sample to revert to a lower energy state during analysis as this would mean that the material is not studied in its original structure.

Depending on the time-frame of the structural reorganisation it is often not possible to study metastable materials with conventional DSC methods as the material will reorganise during the measurement itself.

To be able to measure materials in a defined structure or to analyse crystallisation behaviour of specimens at various degrees of supercooling, very fast heating and cooling rates are needed. These very fast rates can now be achieved with the Mettler-Toledo Flash DSC 1 (FDSC); this instrument allows heating rates of up to 40,000 K/s and cooling rates of up to 4,000 K/s.

Several examples will be shown for different types of experiments and materials. Heating, cooling and isothermal experiments will be discussed, for polymers, fillers, metal alloys and organic materials.

Co-gaseification of coal and sludge

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In Slovenia, as well as in other countries in the world, people are facing waste and wastewater problems on a daily basis. In the capital city of Slovenia, Ljubljana, the cleaning plant consists of mechanical and biological procedures for removing mechanical impurities, organic nutrients and nitrification. The largest proportion of side products represents the excess sludge, generated in the biological treatment. After the process of anaerobic stabilization and machine condensation is completed, the final product of sludge is heated and dried to the point where the content of dry substance is above 90 %. The free-flowing, hygienic waste in the form of pellets is then exported to foreign countries, which causes an additional cost for us.

Coal is one of the most important fossil fuels in the world and it is the dominant energy source for electricity generation. Thermoelectric plant in Ljubljana (TE-TOL) uses Indonesian coal because it contains less sulfur and ash content compared to the Slovenian and is also environmentally appropriate.

In the research a lot of analysis were conducted to get as many information as possible on addition of active sludge to coal in the process of combustion. Indonesian coal had to be preprocessed with sieve analysis to get particle size distribution, which was of critical importance for further work. Using microscopic analysis with an optical microscope, X-ray diffraction and determination of the specific surface area, information was obtained on the physical properties such as porosity, structure, shape and particle size of the studied sample. Thermal methods in this case carried out a major part of the analysis, including thermogravimetry (TG), differential thermal analysis (DTA) and evolved gas analysis (EGA). Using TG method, the comparison for/of 20 wt. % mixtures of sludge and coal as well as for 50 wt. % sludge was conducted to predict decomposition temperatures. The analysis was based on the weight loss at different heating rates in a time period and controlled atmosphere Ar-O_2.

It was found that co-gasification led to successful thermochemical conversion of sludge as opposed to mono-gasification. It was obvious that the co-incineration of coal and sludge was more efficient of coal alone because of lower decomposition temperatures. Most importantly, the sludge would not be necessary to export, which represents the significant cost.

Thermal analysis of five types of second oxidized coal by STA

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In China, the frequency and severity of spontaneous fire in coal mine are relatively higher among coal manufacturing countries. During the process of mining in the re-mining face and the lower part of the thick coal seam (or coal seam group), the second or multiple oxidation of the residual coal can readily occur in the goaf, and the spontaneous fire risk will be much more dangerous.

Study of multiple oxidation of coal is conducive to early detection of the spontaneous combustion of remaining coal in the goaf. Characteristics of spontaneous combustion were shown using unoxidized coal samples (initial oxidation) and oxidized coal samples (second oxidation) from five different ranks of coals. Through temperature-programmed system, the obtained data were applied to investigate the macro-spontaneous combustion in terms of characteristic parameters of the initial and second oxidized on the five coal samples. Furthermore, simultaneous thermal analysis (STA) was adopted to acquire the related kinetic parameters during evaporation of water, mass loss due to desorption, and oxygen-adsorbed stages.

Compared with initial oxidized coal, the results depicted corresponding apparent activation energies during three stages, and explained the relevant macro-parameters. This study came to the conclusion that the five selected second oxidized coals were much easier to court fire under the same conditions.

An isoconversional incremental method employing non-Arrhenian temperature functions

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A direct incremental isoconversional method based on orthogonal distance regression has been proposed in our recent paper [1]. One of its advantages is that it is not tailored to the Arrhenius equation so it can easily be adapted to kinetic analysis using non-Arrhenian temperature functions. For example, if we employ the Berthelot–Hood temperature function $k(T) = A\exp(DT)$, we obtain the following regression model:

$$T_{i+1} = \frac{1}{D} \cdot \ln[AD\beta + \exp(DT_i)], \tag{1}$$

where β is the heating rate and T_i and T_{i+1} are the isoconversional temperatures corresponding to conversions α_i and α_{i+1}, respectively. In fact, Eq. (1) is a non-Arrhenian counterpart to the infamous "temperature integral", usually expressed as

$$\beta = \int_{T_i}^{T_{i+1}} \frac{\mathrm{d}T}{A\exp(E/RT)}. \tag{2}$$

This work deals with practical application of the non-Arrhenian temperature functions in the kinetic analysis of ambuphylline decomposition. Ambuphylline, a muscle relaxant, is administered as a relatively unstable solvate of theophylline with aminoisobutanol. The proposed incremental isoconversional method has been applied to the first step of ambuphylline decomposition. Both the Arrhenius and non-Arrhenian kinetic parameters are strongly correlated as a result of the kinetic compensation effect. Hence, it is impossible to draw reliable conclusions on the drug stability solely from their values. On the other hand, the kinetic parameters obtained from non-isothermal data enable us to construct the isothermal conversion *vs.* time curves of drug decomposition. In contrast to the kinetic parameters, the isothermal $\alpha(t)$ curves are directly related to drug stability. Since the method [1] is based on statistically well-grounded criterion, trustworthy uncertainties of the kinetic parameters and derived quantities can be estimated.

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Investigation of both reduction and oxidation reactions kinetics of Fe_2O_3 and SiO_2 based ore by TG

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Chemical Looping Combustion (CLC) technology is believed to be one of the most promising fuel combustion methods for Carbon Capture and Storage (CCS). In CLC the oxygen is provided to the fuel by a metal oxide (Me_xO_y). By application of Me_xO_y the direct contact between air and fuel is avoided, leading to significant decrease in CO_2 and NO_X emissions from fossil fuel combustion. The exit stream from the fuel reactor (FR) is a mixture of CO_2 and water. Therefore, after water condensation a pure stream of CO_2 is obtained without any energy penalty for its separation. In the past, simple metal oxides such as CuO, NiO, Mn_2O_3 and Fe_2O_3 have been studied as Oxygen Carriers (OC) candidates. Fe_2O_3 based OCs have the additional advantage of being environmental friendly and also having significantly lower production cost compared to other candidate materials.

The present paper shows the results of a research work on possible utilization of naturally occurring OCs materials in CLC. For the study, Kryvbas, a mineral ore containing Fe_2O_3 and SiO_2, is selected. The reactivity measurements are performed at selected temperatures during multiple redox cycles, at isothermal conditions using a thermogravimetric analyser (TG) instrument. Methane is used for the reduction reaction and synthetic air is used for oxidation of the solid. The kinetic parameters such as the activation energy (E_a), the pre-exponential factor (A_0) and the reaction order (n) with respect to fuel and oxygen concentration are determined using a MathCad software. Suitable reaction models are selected by means of the model fitting method.

The fresh and used in several redox cycles OC samples are characterized by X–ray Diffraction (XRD) and Scanning Electron Microscopy combined with X–ray Microanalysis (SEM-EDS). The crystalline phases present and the morphology of the OCs particles are examined to identify both structural and morphological changes and therefore to determine the stability of the OC in cycling CLC tests.

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TKX-50 Thermal decomposition: kinetics and mechanism

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Dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate or TKX-50, synthesized by T. Klapotke group in 2012, and presented as a new promising energetic material, comprising high enthalpy of formation, high thermal stability with low sensitivity and low toxicity [1]. This paper reports for the first time results of the TKX-50 thermolysis investigation under adiabatic conditions and under vacuum. Kinetic parameters for two stages of decomposition obtained using various experimental and mathematical techniques and verified by comparison with data obtained by accelerating rate calorimetry (ARC). The isoconversional methods shown to be more useful than model-free methods and formal kinetic approaches in prediction of thermal behaviour of the material. Based on experimental ARC data it was concluded that TKX-50 has the thermal stability on the same level as CL-20 and RDX. Thermal decomposition of TKX-50 shown to be a complex two-stage process starting with dissociation into hydroxylamine and bistetrazolediol (BTO) acid. The decomposition of BTO*2H_2O and TKX-50 commences at the same temperature, showing that the bistetrazole diole acid decomposition is a key step in the whole TKX-50 thermolysis. The addition of BTO-compound catalyses TKX-50 decomposition, and *vice versa*. The main condensed product of the first stage of TKX-50 decomposition has been identified and found to be ammonium salt of bistetrazole diole (ABTOX). In turn, the second stage of TKX-50 thermolysis is governed by ABTOX decomposition, and consists of two consecutive steps: (i) reversible dissociation with the activation energy of 189 kJ/mole, (ii) formed BTO decomposition (parallel first-order and autocatalytic reactions) with the activation energy 152 kJ/mole, which is equal to calculated energy barrier for N_2 elimination from BTO molecule [2].

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Structural and destructive transformations of polymer composites in the course of model processing

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Polymer composites based on scrap PET blends in a form of wastes from industry and households have been examined upon their processing. The polymer mixtures were investigated on a specially designed experimental machine modelling the recycling processing.

Special attention has been paid to characterize the evolved volatile components as well as to study the destruction onset by various thermal and spectral methods – TGA, DSC, X-ray, IR and MS analyses.

Some general destruction processes have been acquired originating from the structural changes that take place during the model processing of the composites.

The study of firing the ceramic body made from illite and fluidized combustion fly ash

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In this paper a development of thermal and mechanical properties (dimension changes, mass loss, bulk density, Young's modulus (*E*) and internal damping) of the green ceramic body based on illitic clay and fluidized combustion fly ash (FFA) during firing up to 1100 °C are presented. These results are also supplemented by a differential thermal analysis, evolved gas analysis, X-ray diffraction for phase identification and SEM for a structural study.

The samples were prepared from illitic clay (~80 % of illite; in next referred to as illite) representing a plastic component, thermally stabilized illitic clay (referred to as filler) representing a non-plastic compound and FFA. All samples contained 60 % of plastic component and 40 % of non-plastic compound. A part of filler was replaced with FFA in different amounts so, that the mixtures contained 0, 10, 20, 30 and 40 % of FFA. Compact samples were prepared by mixing the input materials with water and following drying.

DTA, TG and EGA analyses were used for studying the input materials in a powder form. In illite there are three main processes observed – drying, dehydroxylation and burning out the organic parts. Moisture content of FFA is rather high (~8 %). Around 400 °C there is visible reaction that corresponds to the calcium hydroxide decomposition. Calcium carbonate decomposition starts at rather low temperature ~650 °C and ends at ~790 °C. Consequently, we observed CO_2 evolution in broad temperature region (~200-700 °C) associated with burning out the remaining brown coal particles.

In general, *E* increases in the region of removing the physically bound water. It decreases up to ~850 °C, and with the further heating, when sintering begins, *E* increases. The higher is FFA content the lower is maximal value of *E*. Logarithmic decrement decreases significantly in the drying region, increases in the dehydroxylation region and increases significantly when samples are heated above 900 °C when the sintering and vitrification take place.

According to the thermodilatometry, the sintering starts at around 900 °C and this temperature decreases with increasing amount of FFA. The more FFA is added to the mixture the lower is the shrinkage of the sample after firing.

Comparative study of different cements hydration kinetics by thermogravimetry on calcinated mass basis

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This work is part of the activities of a project aiming CO_2 and SO_2 capture by cementitious materials. Its objective is to study and to compare the hydration kinetics of four different commercial cements by thermogravimetry (TG) and derivative thermogravimetry (DTG) on calcined mass basis [1,2, 3]. The capture of those gases from industrial gas effluents has been done usually by lime containing products. For CO_2 capture cement pastes can be used as well [4], due mainly to their calcium hydroxide (CH) content formed during hydration, which indicate this kind of sorbent for SO_2 sequestration as well. There are other factors that act in the capture efficiency, such as sorbent porosity, effluent gases temperature, humidity, CO_2 and/or SO_2 concentrations [5]. To quantify the CH and the other main hydrated phases formed as a function of hydration time, TG and DTG curves on respective initial sample masses of Portland cement pastes (types I, II, III and G) were obtained using a TA Instruments, model Q600 equipment. The analyses were performed at a heating rate of $10^{o}C.min^{-1}$, which were preceded by a drying step at $35^{o}C$, to allow the determination of the unreacted water of each case. The TG and DTG curves of differently aged pastes were transformed in respective cement calcined and initial mass basis, to have common and same composition reference basis for a correct quantitative hydration data comparison. The results show that the higher kinetic differences among each cement type occur during the first 24hours of hydration, which are the most important for CO_2 or SO_2 capture [6]. At 28 day of hydration main hydrated phase contents are more similar, except for type III cement case.

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Thermal analysis in welding simulations

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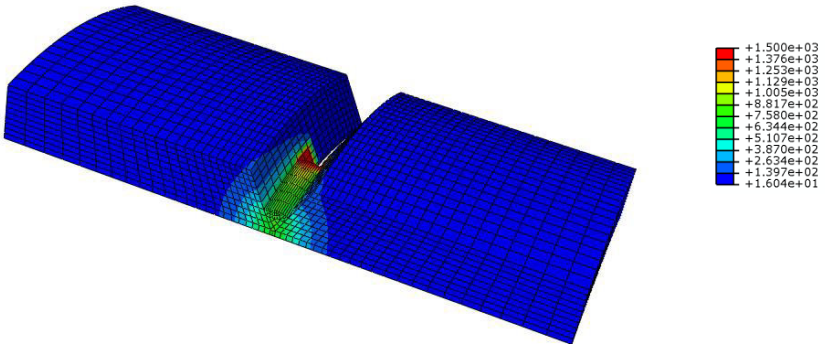
Welding simulations in finite element method models, can be performed using either a sequentially uncoupled approach or a fully coupled thermo-mechanical analysis. In the work present, the sequentially uncoupled approach was used to solve transient thermal fields and subsequent mechanical analysis was performed in multi-pass welds employing a low transformation temperature filler metal. While thermal analysis was calculated as transient heat transfer, the mechanical analysis was considered as quasi static. Element birth technique with moving heat flux was used in the calculation. Temperature dependent material's properties and Von Misses elastic-plastic material's model were assumed. The model presented is capable to calculate latent heat during transformation in addition to transformation strain due to the displacive transformation. Exploitation of transformation strain to minimize residual stress and to optimise stress field distribution after welding is discussed in paper. Results obtained can be used to optimise technological parameters in welding.



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Oral Presentations 2

Thermochemistry & Calorimetry and Thin Films & Nanomaterials

Influence of inorganic fillers on PLA crystallinity and thermal properties

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Polymer composites represent an increasing approach to implement new class of materials for specific application. Polylactide (PLA) is among most widely studied bio-based products during last few decades. That is mainly due to its biodegaradable nature as well as due to a search for the conventional petrol based plastics replacement [1-3]. In this work we have studied thermal behaviour of PLA composites based on three kinds of commercial fillers: *Cenosphere*, *Schwerespat* and *Socal*. The concentration of added fillers was: 0.1, 0.5, 1 and 5 wt %. Composites were prepared using a Brabender plasticorder at 190 °C. Thermal properties of prepared composites were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

The obtained results reveal influence of sample's thermal history. Therefore, the second heating run results were compared. The glass transition temperature (T_g) of composites is in a range 56 to 61 °C, which is close to a value of PLA matrix (57.7 °C). All prepared composites display resembling crystallization enthalpies of cold crystallization as well as enthalpies of fusion. Consequently, added fillers provoke disappearance of crystallinity of PLA matrix that was noticeable originally.

The results of TGA show increase of thermal stability in all composites. The thermal decomposition onset temperature in PLA matrix is below 200 °C while in some composites it is shifted fare above 300 °C.

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Optimizing the Parameters for In-situ Fabrication of Al-Al_2O_3 Composites

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Reinforcement with ceramic particles is an already consecrated method for improvement of aluminum alloys. Mechanical properties such as tensile strength, Young's modulus, yield strength and wear resistance are considerable enhanced. Reinforcements produced inside metallic matrix via chemical reactions or structural transformations could be smaller, more uniformly distributed and could have chemical compatibility with the matrix. Composite materials were produced via powder metallurgy technique using a blend of powders containing Al + 20% vol. Al_2O_3 and 10% vol. Fe_2O_3. Cylindrical preforms 10 mm in diameter and 5 mm thick were produced from powder by hot pressing at 550°C for 5 minutes with a pressure of p = 900 MPa. Sintering treatment was used to produce in-situ particles of Al_2O_3, following exothermal reaction between Al and Fe_2O_3. Differential scanning calorimetry (DSC) was used to determine optimum temperature and duration of sintering in relation with development phase transformations and in-situ reaction. Results were validate by mean of X-rays diffraction (XRD) and scanning electron microscopy / energy dispersive X-ray analysis (SEM/EDX) to evidence formation of in-situ particles of Al_2O_3 and total decomposition of Fe_2O_3.

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Thermoporosimetry of n-alkanes for characterization of mesoporous SBA-15 silicas

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A comprehensive characterization of nanoporous materials, with regards to porosity, pore size distribution, surface area and pore volume, is important because these materials offer a wide range of potential application (e.g. catalysis, adsorbents, electronics, or drug delivery [1]). Although development of various experimental techniques, such as gas sorption, X-ray diffraction, neutron scattering, mercury porosimetry or electron microscopy allows performing pore size analysis over the micro/mesopore size range, none of these approaches can be considered the absolute one and used without reflection on the hypotheses and assumptions hidden in its background.

A promising alternative method for studying porosity is known as thermoporosimetry (TPM), however, it is still not well recognized and developed [2]. It is based on the fact that a fluid confined in the pores of a solid material experiences an important shift of its liquid to solid transition temperature (ΔT) and this shift is related to the size of the pores, in which the liquid is trapped, according to the Gibbs -Thomson equation. Soaking the porous material in the liquid and measuring the melting or crystallization profiles by DSC is enough to perform the porosity characterization. Moreover, it turned out that application of this technique is very simple, fast, inexpensive and nondestructive.

Although several liquids have been used to probe porous properties n-alkanes, with non-polar molecules that should mitigate surface-fluid interactions, seem to be one of the most important and promising. They may also reveal differences in surface chemistry of the porous materials thanks to the variation in their molecular size [3]. This work focused on summarizing the experimental protocols giving valuable results basing on the examination of n-hexane, n-heptane and n-octane confined in the pores of mesoporous silicas SBA-15 [4]. The deeper insight in the influence of heating and cooling rate, activation temperature and liquid and solid mass on n-alkane-TPM measurements was performed. Additional gas sorption experiments gave parameters used for the retrieval of calibration equations. Moreover, during the study, important differences in the behavior of odd and even-numbered alkanes in TPM experiments were observed. We attributed them to different packing of alkane molecules in the solidified state [5].

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Thermoanalytical approach to evaluate mesoporous organic and carbon materials

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Thermoporometry (TPM) is a thermoanalytical method using DSC to obtain textural parameters of mesoporous and macroporous materials. The method is based on a measurement of melting/freezing of liquid entrapped in a porous material. Because of small size of solid phase forming inside the pores this transition occurs at a lower temperature than melting/freezing of bulk liquid surrounding the material. Therefore, size of the pores can be determined by observing the melting/freezing transition.

The objective of this work was to optimise TPM measurements for the selected porous organic and carbon materials by finding a suitable method of a sample pretreatment and by adjusting experimental parameters of DSC measurements. The optimization allows for accurate calculations of textural parameters even for materials with pores larger than 50 nm in diameter.

A group of porous organic materials based on melamine-resorcinol-formaldehyde or cellulose acetate and their carbonaceous variants after pyrolysis were used for TPM experiments. A DSC experiment was performed in a hermetically sealed aluminium pan by measuring the melting of water inside and outside the pores.

Textural parameters obtained from preliminary nitrogen gas sorption (GS) measurements showed lower pore volumes and broader pore size distributions (PSD) than for samples typically used for TPM. Thus, pretreatment and experimental conditions were optimised as follows:

- Washing of the soluble impurities before a TPM measurement was assessed as necessary.
- Heating rate of 1 °C min^{-1} was found to be suitable for the best compromise between sensitivity and ability to separate the melting inside and outside of the pores.
- The optimal ratio of water to solid mass (mg/mg) was determined as 4:14 or 5:14 for the samples with lower mesopores volume (<0.13 cm^3 g^{-1}) and 7:12 or 12:12 for the samples with higher volumes (≈0.4 cm^3 g^{-1}).

There was no need to separate the overlapping peaks of pore and bulk melting (obtaining a single peak of pore melting is generally needed for further calculations of pore volumes and PSDs). The textural parameters obtained on the basis of TPM technique were in a good agreement with the findings from GS and SEM. Only supercritically dried organic sample was not applicable to a TPM method due to sensitivity of its porous structure to water.

In conclusion, porous organic and carbon materials with a broad pore size distribution ($d \approx 4 – 100$ nm) and pore volumes between 0.06 and 0.4 cm^3 g^{-1} can be successfully characterised by TPM, but the experimental conditions have to be carefully optimised.

Application of hydrothermal curing to prepare chemically bonded phosphate ceramics from Calcium Aluminate Cement

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Calcium Alumina cements (shorthand CAC) form a specific group of inorganic binders used as refractory concretes in furnaces and kilns of ceramics, cement, glass, iron and steel industry[1-4]. The main clinker phase and also the major hydraulic one is monocalcium aluminate ($CaO.Al_2O_3$ or CA). Secondary phase may be calcium bialuminate ($CaO.2Al_2O_3$ or CA_2). The hydration of CAC depends mainly upon the temperatures leading to the formation of CAH_{10} (below 21°C), C_2AH_8 and AH_3 (up to 35 °C) or C_3AH_6 and AH_3 at higher temperatures [2]. A new class of products denoted as chemically bonded phosphate ceramic binders (CBPC) were prepared throughout the present paper using sodium hexametaphosphate ($Na_6P_6O_{18}$) and applying hydrothermal curing conditions of 0.3 MPa and 150°C during 3 and 7 days to change the course, kinetics and mechanism of CAC hydration. The hydration of CAC with addition of sodium hexametaphosphate has been investigated at ambient temperature (25°C) with 100 % relative humidity during 365 days and at 50 °C with 60 % RH for 7 days. Thermal analysis method, X-ray diffraction, scanning electronic microscope and Fourier Transform InfraRed were used to identify and characterize different hydration products. Also, mercury intrusion porosimeter was used for the characterization of the pore structure parameters of the composites and mechanical properties determined. While sodium hexametaphosphate did not influence the nature of CAC hydration at ambient temperature though after long term of exposure, at 50 °C $NaCaPO_4.xH_2O$ and $Al_2O_3.xH_2O$ where identified as amorphous phases formed by acid-base reaction between mono calcium aluminate and sodium polyphosphate. Under hydrothermal curing, the main hydration products was hydroxyapatite ($Ca_5(PO_4)_3OH$), known as ceramic materials with potential application in biomedicine supplemented by gibbsite ($Al(OH)_3$). The formation of these hydroceramics results from the transformation of amorphous phases $NaCaPO_4.xH_2O$ and $Al_2O_3.xH_2O$ by effect of hydrothermal treatment.

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Functional oxides from low temperature CSD routes using aqueous and organic precursors

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Chemical Solution Deposition (CSD) processes are applied for the synthesis of a variety of functional metal oxide materials, *e.g.* ranging from ferroelectrics ($PbTiO_3$) over semiconductors (Al doped ZnO) to cathode materials for Li battery materials ($LiMn_2O_4$). Independent of envisioned oxide, tailored precursors are to be developed, always involving the presence of a liquid phase. By subsequent chemical reactions triggered by an energy providing method, these systems are transferred into the desired oxide. The temperature at which these reactions occur, depend on the method and chemistry applied and are steered by the thermodynamics and kinetics involving the concerning transitions.

In this overview, we present low(er) temperature routes which we've already applied for the synthesis of different metal oxides with practical importance in consumer electronics. Insights into the decomposition process involved and precursor properties based on chemical analysis and feedback from the final material's functionality, have led to different approaches for reducing processing temperatures. Here, focus will be on the molecular precursors in which the oxide is formed in-situ at reduced thermal budgets after its deposition on the substrate. Results from (auto)combustion processes starting from water or organic solvent based precursors are discussed and their potential and limitation compared to other methods. From the presented results, general conclusions concerning the low temperature processing from CSD based routes will be drawn.

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The effect of strontium doping on solid-state synthesis of $K_{0.5}Na_{0.5}NbO_3$ studied by thermal analysis and high-temperature X-ray diffraction

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Ceramic materials based on $K_{0.5}Na_{0.5}NbO_3$ (KNN) are one of the most studied possible lead-free substitutes to the currently used lead zirconate titanate piezoelectric ceramics. KNN ceramic has a major drawback – it is difficult to densify. Doping with 0.5 and 1% of Sr was reported to improve density and electrical properties of $K_{0.5}Na_{0.5}NbO_3$.[1, 2] Besides the improved functional properties, Sr doping has a number of unintended effects with the increasing amount of Sr, like dramatic decrease of the grain size, tendency to decrease the monoclinic unit cell distortion and segregation of a secondary phase.[3]
In this study, we investigated the influence of Sr^{2+} doping on the solid-state reaction of KNN ceramics. Ceramics with the formula $(K_{0.5}Na_{0.5})_{1-2y}Sr_yNbO_3$, for y = 0, 0.01, 0.02 and 0.06 were prepared by solid-state synthesis. The homogenized powders were calcined twice at 800°C, 4 h with intermediate and final milling before the pressed pellets were sintered at 1120°C, 2 h. The techniques of high-temperature X-ray diffraction and thermogravimetry coupled with evolved gas analysis together with differential thermal analysis were used to understand the solid-state reaction and its changes with the increasing amount of Sr dopant.

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Influence of chromium substitution on Néel transition and thermal expansion in $GdFe_{1-x}Cr_xO_3$ mixed oxides

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Lanthanide-transition metal mixed oxides emerged in recent years as potential catalysts[1]–[3] and material for harvesting of green energy[4], [5]. Two of those examples are lanthanide orthoferrites ($LnFeO_3$, where Ln represents a lanthanide trivalent ion) and lanthanide orthochromites ($LnCrO_3$), who may serve as oxide semiconductors with the ability to absorb light from the visible spectrum region.

However although structurally similar their magnetic properties exhibit a significant difference. The Néel transition temperature (T_N) is usually higher for orthoferrites than for the orthochromites, e.g. T_N = 657K for $GdFeO_3$[6] but for $GdCrO_3$[7] T_N = 167K. The internal magnetic field is disadvantegoues for electrical carrier propagation, generating additional losses in the electrical flux. It is therefore of high importance to pinpoint that composition range, in which the effective magnetic momentum would be null above room temperature (RT).

We give as an example the $GdFe_{1-x}Cr_xO_3$ and study it by: differential scanning calorimetry, dilatometry, x-ray diffraction, Mőssbauer spectroscopy and UV-Vis spectroscopy. We find the shift of the transition temperature with chemical composition and conclude that the mixed gadolinium ferrochromite is non-magnetic in RT for $0.5 \leq x \leq 1$.

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Effect of crystal field parameters of Cr^{3+} on colour hue of $Li_{1+x}Cr_xZr_{2-x}(PO_4)_3$ solid solutions

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For many years our department has been engaged in the development of new high performance inorganic pigments. Inorganic pigments are widely applicable technological colourants which are chemically and thermally stable, lightfast and, therefore, durable under the most aggressive utilization conditions. One of the groups of inorganic colorant with high performance characteristics and wide range of colours belongs to NASICON phosphates. In this view, NASICON-related phosphates containing Cr^{3+} represent a particular case, because colouration of such compounds highly depends on the crystal field strength of Cr^{3+} and, accordingly, on co-substitutions in the crystal lattice. By simple control of the chemical composition within NASICON crystal lattice, it is possible to shift the absorption bands in the visible range of the spectrum of light with the purpose to obtain the desired colouration.

In this contribution, a series of the NASICON's representatives – solid solutions of $Li_{1+x}Cr_xZr_{2-x}(PO_4)_3$ and their chromatic characteristics are discussed. Special attention is paid to effect of crystal field parameters on the shift of the absorption bands in VIS reflectance spectra and the resulting colour hue of the samples. The colour of the samples is explained by means of crystal field theory. Accordingly, two observed adsorption bands in VIS range of electromagnetic irradiation are associated with the electronic transitions between different energy states of d-electrons of Cr^{3+}, which are determined by surrounding crystal environment and crystal field strength of the chromium ions. In particular, Cr^{3+} has an octahedral oxygen environment in $Li_{1+x}Cr_xZr_{2-x}(PO_4)_3$ solid solutions and the crystal field strength is controlled by substitution degree x. With increase of the substitution degree, the crystal field changes from a very weak to weak. Accordingly, the absorption bands in the visible spectrum of light are also shifted to higher energies (UF direction) and the resulting colouration changes from light pink via brown to bright green.

$Li_{1+x}Cr_xZr_{2-x}(PO_4)_3$ samples have been prepared by solid state reaction. Thermal behaviour of the reaction mixtures was investigated using simultaneous TG/DTA analysis with temperature intervals between 20-1200 ^oC. Evolution of the phase composition in the system was analysed using powder XRD analysis. The obtained pigments were characterised by thermal stability test in temperature intervals between 20-1500 ^oC and also by particle size distribution measurement. Relations between the colour hue and crystal field parameters of the samples were analysed using VIS-spectrophotometry in the range of 400-700 nm. The crystal field strength (Dq) and electronic interaction of Cr^{3+} with its coordination polyhedron (B') were evaluated for the samples with different substitution degree x on basis of the position of the absorption bands in VIS spectra.

Study of thermal behaviour of Y_2O_3-Al_2O_3 glass microspheres

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Yttrium-aluminate glasses are attractive technological materials with interesting mechanical and optical properties, good structural stability under extreme mechanical, electrical, thermal and chemical conditions. For these properties (comparable with those of sapphire single crystal or polycrystalline alumina), are these glasses successfully used for many application (e.g. transparent ballistic protections, infrared transparent windows and solid state lasers materials [1]).

In this work A60Y40 glass sample with the eutectic composition (76.8 mol. % Al_2O_3,23.2 mol % Y_2O_3) was prepared in the form of microspheres by flame spraying technique [2] and its thermal properties were studied to examine possibility of preparation of bulk glasses or glass ceramic materials by pressure assisted viscous flow sintering at temperatures $\geq$ 900°C. Optical microscopy, SEM and X-ray powder diffraction analysis were used for basic characterisation of prepared glass microbeads. HT XRD records in the temperature interval 750-1200°C with the step of 5°C were measured for better understanding of crystallisation behaviour and phase evolution in prepared glass during sintering. DSC analysis in the temperature range 35-1300°C and the heating rate 10°C/min, and isothermal DSC experiments with different dwell times (30, 60 min) at various temperatures were carried out. The onset of exothermic (crystallization) peak temperature T_x, and the maximum of the exothermic peak temperature T_p were determined and the mechanisms of crystallisation investigated. The isothermal crystallisation experiments at 875, 935, 998 °C, 1300 and 1600°C with 6h dwell times were performed and crystallized microspheres were studied by SEM, X-ray powder diffraction analysis (Diamond Light Source, Beamline I11), and TEM.

The crystallisation of the yttrium-aluminium garnet (YAG) phase was observed at all temperatures, with the highest crystallisation rates at 935 and998°C. The formation of α-Al_2O_3 phase was only observed at the temperatures exceeding 1300°C). The SEM and TEM examination of crystallised microspheres confirmed the nucleation and growth of YAG crystals both through volume and surface crystallisation. The relationships between the temperature and time of annealing, microstructure and content of individual crystalline phases are evaluated and discussed, and possibility of preparation of composite α-Al_2O_3-YAG ceramics with fine grained microstructure is investigated.

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Thermoanalytical characterization of boron-containing alumina ceramics

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Alumina is one of the most promising ceramic materials for a wide range of structural and other special technical applications due to a combination of hardness, high heat-resistance, chemical inertia, on the one hand, and availability on the other. Ceramics based on phosphate binders is special group among refractory materials [1]. Its characteristic feature is the ability to form a strong structure at relatively low temperatures (550-600 °C) and maintain its properties when heated to high temperatures. Aluminophosphate binders are colloidal solutions of aluminophosphates produced by a reaction between orthophosphoric acid and aluminum hydroxide at 70 - 90 °C. Properties of aluminophosphate binders are determined by certain ratio of a water, phosphoric acid and aluminum hydroxide. In order to improve the properties of oxide ceramics used for protection against ionizing radiation, promising introduction to its structure of modifying components containing ultrafine boron-containing compounds.

The object of the study is alumina ceramics based on inorganic (aluminophosphate) binders modified by crystalline or amorphous boron, which can operate at high temperatures. Samples were performed in the Belarus State University [2]. The effect of the composition and filler's concentration on the heat transfer characteristics of new boron-containing composite materials was investigated.

Thermoanalytical and thermophysical research methods are successfully used for the determination of phase transitions, thermally induced chemical reactions, destructtion and thermophysical properties of materials.

Simultaneous TG-DSC analysis was carried out by STA 449 F3 Jupiter (NETZSCH) in the temperature range 25 - 900 °C. Thermophysical properties were determined on the LFA 457 MicroFlash (NETZSCH) by a laser flash method in the temperature range 25 - 500 °C. Experiments were carried out in a vacuum (1 Pa) and helium gas atmosphere at atmospheric pressure (1 kPa).

It has been shown desorption of liquid component of inorganic binder from ceramic samples even from those have been performed at elevated temperatures. There is an exothermic process in the temperature range 580-740 °C in unmodified samples. Doping of amorphous boron in the ceramics leads to additional exothermic process at 800 °C, which combines with exothermic process in unmodified material when boron concentration is equal 80%. (When boron concentration is equal 80% exothermic process are combined.) The temperature dependence of the specific heat repeats DSC-curve with similar extremums. The thermal conductivity and the thermal diffusivity of ceramic samples with a high concentration of amorphous boron is an order of magnitude less than that of the unmodified material.

It should be draw attention on the correct calculation of the thermal conductivity of such materials. The thermal conductivity is defined as $\lambda = a \bullet \rho \bullet C$, and if the specific heat capacity (C) depends on the processes occurring in the material, the thermal conductivity will also depend on these processes.

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A novel method for thermo-electrical properties of GaSb by Electro-Pyroelectric technique

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A novel method for thermo-electrical properties of GaSb based on Electro-Pyroelectric technique (EPE), which integrated experimental and theoretical model, is reported in this paper [1]. The rise temperature over the time at a thin PVDF film (PolyVinyliDene Fluoride) interface via a modulated electrical current produced an electropyroelectric current [2-3]. So, a measurement of thermal properties upon a thick GaSb semiconductor using the EPE signal combined with electrical impedance analysis over the frequency range from about 10Hz to 100 KHz are performed. The experimental results were found to be in good agreement with the literature and the impedance analyzer values.

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Modelling of advanced aluminium alloys using thermal analysis

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It is well known that various thermal analyses are excellent tools for planning new special alloys for new applications. Thermal analysis provides new information about thermodynamic properties, phase transitions and phase precipitation. In this work the use of thermodynamic equilibrium calculation using Thermo-Calc program, simultaneous thermal analysis and simple thermal analysis will be used to present the use of these methods for development of new alloys. Phase diagrams are used in materials research and engineering to understand the interrelationship of composition, microstructure and process conditions for better visual representation and interpretation of solidification path of studied alloys. The effect of rare elements addition on the Al systems Al-Cu, Al-Si-Mg and Al-AlCu5.5 was investigated using thermodynamic modelling, simple thermal analyses, differential scanning calorimetry (DSC), optical and scanning electron microscopy (SEM) were employed to identify the generated microstructures. Characteristic solidification and precipitation temperatures of individual phases were recognized.
Rare earth metals have been found to influence the solidification and precipitation path. Increase of additions decreased the precipitation temperature of primary silicon phase. Ce addition reduces the melting enthalpy and solidification enthalpy at both AlSi12 and AlSi17 alloy. Such alloys have better mechanical properties because rare metals modify the microstructure and enhance the tensile strength and hardness when suitable concentration is added. Addition of neodymium increased eutectic solidification temperature and solidus temperature, which lead to a narrower solidification interval. It was also discovered that neodymium formed binary eutectic (α_{Al} + $Al_2Cu(Nd)$).

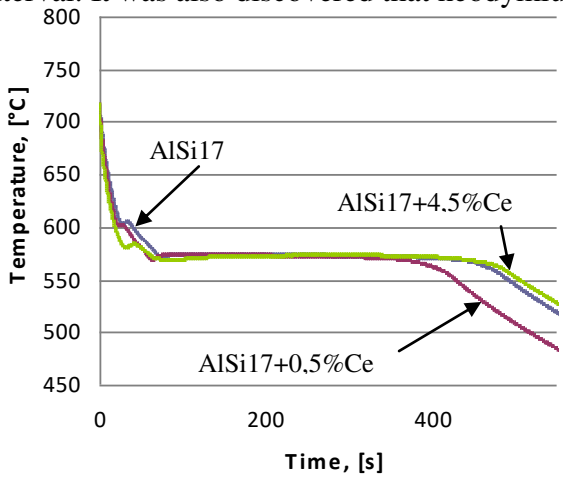

Fig. 1: Effect of Ce addition on the Al alloys solidification

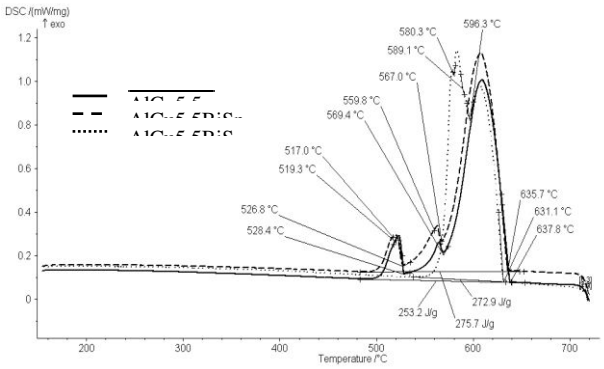

Fig. 2: Cooling DSC-curves for the Al-Cu5.5 alloy with additions of neodymium.

Dilatometric analysis of Al–Si alloys during solidification

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Solidification of AlSi12 alloy was described using different techniques such as thermal analysis, dilatometric analysis in accordance with thermodynamic calculation carried out by ThrmoCalc software. The aim of the paper is to investigate dimensional changes of a casting during solidification. In order to study such phenomena the permanent measuring cell from calcium silicate brick was produced. The casting from the cell was a 220 mm long bar with the square cross-section of 295 mm^2. At the end of the bar two quartz rods were inserted into measuring cell connected to two linear variable differential transformers (LVDT) which were measuring the dimensional changes during solidification and cooling. At the same time the thermal analysis was carried out in the thermal centre of the casting. Four samples of AlSi12 alloy were prepared. One was without additions and at others the Ti, Sr and both of additions were added simultaneously. Samples were marked as 12, 12T for Ti addition, 12S for Sr addition, 12TS for Ti and Sr addition. Ti and Sr were in forms of master alloys AlTi5B1 and AlSr10.

Solidification of aluminium alloys is well described in literature in terms of thermal analysis [1]. Solidification of castings is connected with dimensional changes or shrinkage during solidification of the castings which can produce defects such as shrinkage porosity. Shrinkage porosity is a consequence of shrinkage of metal during solidification which can be up to 7 vol. % in case of aluminium. Not many authors have reported about dimensional changes measurements of castings during solidification. Some has reported about dilatometry of casting and measuring cell and relationship between casting and mould connected with gap formation [2].

Results of thermal analysis are presented in Fig. 1a. Cooling curve (T) of sample 12 is showing the solidification of AlSi12 alloy. Cooling curve is in accordance with thermodynamic calculation of solidification. In the first sequence of solidification the α_{Al} precipitates followed by $Al_9Fe_2Si_2$ phase precipitation. At eutectic part of the curve the solidification of (α_{Al} + β_{Si}) eutectic takes place and solidification is finished by $Al_{14}(Fe,Mn)_4(Al,Si)_5$ phase precipitation. All phases were detected in microstructure and analysed by EDS-analysis.

The measurement of dimensional changes of sample 12 is presented in Fig. 1b. It is seen on dilatometric curve (Δl) that casting is first expanding due to measuring cell expansion because of warming of a cell and casting is still liquid at the time. When the solid skin is formed in the casting it starts to move the quartz rods and shrinkage of casting starts and takes place till the room temperature. Derivative dilatometric curve ($d\Delta l/dt$) is showing that some effects on the curve are seen. These effects are in accordance with effects on derivative cooling curve (dT/dt) which presents the path of solidification. Fig. 1b is showing shrinkage of casting versus temperature and it is clearly seen that modification of AlSi12 alloy has an effect on shrinkage of casting. The samples with addition of Sr are shrinking less then castings without Sr addition. The reason for lower shrinking must be found in the different solidification morphology of an alloy and ability of feeding of casting. At the same time the Sr addition can cause higher gas porosity in casting which can compensate shrinkage.

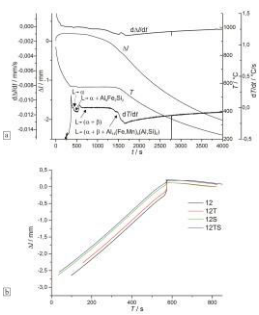

Figure 1: Results of measurement of sample 12 with cooling curve, dilatometric curve and both differentiated curves (a) and dimensional changes of all samples versus temperature (b)

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Thermodynamic stability of microconstituents in AlSi11 alloy

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An AlSi11 alloy (EN AC 44000) belong to the group of "eutectic alloys" and is characterized with relatively low melting point and narrow solidification interval which both brought to the uniformly distributed eutectic microstructure indicating superior mechanical and technological properties [1]. Silicon is one of the most important alloying elements which comprehend to good castability of aluminum alloys. Addition of silicon improves resistance to hot cracks and feeding capability [1,2]. Synergy of influenced alloying and trace elements effect comprehend to different intermetallic phase evolution. The content of secondary alloying elements (Mg, Cu) and trace elements (Fe, Mn, Cr, Zn) significantly influence on solidification manner of an AlSi11 alloy [3-5].

Investigation of an AlSi11 alloy comprehends modelling of equilibrium phase diagram, simultaneous phase analysis and microstructural investigations. Polythermal section of phase diagram of AlSi11 alloy indicates solidification sequence as follows: dendrite evaluation α_{Al} beside precipitation of high temperature intermetallic phases on iron base, silicon (primary and eutectic) evaluation, and precipitation of complex secondary eutectic intermetallic phases $Al_8FeMg_3Si_6$ and Mg_2Si. Since liquid is stable till 566 °C, and secondary eutectic phases evaluation is occurring below this temperature which indicate limited sources and positions for its precipitation. Equilibrium thermodynamic modelling also indicates precipitation of other intermetallic phases such as $Al_{13}Cr_4Si_4$, $Al_5Cu_2Mg_8Si_6$ and Al_3Ni, all below 400 °C as a result of solid state reactions. Metallographic analysis resulted in following microstructural constituents: primary aluminium α_{Al}, main eutectic $\alpha_{Al} + \beta_{Si}$, high temperature iron phase Al_5FeSi, intermetallic phases in form of secondary eutectic Mg_2Si and $Al_8FeMg_3Si_6$.

Correlation of established microstructural constituents with thermodynamic modelling and differential scanning calorimetry indicates thermodynamic stability of particular microstructural components as well as exact solidification sequence for this particular chemical composition.

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Phase and magnetic transformations in cast Fe-Cr-C alloy

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The paper presents the results of phase and magnetic transformations analysis in cast Fe-24Cr-0.8C alloy. The investigated alloy was synthesized in an arc furnace under a high purity argon atmosphere. Microstructure observation in the as-cast state was carried out using scanning electron microscopy (SEM). Analysis of phase and microstructural changes were performed using differential scanning calorimetry (DSC), high-resolution dilatometry and high temperature X-ray diffraction (XRD). Magnetic transformations were analyzed using vibrating sample magnetometer (VSM) and a power signal from dilatometer heating device. The microstructure of the as-cast investigated alloy is composed of primary dendrites with secondary branches of Fe-Cr solid solution with eutectic $M_{23}C_6$ and M_7C_3 carbides in interdendritic zones. Sequence of carbides precipitation and phase transformations were explored. Magnetic transformation from ferromagnetic to paramagnetic material proceed in the range between approx. 600÷750°C and exhibit two maxima in 687°C and 727°C. The obtained results are useful to design new materials from the Fe-Cr-C system, dedicated to work at elevated temperatures.

Atmosphere effects on sintering of steels containing oxygen-sensitive alloying elements

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The possibility of sintering steels containing oxidation-sensitive elements such as Cr, Mn and Si is an opportunity for the Powder Metallurgy (PM) industry that could open the door to a new variety of compositions, properties and prices. However, this is a difficult matter in PM, where the alloying elements are added in the form of powder particles with a high specific surface area available for oxidation. A possible way is to combine these elements with other elements with a lower oxygen affinity – such as Fe- in the form of a "master alloy" powder. The master alloy powder is then mixed with an iron base powder to provide the final composition of the steel after sintering. However, protecting the master alloy particles against oxidation is still a challenge. Recent studies have shown how the reduction of the surface iron oxides from the base powders takes place at temperatures at which these elements are still avid for oxygen, which causes an oxygen transference from the base powder to the master alloys through the atmosphere [1]. Further knowledge on the interaction of these oxygen-sensitive powder particles with different gaseous species from the atmosphere is required to find suitable sintering parameters (atmosphere, temperature, heating rate, etc.) [2].

Thermogravimetry analysis coupled with mass spectrometry has proved to be the most effective method for analyzing the oxidation/reduction reactions at different stages of sintering [3]. Identification of critical temperature ranges with these techniques has provided the tools for an optimum design of the sintering cycles for conventional steels and even for Cr-prealloyed grades [4].

In the present work, thermogravimetry analysis coupled with mass spectrometry are used to assess the effect of the atmosphere on the reduction/oxidation reactions in steels containing oxidation-sensitive elements. A systematic study is presented starting from mixes with elemental Cr, Mn and Si powders in different atmospheres (Ar, H_2, Ar-CO and Ar-CO-H_2 mixes), with a further study on mixes containing Fe-Mn-Si-Cr master alloys. The results allow an accurate description of the interaction between gaseous species, metallic powders with different oxygen affinity and graphite, setting the basis for defining the required conditions for sintering of steels presenting new and challenging alloying compositions.

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Thermal analysis of indefinite chill cast iron modified with ferrovanadium and ferrotungsten

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In roll production optimisation of the technological process is crucial. Alloy modification is a method commonly used when enhancing mechanical or microstructural properties. The addition of heterogeneous nucleation sites refines the given microstructure and enhances toughness of the material. As such, heterogeneous modifying agents must have a high melting point to ensure an appropriate crystal composition for stable atom deposition of the base material from the metal melt. Ferroalloys based on high-melting metals, such as vanadium and tungsten require a longer incubation time in the melt which makes them liable candidates for modification [1]. Thermal analysis (TA) along with thermodynamic modelling using the CALPHAD approach enables a thorough investigation and understanding of the modifying effect.

A trial indefinite chill alloy was prepared using ground ferrovanadium and ferrotungsten as melt modifiers. The alloy was then centrifugally cast to make a cylindrical working layer of a roll. Simple thermal analysis (ETA) of the alloy prior to and after modification was conducted. Samples were then taken from the working layer for metallographic investigation using optical and scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS). Differential scanning calorimetry (DSC) was additionally used for further characterisation of the modified alloy. Using the Boettinger-Kattner [2] model theoretical DTA curves were also calculated which were then compared to the experimental ones in order to understand the sequence of solidification and the impact of modifier addition.

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Non-destructive analyse of phase transformation in shape memory alloys by infrared thermography

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The aim of this article is to study characteristic microstructure, phase transformation and temperature variation to the surface of shape memory alloys [1] specimens cooper base during mechanical charging, using a non-destructive technique: infrared thermography. This analysing method in SMA microstructure is relatively new and is based on tracking evolution of temperature field during tensile tests. Temperature variation were revealed using coupling between infrared camera and mechanical traction machines [2]. For this purpose we use polycrystalline shape memory alloys cooper base (Cu-Zn-Al), in different state at room temperature, which are subjected to cyclic mechanical tests under 3 different strains: 1 %, 2 % and 3.2 %. Mechanical tests are performed in normal conditions of temperature and pressure. All tests are performed following same testing procedure. During the mechanical loading, austenite specimens are transforming partially or totally in martensite specimens revealed by temperature variation. Variation of temperature field on the surface of specimens were analysed by infrared camera during first cycle of mechanical charging. We have measured specific temperature field, with characteristic spatial resolution and temperature variation function of initial state of specimen [3]. Coupling between infrared camera and traction machine give us information to discover initial state of SMA specimens Cu-Zn-Al without any other methods.

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Oxidation resistance of various Ti-alloys

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Since titanium metal first became a commercial reality in 1950, corrosion resistance has been an important consideration in its selection as an engineering structural material. Titanium has gained acceptance in many media where its corrosion resistance and engineering properties have provided the corrosion and design engineer with a reliable and economic material. [1] Titanium, like any other metal, is subject to corrosion in some environments. In this work high temperature stability of Ti and various Ti-alloys was investigated. The best results showed new trademark alloy Ti-exhaust, developed for exhaust application in Akrapovič d.d., whereas the oxidation at 800 °C was 0.41 % and at 900 °C 6,81 %. For the comparison commercial pure Ti-alloy Ti–Gr.2 and some other Ti-alloys were used, whereas the oxidation at 900 °C was much worse and the only comparable Ti-alloy was KS-1,2ASN (Fig.).

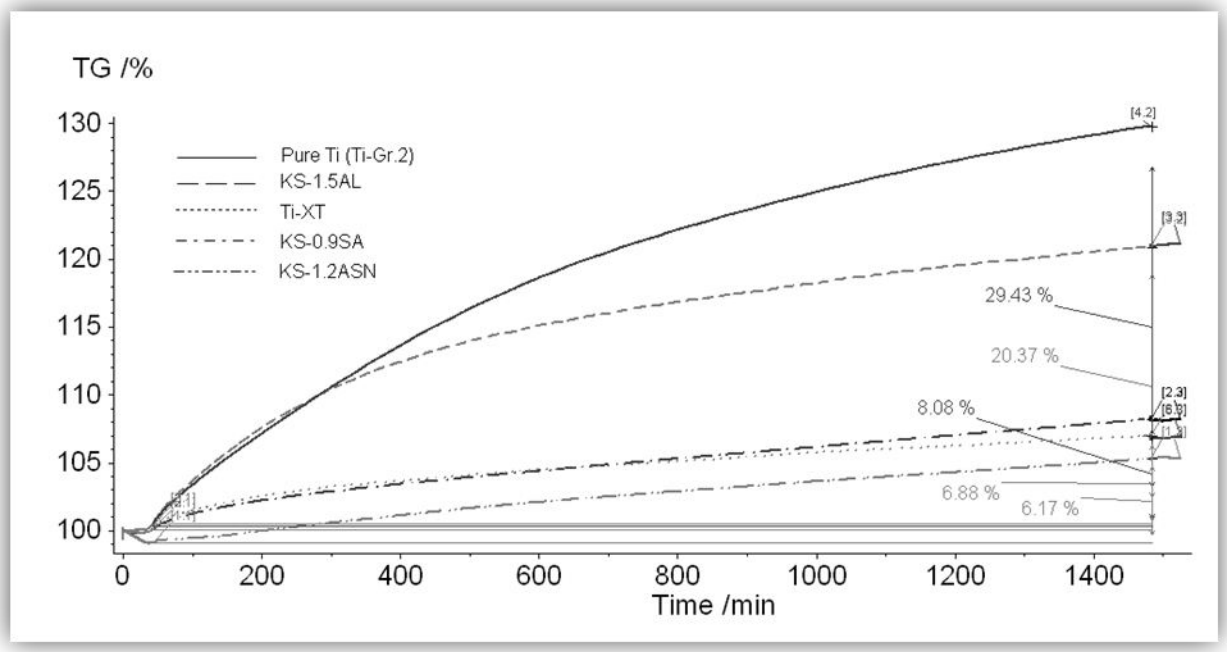

Fig. 1: Thermogravimetric curves of investigated samples at 900 °C for 24 h.

[] Corrosion resistance of titnium, Printed in USA, 1997 Titanium Metals Corporation

A thermal analytical study of the phase stability of unalloyed and alloyed plutonium

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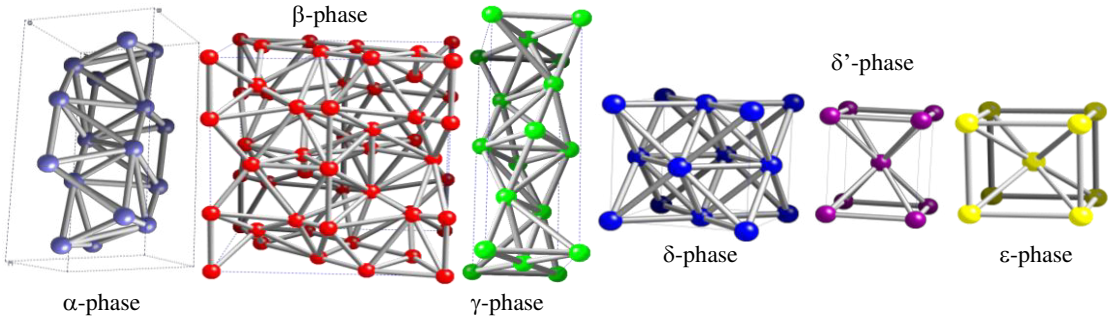
Plutonium is a challenging material even in its elemental form, which is then greatly complicated by the effects of chemical additions and impurities, differences in production, treatment conditions and the consequences of its radioactive decay. The uniquely complex character of plutonium is evidenced by the fact that it can adopt as many as six different allotropic forms between room temperature and its melting point at 640ºC. The transformation from one crystal structure to the next occurs readily for relatively small changes in temperature and pressure and there are large differences in the properties of the phases.



Plutonium allotropes from ambient temperature to its melting point at 640 °C.

The ambient temperature □-phase (monoclinic) is hard, brittle and has a high density, whereas the high temperature □-phase (face centered cubic) is soft and ductile with a 20% lower density than the □-phase. Alloying plutonium with a few atomic percent of an element such as gallium, aluminium, cerium or americium can stabilise the face centred cubic □-phase, which has typical metallic characteristics, from ambient temperature to 450°C. However the □-phase (monoclinic), may be induced to form within the stabilised □-phase depending on the degree of homogeneity of the alloy and the alloying content, thermal treatment and applied pressure.
The focus of my work has been to establish the conditions for reproducible reaction parameters for the solid phase transformations of unalloyed and alloyed plutonium. This work progressed to investigate the transformation kinetics, the reaction paths and mechanisms under a wide range of conditions.

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Oral Presentations 3

Materials: Functional Materials, Ceramics, Metals & Alloys, Cements, Glasses and Polymer Composites

Thermodynamic and transport properties of M_3DyBr_6 (M = Li, K, Rb, Cs) compounds

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Thermodynamic (phase transition temperatures and enthalpies, heat capacity of solid and liquid phase) and transport properties (electrical conductivity) have been determined for M_3DyBr_6 congruently melting compounds that are formed in $DyBr_3$-MBr (M = Li, K, Rb, Cs) binary systems. It was found that K_3DyBr_6, Rb_3DyBr_6 and Cs_3DyBr_6 belong to the group of compounds having two modifications, with two different types of crystal structure. High-temperature modification has cubic, elpasolite-type structure, whereas low-temperature modification has monoclinic, Cs_3BiCl_6-type structures. Transition from the low- to high-temperature modification is a non-reconstructive phase transition. The molar enthalpy corresponding to this transition is relatively small and ranges from 7 to 8 $kJ \cdot mol^{-1}$. The specific behaviour of the relationships: molar heat capacity – temperature, and electrical conductivity of a solid phase – temperature for the compounds under consideration is most likely connected with a disordering of cationic sublattice formed by alkali metal ions taking place in a continuous way. These compounds are stable or metastable at room temperature.

Li_3DyBr_6 with monoclinic crystal structure is the only one compound under investigation that has no solid-solid phase transition.

Experimental temperatures and enthalpies of phase transitions as well as molar heat capacity dependence on temperature for the M_3DyBr_6 congruently melting compounds were used to determine the thermodynamic functions (H_T - H_{298}, $S_{m,T}$, $-(G_{m,T} - H_{m,298}) / T$) of both solid and liquid state.

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The work was financed by a statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of Wroclaw University of Technology. Studies co-financed by EU under the European Social Fund.

Thermodynamic study of the polyselenides $Ln\mathrm{Se}_{2-x}$ (*Ln* = Sm, Gd, Dy, Ho)

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Characteristic property of rare-earth polyselenides of $Ln\mathrm{Se}_x$ composition ($1.5 < x < 2.0$) consists in ability of selenium atoms to create low-dimensional structures in anion sublattice. This ability is revealed in a rich variety of superstructures whose period grows with decrease of x. The displacement of selenium atoms in new positions of superstructures results to charge density wave formation and under external fields the electronic-structural transitions can take place in such superstructures. Thanks to this phenomenon rare-earth polyselenides show anisotropy of physical properties and have ability to the same interesting behavior, as the compounds with cationic clusters. For experimental investigation of their properties the high-quality crystals of rare-earth polyselenides are needed. These crystals are difficult to obtain without knowledge of the thermodynamic parameters (p_{Se}-T-x) which define the conditions of their growth.

Earlier we have investigated the light (La, Ce, Nd, Pr) rare-earth polyselenides and revealed the regularity in the change of solid phase compositions under stepwise removing the selenium atoms from anionic lattice: $Ln_n\mathrm{Se}_{2n-1}$ where n is equal to 5, 7, 10, 20 [1]. The aim of this work is to clarify the implementation of this regularity for heavy (Sm, Gd, Dy, Ho) rare-earth polyselenides and to obtain for them a set of standard thermodynamic functions.

The initial samples for investigation were the single crystals of higher polyselenides of Sm, Gd, Dy and Ho. The selenium vapour pressure over samples studied has been measured by static method with quartz membrane-gauge manometers. Limiting errors in values of pressure, temperature and solid phase composition were 0.5 Torr, 1 K and 0.01 formula units, accordingly. The measurements have been realized in the wide intervals of temperature ($758 \le T/\mathrm{K} \le 1298$), pressure ($1 \le p/\mathrm{Torr} \le 760$) and composition ($1.5 \le x/\text{f. u.} \le 1.9$).

The detailed thermodynamic study has revealed that the phase regions in the studied composition intervals consist of discrete intermediate phases whose stoichiometric composition can be described by the same general formula $Ln_n\mathrm{Se}_{2n-1}$ found earlier for light rare-earth polyselenides but with somewhat another set of n values (n = 3, 4, 5, 7, 8). The main result of this study is the thermodynamic parameters (p_{Se}, T) which define the fields of stability and the growth conditions of homogeneous polyselenide phases. These fields are very narrow for the polyselenides with small n values therefore it isn't surprising that they weren't still synthesized. A set of thermodynamic characteristics ($\Delta_f H_{298}$, S°_{298}, $\Delta_f G^\circ_{298}$) obtained in this work can be used for thermodynamic simulation of crystal growth processes of Sm, Gd, Dy and Ho polyselenides.

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Thermal treatment influence on structure, texture and oxidation of ZnS precipitate

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Zinc sulphide (ZnS) has applications in various fields: luminescent materials, sensors, solar cells, semiconductors and photocatalysis due to its electronic properties, which can be tuned easily by slight variation of composition, crystalline structure and particle size [1].

In this work, the effect of heating temperature on the structure and size of ZnS nanocrystals prepared by chemical precipitation method were studied. Thus, aqueous solutions of $Na_2S{\cdot}9H2O$ with pH of 8 (controlled by adding of glacial acetic acid) and $ZnSO_4{\cdot}7H2O$ (Na_2S: $ZnSO_4$=4:1 molar ratio) were used. The precipitate from a part of the suspension was separated by centrifugation (denominated ZnS-P) and the other part of suspension was heated to 200 ° C in an autoclave before centrifugation (denominated ZnS-C). The both solid samples were washed and dried under vacuum at 65 ° C for 8 hours. The heating was used to improve the crystal quality and to stabilize their structure.

The structure and texture of ZnS-P and ZnS-C were studied by XRD, SEM-EDX and low temperature nitrogen adsorption technique. The XRD patterns had shown a single phase of sphalerite in both samples, but with narrow and stronger diffraction peaks for ZnS-C, in agreement with the particle size of 7.5-8 nm for ZnS-P and 70.1 nm for ZnS-C.

The texture parameters are: specific surface area S_{BET}= 70.3 m^2/g, V_p=0.168 cm^3/g and the curve of pore diameter with maximum at 9.4 nm for ZnS-P, respectively, S_{BET}= 13.8 m^2/g, V_p=0.040 cm^3/g and the pore-size distribution curve with maximum at 3.4 nm for ZnS-C.

Nano-ZnS could be oxidized easily in the process of preparation and application, causing the degradation of its performance depending on the rate of oxidation. For that reason the kinetics of oxidation was studied through non-isothermal thermogravimetric method according to [2]. The Friedman isoconversional method (differential model-free) was used for checking the activation energies because this provides more accurate values of activation energies compared with the integral model-free methods [3].

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Enthalpies of solution and enthalpies of fusion of organic compounds: nothing in common or close relations

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The enthalpies of "liquid-gas" and "solid-gas" phase transitions are fundamental characteristics of chemical compounds. Knowledge of these values is of great importance for different fields of chemistry and physics. They have practical application in separation process, studies of solubility of substances and their distribution in environment. Numerous experimental techniques have been developed for determination of phase transitions enthalpies. Their advantages and disadvantages are well documented in the literature. However, there is another way for determination of phase transitions enthalpies directly at 298.15 K without heating and transfer of compounds to the gas phase. In our previous works [1-2] we proposed the method of determination of vaporization/sublimation enthalpy through the measurements of solution enthalpies of studied compound in different solvents. The method is based on the general relationship between vaporization/sublimation enthalpy of compound and its enthalpies of solution and solvation in any solvent.

Enthalpy of solution can be measured experimentally using different experimental techniques (solution calorimetry, gas chromatography and etc.). The problem is how to obtain enthalpy of solvation. Group-additivity scheme for calculation of solvation enthalpies was developed on the basis of experimental and literature data. According to this scheme enthalpy of solvation is calculated as a sum of additive contributions of fragments that construct the molecule of interest. Solvation enthalpy calculated by this way together with solution enthalpy at 298.15K allows to determine enthalpies of vaporization and sublimation of any aromatic compound directly at 298.15K. Method proposed in this work was tested on a number of pyridine and aromatic hydrocarbons derivatives.

Enthalpy of solution of crystalline solutes in any solvent includes the contribution of crystal package breaking. Enthalpy of fusion of these compounds has the same meaning. In this work we have compared enthalpies of solution and enthalpies of fusion of different organic molecules. Some general relations between these data were found. They can be used to predict one value from another without any temperature adjustment.

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Thermodynamic analysis of transcritical CO_2 refrigeration cycle

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Carbon dioxide (CO2) has been widely investigated for use as a working fluid in refrigeration cycles, because compared to conventional refrigerants such as HCFCs (R22) or HFCs (R134a and R404A), CO2 is more environmentally friendly due to its zero Ozone Depletion Potential (ODP) and very low direct Global Warming Potential (GWP < 1), therefore attaining favourable thermo-physical properties.

Carbon dioxide as a safety and green natural refrigerant has many excellent advantages such as no toxicity, no inflammability, lower price, higher density, latent heat, specific heat, thermal conductivity and volumetric cooling capacity, and lower viscosity. However, CO2 has a relatively high operating pressure due to its low critical temperature (31.1 C) and high critical pressure (73.8 bar).

Alongside all the other application areas, CO2 has recently acquired significant attention for its application in supermarket refrigeration.

The objective of this paper is to investigate the performance of a transcritical CO2 compression refrigeration cycle for different parameters and evaluate its COP. To achieve that, a refrigeration cycle was modelled using thermodynamic concepts. Then, the model was simulated for various parameters that were manipulated to investigate the cycle performance.

Simulations were conducted using Engineering Equation Solver (EES) developed program. The results can be used in the design of CO2 refrigeration cycle.

Is classic combustion calorimetry in danger of extinction?

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A key problem in chemistry is to predict the feasibility of a chemical reaction with respect to a good yield of a product in a reasonable time. Knowledge of enthalpies of formation, is particularly important because they contribute to the relative thermodynamic stability of the species involved in a chemical reaction. The conventional method for measuring enthalpy of formation of stable species in the condensed state (solid or liquid) have been largely combustion bomb calorimetry. Regrettably, that there are very few labs in the whole world still remain currently involved in the thermochemical studies with the goal of measuring enthalpies of formation. In the Europe (except for Rostock) there are still two working groups in Portugal. Some very active in the past working groups in Madrid and from the post-USSR are also practically disappeared. *Is there any reason for such an extinction of the thermochemistry from the scientific landscape?*

May be one of the possible explanation could be a reasonably sophisticated calorimetric equipment which required special knowledge as well keeping alive a certain traditions and the knowledge transfer from generation to generation of scientists working with these devices. Another important issue could be the amount and purity of samples required for combustion calorimetry. For the successful experiment about 10 g of the sample with the purity better than 99.9% are usually used. The reliable experimental determination of the standard molar enthalpy of formation is difficult due to highest sensitivity of this property to ever possible experimental inaccuracy (e.g. small amount of an impurity, even less than 0.05%, in a sample for combustion experiment is able to falsify the value of the measured enthalpy of formation up to 20-30 $kJ \cdot mol^{-1}$). As a rule compounds with structural peculiarities which are interesting for the thermochemical studies could be obtained by colleagues from organic chemistry only with very poor yields. That is why the option to synthesise 10 g of the extremely pure compound and to convert it into CO_2 and H_2O during the combustion experiments attract very restricted interest from synthetic chemists or chemical companies without an additional financial stimulus for a customer synthesis.

As a rule the accuracy of measurements of the energy released in a calorimeter is required to be close to 0.01%. In order to reach such a precision, the commercial combustion calorimeters are usually modified in scientific laboratories towards stabilization of the temperature constancy in water bath as well as enhancement of the temperature resolution inside the insulated container. However, recent constructive developments of the some commercially available combustion calorimeters meet requirements for using this device for highly precise scientific measurements. For example, we tested precision and accuracy of the commercial Parr-6200 calorimeter with a set of 5 substances. Results of the test measurements have definitely revealed that accuracy close to 0.01% could be achieved with the commercial calorimeter, furnished with the Pt-crucible, provided that weightings procedures are performed at the level of 0.00001 g for the sample and 0.01 g for the water amount in the system.

Development of calorimetric methods for the characterization of different aqueous de-icers

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Recent research work regarding the characterization of different aqueous de-icers using calorimetric methods will be presented. A dynamic DSC procedure based on [1, 2] was developed to determine the thermal properties (freezing point, melting enthalpy) of aqueous brines. Phase change temperatures were characterized for the eutectic melting peak by the onset temperature. And for the broad melting peak, two temperatures were determined, the peak maximum temperature and the temperature corresponding to the inflection point of heat flow curve, which represents the end of the phase change [3].

Heating rates of 0.2, 0.5 and 1.0 K/min were used to extrapolate the characteric temperatures at the null heating rate. For each sample, at least three runs were performed to check the reproducibility. Thermal analysis was conducted with Setaram microDSC and with Netzsch DSC. Additionally the influence of different kind of sample cells were compared.

The results demonstrated that the developed calorimetric method is suitable for the characterization of aqueous de-icers. Our studies confirmed that the enthalpy of fusion is suitable to assess the performance of aqueous de-icers [4]. The extrapolated temperatures at null heating rate matched literature values very good [5]. An empirical correlation between enthalpy and ice melting capacity described in literature [6], was attested qualitatively.

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Complementarity between methods of thermal analysis for the study of water intercalation into the crystal structure

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Phenomena of water intercalation (reversible introduction of water molecules into the interlayer space) is intensively investigated due to significant difference in physical and chemical properties of intercalates and parent crystal structures. Among such properties are conductivity, catalytic and photocatalytic activity, thermal stability, reactivity of solids. Intercalation of water molecules could occur in aqueous medium and humid atmosphere and could be investigated by two ways – a study of the hydration of compounds and study of the dehydration of intercalates.

Herein it will be presented advantages of complementarity between methods of thermal analysis and calorimetry for the investigation of water intercalation into the structure of promising photocatalysts.

TG, DSC, STA-QMS, HT XRD, water sorption analysis were used for the estimation of the deviation in content and structure during hydration, energetic characteristics of hydration/dehydration, temperature and RH regions of the stability of intercalates.

Examples of complex investigation of perovskite-type layered titanites $A_2Ln_2Ti_3O_{10}$, tantalates $ANdTa_2O_7$ and niobates $ANdNb_2O_7$ (A = H, Li, Na, K, Rb, Cs) reveal the presence of intercalated water only in the structure of tantalates and niobates with sodium cations and protons in the interlayer space. Titanates are able to undergo protonation (substitution of alkali cations to protons) and intercalation of water molecules into the interlayer space. It was found that the protonation is typical for all forms of layered titanates. In addition to the protonation process the intercalation of water into the interlayer space was observed for $K_2Ln_2Ti_3O_{10.}$ Thus, titanates exist in aqueous solution in the form of compounds with the general formula $H_xK_{2-x}Ln_2Ti_3O_{10}*yH_2O$ or $H_xA_{2-x}Ln_2Ti_3O_{10}$ (A = Li, Na). XRD and TGA showed the existence of stable forms of intercalated compounds in different temperature ranges and determined the content of water in each sample. The method of simultaneous thermal analysis (TGA + DSC) combined with mass-spectrometric analysis of the gas phase served as evidence that the weight loss under heating is caused by water liberation. The thermal desorption and deintercalation effects were determined. Results of different methods correlate and conferm each other.

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Dielectric, mechanical and heat capacity spectroscopy of an epoxy and hyperbranched polymer system

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In this work we examine the molecular mobility associated with the glass transition and the secondary relaxations of a system based upon an epoxy resin cross-linked with an amine-terminated hyperbranched polymer (HBP). The HBP is a commercial polyethyleneimine, Lupasol PR8545, with a molecular weight of 2000 g/mol, and the epoxy resin is a commercial diglycidyl ether of bisphenol-A (DGEBA), DER331, with an epoxy equivalent in the range 182 to 192 g/eq. The molecular dynamics have been studied by dielectric analysis (DEA), dynamic mechanical analysis (DMA) and by differential scanning calorimetry (DSC) and temperature modulated DSC (TOPEM). The samples studied include the neat HBP, the neat epoxy, the stoichiometric mixture of HBP and epoxy (ELP) in the uncured state and during a dynamic cure at constant heating rate, and the fully cured HBP/epoxy system.

The HBP and the epoxy both show two secondary relaxations by DEA: a γ-relaxation, with activation energies of 41.5 and 27.7 kJ/mol, respectively, and a β-relaxation, with much higher activation energies of 167 and 80 kJ/mol, respectively. The glass transition for the epoxy has an apparent activation energy of 306 kJ/mol by DEA and 358 kJ/mol by DMA, in reasonable agreement, whereas the HBP has a much higher apparent activation energy by DMA (209 kJ/mol) than by DEA (63 to 78 kJ/mol), implying a quite different molecular origin for the dielectric and mechanical relaxations.

The uncured mixture, ELP, also displays two secondary relaxations, which correspond closely with those of the neat epoxy, but differ significantly from those for the HBP, implying that the epoxy dominates the molecular mobility in the mixture. The α-relaxation in the ELP mixture is complex: the relaxation is seen as a combination of two peaks, which correspond to the glass transitions of the two phases which are seen by optical microscopy in the uncured mixture. The higher temperature peak, corresponding to the epoxy-rich phase, closely mirrors that of the neat epoxy, while the peak corresponding to the HBP-rich phase does not shift with frequency. The α-relaxation is followed by the curing reaction, in which a peak due to vitrification is seen by DEA, at a temperature which is consistent with that seen by TOPEM in a lower frequency range.

The fully cured system, when cured isothermally in two steps, displays two glass transitions in DEA, corresponding to the two phases observed in the ELP mixture. These two glass transitions are also seen by DSC and TOPEM, occurring at temperatures which are consistent with those found by DEA at higher frequencies. Strangely, the DMA results only show a peak corresponding to the lower glass transition temperature.

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The technique of multicomponent phase diagrams construction with volatile and aggressive components

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Investigations of systems with volatile and aggressive components such as S, Sn, As, etc. are of high level importance for metallurgical and technological purposes. But volatility of these elements and tendency to react with different materials create the methodological difficulties under providing investigation with applying of experimental techniques. For this reason there is a lack of available papers, devoted to construction of phase diagrams with S and Sn, especially for Fe-Cu-S and Fe-Sn-S systems [1-3].

Based on the long-time experience in construction of phase diagrams, authors of this work proposed the technique of thermoanalytical investigation of systems with volatile and aggressive components, combining the standard DSC cell and quartz ampoule. At described technical solution sealed quartz ampoule is placed directly in the standard alumina DSC crucible. Thus, the mass of the investigated material is minimized, allowing receiving more correct results due to the decreasing of thermal gradient through the sample volume. From the other hand, quarts tube prevents the interaction between aggressive S, Sn and platinum wires of differential thermocouple. Discussed technique can be implemented in any modern thermoanalytical device, independent from company – manufacturer.

Proposed technique coupling with standard methods of phase diagrams construction (DSC, SEM, EPMA, and XRDA) is used for investigation of phase transformation in Fe-Cu-S and Fe-Sn-S systems. The results of this work are liquidus surfaces projections of the ternary Fe-Cu-S and Fe-Sn-S systems in a wide range of compositions.

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Rules of the formation of supermolecular structures in the presence of a non-selective β-nucleating agent in isotactic polypropylene

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Commodity iPP has several crystalline modifications, like the monoclinic α-, the trigonal β- and the othorombic γ-modification. iPP crystallizes into α-form under conventional processing conditions. The formation of β-modification can be induced by nucleating agents, which can be either completely selective to the β-modification like Ca-suberate and Ca-Pimelate, or may have dual nucleating ability resulting in mixed polymorphic composition like N,N'-dicyclohexyl-2,6-naphthalene-dicarboxamide [1]. In fact most of the β-nucleating agents available recently have dual nucleating ability [2,3] thus the polymorphic structure formed in their presence depends predominantly on the conditions of crystallization. The nucleating agents developed recently are often partially soluble in iPP in order to ease their dispersibility in the melt during processing. Therefore the structure form in the presence of a soluble nucleating agent with dual ability depends both on the recrystallization condition of the nucleating agent as well as the thermal conditions like melt temperature and cooling rate.

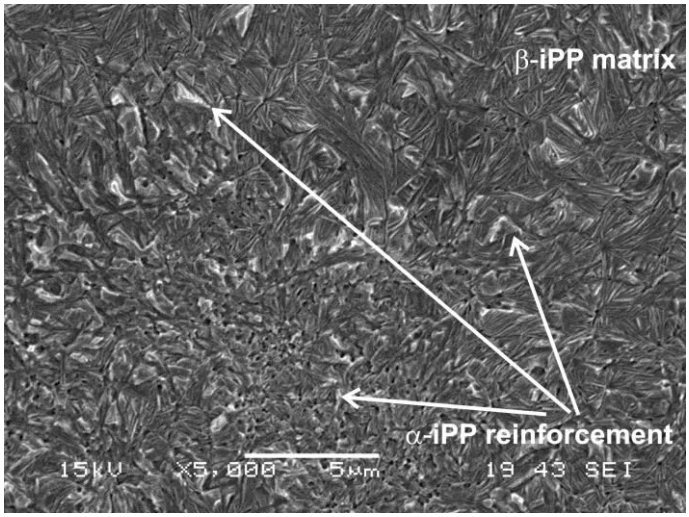

Fig 1 *Supermolecular structure formed in thin film melted at 250 °C and cooled to room temperature at 40 °C/min (300 ppm nucleating agent)*

Calorimetry (DSC), polarized optical microscopy (POM) and scanning electron microscopy (SEM) was used for detailed characterization of the crystallization process and the structure formed in the presence of a soluble nucleating agent possesses dual nucleating ability. It was found that the α- and β-modifications develop simultaneously in the early stage of crystallization, but α-iPP includes into the β-phase due to its slower growth rate (Figure 1). Consequently, this polymorphic structure has good impact resistance without decreasing of stiffness.

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Low temperature oxidation of carbon thin films, as evidenced by the real time thermo-optical measurements

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One of thin films´ characteristic features is their low sheet mass density which sets certain limits to an evaluation of films´ thermal properties by the classical methods of thermal analysis. In this contribution we tentatively do a kind of thermal analysis measuring the carbon films´ optical transmittance (OT) in order to be able to follow the carbon combustion to a range of the very thin films. The carbon films containing the graphite related phases (domains) are especially suitable samples for this kind of analysis since they yield robust changes in the optical signal even at film thickness deeply in the submicron range. In measurements the 200 nm thick carbon films underwent the controlled oxidation (combustion) at temperature of 300 °C. The samples were horizontally placed in the upward air stream of an electric oven. The films were deposited by vacuum arc plasma method. In separate measurements the films were heated and subsequently quenched at different time intervals. The purpose was to capture various films oxidation states using additional characterization methods like film thickness measurement, UVVIS, Raman spectroscopy, AFM and SEM. The optical transmission method operated with a simple optical scheme using a beam of modulated LED (λ=624 nm), passing the sample by a normal incidence angle. The light beam intensity was detected with standard Si photodiode. By curve fits, the obtained OT curves were ascribed as a convolution of the two ascending sigmoidals, with only a small time interval of their overlay (R2=0.9996). The first sigmoidal is of the slow OT increase and the second one of the rapid OT increase. Importantly, according to the film thickness measurement only the second wave portion of the OT curve (the second OT sigmoidal) is associated with the own combustion process. Rather to surprise, the prolonged small rate, small OT increase processes are necessary to be finished before the own film combustion can proceed. On the other hand, the second wave of the OT curves proves that the thin carbon film combustion can be controllably maintained for the prolonged time, i.e., at a small rate. The kinetic interpretation of OT curves is problematic yet since the OT signal is primarily composed of the light absorption and light scattering contributions. Especially the light scattering contributions are hard to be deliberately accessed because of the plethora of the carbon nanostructure arrangements.

Measurement of Thermophysical Properties on Thin Film Materials

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Due to new research efforts in the field of thin film materials with a focus on size effects, there is a growing need for measurement setups dedicated to samples with small geometrical dimensions like thin films and nanowires with considerably different physical properties than bulk material. The characterization of these samples is important to learn more about their structure and conduction mechanism but also important for technical applications e.g. in the semiconductor industry.

We report about new developments to characterize thermoelectric thin films. The presented chip based system measures simultaneously the electrical and thermal conductivity, the Seebeck Coefficient and the Hall Constant of a thin film sample in the temperature range from liquid nitrogen up to 350°C. Due to the simultaneous measurement at only one sample, errors caused by different sample compositions, different sample geometries (thickness) and different heat profiles can be avoided. The system consists of two main parts, a structured Si-wafer and a suitable measurement setup [1]. The sample deposition and handling is kept easy and optimized to meet a very broad range of use.

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High-temperature behaviour of novel ceramic Hf-B-Si-C-N films

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Using magnetron sputtering, which is one of the plasma technologies, it is possible to prepare new advanced thin-film materials from multi-element system which exhibit unique combination of physical and functional properties. The ability to maintain these properties at elevated temperatures in various environments is essential for many industrial applications. The efficient way how to investigate the high temperature behaviour of a material is to combine thermogravimetric analysis, where the mass changes during heating are practically continuously recorded, with additional ex-situ analyses.

Recently, we have shown that a silicon addition into Hf-B-C films can result in the films with a high hardness of ~22 GPa, low electrical resistivity of 6 μΩm and excellent oxidation resistance in air up to 800°C [1]. In this study we investigated the oxidation resistance and thermal stability of novel magnetron sputtered Hf-B-Si-C-N films. The oxidation resistance of these films was investigated in synthetic air using a symmetrical high-resolution Setaram TAG 2400 thermogravimetric system during dynamical heating. The attention was also paid to the thermal stability of the electrical resistivity and hardness of these films. In addition, changes in the structure, elemental composition, microstructure and surface morphology of the films subjected to oxidation tests were analysed by X-ray diffraction, Rutherford backscattering spectroscopy, high-resolution transmission electron microscopy and optical microscopy.

Based on the nitrogen content in the gas mixture during deposition, the Hf-B-Si-C-N films can be divided into two groups. The films prepared at a N_2 fraction from 0% to 10% in the gas mixture exhibit hardness about 22 GPa and electrical resistivity ranging from 4 to 1500 μΩm. Thermal stability of these properties is high and reaches 950°C in air when the films are dynamically heated. A further increase of the N_2 fraction in the gas mixture leads to a rapid growth of the electrical resistivity up to non-measurable values and a slight decrease of the hardness. Such films exhibit, however, the highest oxidation resistance with negligible mass changes up to 1500°C. The mechanism of the oxidation process of these materials will be also discussed.

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Thermal investigations on Ag2S thin films by Electropyroelectric technique

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Thermal properties have long been recognized as potentially transformative parameters due to their role to transfer heat energy. First, we present a theoretical model of the new so-called electropyroelectric technique in the front detection configuration (FEPE) for thermal parameters investigation of semiconductor thin films [1]. A normalization procedure relative to an empty pyroelectric sensor is used. Then, we determine thermal conductivity and thermal diffusivity of silver sulphide (Ag2S), using the best concomitance between experimental and theoretical curves, while giving the normalized amplitude and phase variations versus modulation frequency offered by EPE technique.

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Thermal modification of polyfurfuryl alcohol-montmorillonite (PFA-MT) nanocomposites as precursors of porous carbon materials

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Clay-polymer nanocomposites (CPNs) have become the subject of intensive studies in many fields of science and industry. The application of layered aluminosilicates as inorganic fillers in CPNs usually leads to improve physical, mechanical and chemical properties of polymers, e.g. thermal stability, stiffness and strength, flame retardancy, biodegradability, gas barrier and electrical properties [1]. However, polymer-inorganic composites can also be used in preparation of mesoporous carbons. One of the best known example of such materials is ordered mesoporous carbon CMK-3, obtained based on mesostructured silica SBA-15, being a hard template, and polymeric carbon source (e.g. sucrose, polyfurfuryl alcohol, polyacrylonitrile) [2]. In the presented work, thermal decomposition of polyfurfuryl alcohol-montmorillonite (PFA-MT) nanocomposites was studied. The structural properties of porous carbons, obtained by removal of clay template, was also discussed. Such materials can be used as attractive and low-cost carbon adsorbents, catalysts and electrode materials for lithium ion batteries.

A series of PFA-MT nanocomposites was synthesized by in situ polycondensation of furfuryl alcohol in the presence of natural montmorillonite. In syntheses, various PFA/MT mass ratios (1:1, 2:1 and 3:1) were used at a constant concentration of monomer solution (5 wt%). In each case, the polycondensation reaction was catalyzed by an addition of hydrochloric acid. The PFA/MT nanocomposites were characterized by thermal analysis (TGA). The thermogravimetric measurements were performed in an inert and oxidative atmosphere in order to determine a real content of polymer and its thermal stability as well as to find optimal conditions of further thermal modification of the formed PFA-MT materials.

The obtained composite materials were carbonized at elevated temperature, and then the aluminosilicate template was leached two times by sodium hydroxide and hydrofluoric acid. The XRD results revealed that exfoliation of clay structure in the PFA-MT composites (before and after carbonization) with the higher PFA content was observed. The final carbon materials exhibited a high BET surface area (above 350 m^2/g), resulting mainly from a presence of slit-shape mesopores.

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Application of thermal analysis in the study of organoclay nanocomplexes

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The delamination of kaolinite is a „hot topic" in the light of its possible application as nano-additive in polymers, rubber, etc. Complete delamination of the mineral can be achieved through stepwise intercalation and it is also possible to make halloysite-like nanotubes from the delaminated kaolinite sheets.

Among the analytical techniques used for the characterization of the nano-complexes formed (e.g. XRD, FTIR, Raman microspectroscopy, TEM, etc.) thermal analysis plays a key role. Intercalation complexes made with potassium-acetate, hydrazine, dimethyl-sulphoxide, urea and formamide can be quantitatively characterized by thermal analysis. In addition, the use of controlled rate thermal analysis (CRTA) offers a unique possibility to separate (surface) adsorbed and intercalated reagents. Also, the steps of the delamination process with multiple intercalation can be followed with thermal methods.

Delamination of the TOT-type minerals (e.g. montmorillonites) can be made with ion exchange through the replacement of the interlayer cations with long-chain (e.g. alkyl-ammonium) ones. In this case the interlayer distance can be controlled and the hydrophilic nature of the mineral can be modified and converted to hydrophobic one. With the adsorption of non-polar compounds onto the surface, composites suitable for the removal of hazardous compounds (e.g. phenols) from waters and waste waters can be produced. Again, the use of thermal analysis is indispensible when the evaluation of thermal stability and the quantitative characterization of these complexes are necessary.

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Nanocrystalline anatase derived from modified alkoxide mesostructured gel

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A sol prepared by chelation of titanium *n*-butoxide, $Ti(OC_4H_9)_4$, with ethyl acetoacetate, $C_6H_{10}O_3$, in 1:1 molar ratio was slowly hydrolyzed and the obtained gel was thermally treated in order to produce anatase. The gel and thermally treated samples were investigated by means of Fourier transformed infra-red spectroscopy (FTIR), X-Ray Diffraction (XRD), Differential Thermal and Thermogravimetric Analysis (TGA/DTA), N_2 adsorption-desorption isotherms, Field Emission Scanning Electron Microscopy (FESEM) and High Resolution Transmission Electron Microscopy (HRTEM). From the results obtained, gel structure and gel crystallization behavior as well as crystallized sample properties are discussed.

It was determined that modified alkoxide is partially hydrolyzed leaving small amount of butoxide and ethyl acetoacetate groups attached to titanium. XRD pattern of gel exhibited broad, low-angle reflection, which indicates the existence of some degree of ordering on the mesostructure scale. HRTEM of the gel also revealed the presence of mesostructure. Observed mesostructure was found to be consisted of inorganic-organic nanoclusters, exhibiting some polydispersity in the size and variations in composition. The random packing of nanoclusters enables development of three-dimensional mesostructured framework.

Thermal decomposition of the complex in air up to 1000 °C shows seven decomposition steps: evaporation of water and butanol at ~110 °C, elimination of ethyl acetoacetate at ~180 °C and butoxy groups between 200 and 300 °C, carbonate removal at 380 °C, crystallization of anatase at 420 °C and its transformation to rutile between 655 and 800 °C and, finally, oxidation of carbonaceous species between 600 and 1000 °C. Thermal treatment at 200 °C yielded with collapse of the mesostructure and disappearance of low-angle XRD peak.

After thermal treatment of the gels at 350 °C for 2 h, pure nanocrystalline anatase was obtained with average crystallite size of 16.4 nm. A nanocrystalline character of prepared anatase was confirmed through HRTEM micrographs revealing the exposed {101} facets. Nitrogen absorption/desorption isotherms and pore size distribution of sample thermally treated at 350 °C is of type IV, typical for porous aggregates of anatase nanocrystals, with a relatively narrow pore size distribution in the range of mesopores. Relatively low specific surface area of 26.09 $m^2 g^{-1}$ was ascribed to the reduction of mesopores volume due to blockage with carbonaceous material.

Epoxy-matrix composites filled with surface-modified SiO_2 nanoparticles

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To prepare polymer-matrix composites with good mechanical properties, inorganic fillers are modified by coupling agents in order to create an interphase. Composites based on epoxy resin and commercially available SiO_2 nanoparticles were prepared. Nanoparticles were previously treated with a coupling agent, 3-glycidyloxypropyltrimethoxysilane (GLYMO), dissolved in toluene or in ethanol/water mixture (1/1 volume ratio). Successful modification of the nanoparticles was confirmed by infrared spectroscopy (FTIR), which displayed bands characteristic of C-H and epoxy group, and combined differential scanning calorimetry and thermogravimetric analysis (DSC-TGA), which showed the additional mass loss due to organic modification.

Composite materials were prepared by adding 0,5 – 5 phr (parts per hundred parts of resin) of nanoparticles into an epoxy resin (diglycidyl ether of bisphenol A) which was then cured with a poly(oxypropylene) diamine. Curing was followed by DSC, and cured materials were characterised by tensile and hardness testing. Morphology of fractured surfaces (after tensile testing) was investigated by scanning electron microscopy (SEM). Thermal stability of cured materials was studied by TGA, and their glass transition temperature determined by DSC.

Presence of the filler does not influence the curing mechanism of epoxy resin. All composites show improved mechanical properties (both hardness and tensile) in comparison with unfilled resin, especially for smaller nanofiller content, which can be explained by better dispersion of unmodified nanoparticles at lower contents. Poor dispersion at 5 phr is clearly visible in SEM micrographs. Samples prepared with nanoparticles modified in ethanol/water mixture exhibit significant increase of elongation at break, instead of brittle fracture characteristic of cured epoxy resin. We suggest that modified nanoparticles form loosely bonded agglomerates which act as a separate, elastic phase and have a toughening effect on the epoxy matrix. Glass transition shifts to higher temperatures in composites, and they exhibit improved thermal stability.

One pot synthesis of tungsten bronze nanoparticles for heat-ray shielding

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Recently, much attention has been attracted for the smart windows to reduce the energy consumption for air conditioning, and, thereby, to decrease the carbon dioxide emission by shielding the heat-ray from the sunlight into the room in summer, and from the room to the outside in winter for automobiles, buildings, etc. Nowadays, the thin films of various nanosized conductive compounds such as silver, indium tin oxides (ITO) , etc. are widely used as solar filters, however, the performances of the these materials are not satisfactory. We focused the attention on the hexagonal tungsten bronze compounds with the chemical formula of M_xWO_3 consisting of the mixed valence of W^{6+} and W^{5+}, where M is alkali metal ion which locates in the space of the WO_3 layer. In the present paper, the monodispersed nanocrystals of tungsten cesium were directly synthesized by the solvothermal reaction using an ethanol-acetic acid mixed solution as a reaction solvent.

After dissolving a certain amount of WCl_6 in the dehydrated ethanol-acetic acid mixed solution, CsOH was introduced to precipitate an amorphous precursor, followed by heating in an electric oven around 240^{o}C for 20 h, where the amounts of acetic acid in the solvent were adjusted to 0-40 vol.%, and concentration of WCl_6 was adjusted to 0.015 M with nominal Cs/W atomic ratio of 0.5. During the solvothermal reaction, the etherification of ethanol and esterification reaction between ethanol and acetic acid proceeded to generate water, which plays an import role on the crystallization of the product. By controlling the amount of acetic acids, it was possible to control the amount of water generated, and consequently, control the particle size, morphology and agglomeration of the products.

The thin film constructed with well-dispersed Cs_xWO_3 nanocrystals showed excellent visible light transparency as well as near infrared ray shielding performance. The simulated experimental results confirmed the heat-shielding performance of Cs_xWO_3 film superior to commercial ITO glasses, indicating the high-potential as a heat-ray filter. It was also confirmed that the nanoparticles of various tungsten bronze compounds, such as Na_xWO_3, K_xWO_3, $(NH_4)_xWO_3$ and $W_{18}O_{49}$ could be synthesized via similar solvothermal reactions, and all of them showed excellent heat-ray shielding abilities.

Leak testing of carbon-tin nanocomposites by thermal analysis methods

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In relation to the available anode materials, tin has been shown as one of the best alternatives due to its lithium uptake at low potential and high theoretical capacity (994 mAh/g for $Li_{4.4}Sn$ phase) [1]. However, the major problem during formation of Li_xSn_y alloys is cyclic volume changes, reaching up to 300% [1], which lead to the loss of electrical contact between active material and current collector. One of the ways to overcome this issue is development of tin-carbon nanocomposite, in which nanometric tin grains will be encapsulated in a flexible and conductive carbon layers matrix [2-4]. Nevertheless, such nanocomposites are able to provide appropriate electrochemical properties, only if the formed carbon layer is leak-proof, flexible and porous enough to compensate volume changes.

The goal of the present work was to perform the leak testing of two types of C-Sn nanocomposite anode materials by thermal analysis methods as well as comparison of their morphological and electrochemical properties.

Electrode materials consisted of tin-based nanograins encapsulated in a different origins carbon buffer matrix (starch or water soluble polymer) were obtained in a simple and inexpensive process. The tin precursor was synthesized using a modified reverse microemulsion technique (w/o) and then coated by a source of carbon [2-4]. The C/Sn precursors were pyrolysed, affording formation of tin-based nanograins encapsulated in conductive carbon buffer matrix. In order to verify the structure of the resulting nanocomposites the X-Ray diffraction studies (XRD) were performed. The morphology of the samples was characterized by low-temperature nitrogen adsorption method (N_2-BET). Thermal analysis methods (EGA-TGA/DTG/SDTA and DSC) allowed determining optimal conditions of preparation process and calculating carbon content in obtained anode materials (40-60 wt.%). The same thermal methods also proved to be highly useful in establishing the leak behavior of C-Sn nanocomposites. The electrical properties of the nanopowders were examined by an ac 4-probe method and the electrochemical characterization was performed by cyclic voltammetry (CV) and charge-discharge tests (CELL TEST).

The thermal analysis methods as well as low-temperature nitrogen adsorption method indicate that the composition of carbon precursor has strong impact on leak behavior and morphology of the obtained carbon buffer matrix. The study also showed that columbic efficiency and capacity retention in charge-discharge tests strongly depend on the carbon loading and sort of the carbon precursor.

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Oral Presentations 4

Bio(macro)molecules & Biocomposites, (Bio)Calorimetry, Life science and Functional complex compounds

Heteropolyacids Anchored on Amino-Functionalized MCM-41 and SBA-15 and its application to the ethanol conversion reaction

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Among the variety of catalytic systems, heteropolyacids (HPAs) with Keggin structure unsupported and supported on different materials have received much interest in the area of acid and oxidation catalysis due to their acidic and redox properties, which can be controlled at molecular level [1-2]. In this study was carried out the preparation of molybdophosphoric acid $H_3PMo_{12}O_{40}$ (HPM), and molybdovanadophosphoric acid $H_4PVMo_{11}O_{40}$ (HPVM), by supporting on amino-functionalized MCM-41 and SBA-15 molecular sieves.

Amino-functionalized molecular sieves were synthesized using 3-aminopropyltriethoxysilane as the functionalization agent. Keggin type HPAs were anchored on the surface of amino-functionalized molecular sieves by chemically bonding to amino groups. The modified surface of mesoporous silica has a positive charge, and thus, provides sites for the immobilization of HPM and HPVM. These catalysts were characterized by FT-IR spectroscopy, X-ray diffraction, nitrogen physisorption at 77 K, SEM-EDS and evaluated by vapour-phase ethanol conversion reaction. Thermal stability was investigated by TG-DTA coupled with MS and DSC.

The weight loss of amino-functionalized molecular sieves and HPA - amino-functionalized molecular sieves composites above 280°C was due to the decomposition of aminopropyl functional group. This means that HPA - molecular sieves composites are thermally stable at temperatures below 280°C.

The supported catalyst was applied to the vapour-phase ethanol conversion reaction between 190 - 250°C temperature range. The catalytic performance of HPA - molecular sieves composites was compared to that of the bulk HPA. It is known that ethylene and diethyl ether are formed by the acid catalytic function of HPA while acetaldehyde is produced by the oxidation catalytic function of HPA. The HPA - amino-functionalized molecular sieves catalysts exhibited a remarkably enhanced oxidation catalytic activity (formation of acetaldehyde) and a suppressed acid catalytic activity (formation of ethylene and diethyl ether) compared to the unsupported catalyst. The enhanced oxidation catalytic activity and the suppressed acid catalytic activity of HPA - amino-functionalized molecular sieves was attributed to molecularly dispersed HPA, which was chemically immobilized on the positive site ($-NH^{3+}$) of HPA composites by sacrificing its protons (Brönsted acid sites).

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Thermogravimetric analysis and kinetic study of dairy and swine manure under pyrolysis and combustion conditions

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The thermal degradation behaviour and the kinetics of three different manures (two dairy and one swine (SW) samples) were investigated by means of thermogravimetric analysis. Dairy samples were pretreated by anaerobic digestion (AD). Therefore, the effect of AD pretreatment on the thermal behavior was evaluated before (sample Pre) and after pretreatment (sample Dig R).

Pyrolysis and combustion processes were investigated. The thermal degradation profiles showed three main stages: dehydration, devolatilization and char transformation (char oxidation for combustion experiments). The differences observed among the samples were attributed to their different composition and the pretreatment process.

Regarding the kinetic study, two model-free isoconversional integral methods as Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) and the differential isoconversional method of Friedman at different heating rates were used to calculate the apparent activation energy dependent on the conversion rate[1]. Furthermore, Coast-Redfern was used to evaluate the kinetic behaviour of the samples. The apparent activation energies obtained by all these method were compared.

Generally, the kinetic evaluation showed two regions of apparent activation energy. The first region corresponded to $0.05 < \alpha < 0.4$ and the second one to $0.6 < \alpha < 0.9$. These two regions fitted well with the two abovementioned main stages of devolatilization and oxidation processes, respectively. The apparent activation energy for the devolatilization stage of sample SW (for pyrolysis and combustion experiments) was higher than that for both dairy samples. On the other hand, the apparent activation energy for the second stage in pyrolysis experiments was not calculated. The main stage of the pyrolysis process was the devolatilization of the sample. Therefore, the second region (char transformation) was not significant compared to the devolatilization stage and the oxidation stage in the case of combustion.

Finally, in order to corroborate the kinetic analysis, the reconstruction of the weight loss curves was performed. Two different VBA-Excel applications were developed: one based on the reaction mechanism and the other one based on the distributed activation energy model (DAEM) [2].

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Dehydrogenation of Ammonia Borane with the Addition of Hydrofobic Ionic Liquids

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Ammonia borane (AB) is identified as one of the candidates for solid state hydrogen storage. AB can react with water in the presence of a catalyst to release hydrogen (H_2) at room temperature [1]. However, the thermolysis processes provide the highest dehydrogenation capacity even at temperatures as low as 120°C, even though some volatile byproducts, like borazine and diborane, are formed. An exothermic decomposition process occurs in the temperature range between 107 and 117°C, liberating 1.1±0.1 mol of H_2 per mol of AB [1]. To overcome the problems arising from the exothermic AB thermolysis, it has been proposed to conduct the dehydrogenation in the presence of a ionic liquid; in fact, in this conditions, milder reaction temperatures and better reaction control are achieved, since ILs seem to enhance the formation of the intermediate species in AB thermolysis [2]. ILs are salts with valuable properties. They have low vapor pressure, high ionic conductivity, high capacity and wide chemical stability [3]. Due to these skills, in the last years hydrophilic ILs have been used in the presence of AB. But, they exhibit some restrictions due to a difficult manipulation and use even under vacuum. On the contrary, hydrophobic ILs present an higher chemical stability and they can be applied and handled in air [4]. For this reason, we reported the results obtained by mixing AB with hydrophobic ILs with bis(trifluoromethanesulfonyl)-imide (TFSI) or trifluorosulfonyl-imide (FSI) anions.

The AB dehydrogenation was studied in situ in the temperature range between 65 and 250°C using concomitant thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) combined with mass spectrometry for the H_2 and by-products detection. The release of H_2 is faster with ILs than that in naked AB. Indeed, even without the addition of a catalyst, the dehydrogenation starts already at 70°C without any induction time. Finally, we performed the characterization on the sample residue with infrared spectroscopy. It provides information on the chemical bonds broken during dehydrogenation and confirms the release of the H_2. Thus, through the comparison with TGA results, it is worth to recognize the effective active role of hydrophobic ionic liquids in the dehydrogenation process of AB.

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Thermal behavior study of Meloxicam polymorphs

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Meloxicam belongs to a class of drugs called nonsteroidal anti-inflammatory drugs (NSAIDs) that are used to treat pain and/or inflammation. Derived from oxicam, is suitable for alleviating the symptoms signs of osteo and rheumatoid arthritis. Meloxicam blocks the enzymes that make prostaglandins (cyclooxygenase 1 and 2) and reducing their levels [1,2].

This study aims to investigate the thermal behavior of meloxicam polymorphs and their characteristic physical, chemical and biopharmaceutical properties.

Two different commercial samples hereinafter A and B, were analyzed by DSC (Shimadzu DSC-60, 10 ^{0}C min^{-1}, N_2, up to 350 ^{0}C), TG/DTG (Shimadzu DTG-60), powder X-ray diffraction XRD7000 (Shimadzu, 40kV, 30mA, CuK_{α} (λ = 1.54056 Å) equipped with a Polycapillar focusing optics under parallel geometry, graphite monochromator, 4-70° (2θ), step size of 0.01° (2θ), 5 s step^{-1}, spinning of 30 cpm) and FTIR-ATM.

During the Meloxicam thermal study we found evidences of a thermal induced inter conversion of one Meloxicam polymorph to another at about 213 °C. The melting point onset temperature is unchanged at 262 °C. For sample A there was no change, for sample B, we have observed small and broad exothermic peak at about onset temperature of 213 °C. That may be explained by crystallization or one crystalline transition. We have obtained isotherms at 175 °C, just before the transition peak starts to appears for 15, 30 and 45 minutes Those experiments were follow-up with x-ray diffraction and shown that we have a conversion of one polymorph to another.

We are making a detailed thermal study for the determination of the transition heat to full knowledge the pathways for the observed phenomenon.

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Compositional Analysis of Complex Materials with TGA-GC/MS

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Compositional analysis with thermogravimetrical analysis (TGA) provides precise quantitative data about the composition of complex materials such as e.g. polymers. General content data such as the amount of volatiles, total polymer and carbon black, and the total inorganic residue can be obtained with simple thermogravimetrical measurements.

To obtain more detailed qualitative information, often so-called evolved gas analysis (EGA) is performed. With evolved gas analysis, the decomposition products from the TGA measurement are transferred into a gas analysis instrument such as a mass spectrometer or an infrared spectrometer. TGA-MS or TGA-FTIR data provide detailed information about the decomposition products released during the TGA analysis at certain times or temperatures.

A significant drawback of these techniques, however, is that they are not able to separate decomposition products. Especially with polymers usually several compounds are evolved simultaneously. This complicates the analysis of FTIR as well as MS data considerably. In fact, it is virtually impossible to identify individual decomposition products.

This problem can be remedied by separating different compounds before their identification. This can be achieved by combing e.g. GC and MS. In this contribution we will present a novel approach to combine TGA with GC/MS. We propose to use a dedicated, heated interface allowing collection of up to 16 gas aliquots at predefined temperatures during the course of a TGA experiment. The gas aliquots are then injected one by one into the GC. In the GC the different compounds in the gas sample will be separated and subsequently identified by MS. The power of these TGA-GC/MS measurements will be illustrated with several application examples.

The complexity of contemporary pharmaceutical formulations demands innovative analytical approaches: are we ready?

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Solid and semi-solid dosage forms still dominate the pharmaceutical market; furthermore, the composition and complexity of formulations is becoming more diverse. The foregoing has led to an expansion of ever demanding experimental procedures to understand and improve the performance of the formulations/products developed and monitor the quality of end products.

One of the new initiatives [1] based on chemical mapping using microscopy, thermal analysis and separation sciences has been recently developed in order to provide answers to complex questions such as chemical 3D mapping (tomography) of solid and semi-solid formulations (and many other systems under investigation/interest), solubility assessment and dissolution profiling in the presence of different solvents or mixtures of solvents.

In the new approach, chemical analysis by dissolution assessment (CIDA), material is selectively removed from the surface of the analyte and then analysed (HPLC and IR). Microscopy is used to monitor physical changes at the surface as the material is removed and software (image analysis) enables the analytical data to be correlated with changes in the surface of the sample; this can be undertaken at the nanoscale. The whole system can be analysed isothermally, at different temperatures or via a combination of heating and cooling cycles using thermal analysis techniques. CIDA is an exciting new technique; but, more importantly, significant scientific benefits arise from obtaining many important analytical parameters in a short period of time.

The real power of the CIDA approach is that analysis can be reliably applied to a single sample, a wide variety of solvents can be used, physico-chemical changes in surface properties and detection of removed chemicals are simultaneously monitored at the micro/nano scale; the use of chemicals is minimized. Unique information about surface properties and changes therein is obtained and the methodology used can be easily automated.

Analytical challenges often led to creativity in problem solving and this approach will, no doubt, present new demands in different areas of research; the example(s) provided in pharmaceuticals will influence interdisciplinary scientific developments in other areas of formulation science.

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Use of Solution Calorimetry for Biochemical and Pharmaceutical Applications

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Molecular recognition plays an important role in biological and pharmaceutical systems and can be either intermolecular (ligand binding to macromolecule) or intramolecular (folding of macromolecules).[1] Understanding the relationship between the structure of biological macromolecules and the energetics that dictate stability and binding with other molecules remains one of the most important problems in biochemistry and biotechnology. Such knowledge helps to design proteins with enhanced stability, more stable drug formulations and pharmaceutical ligands.[2,3]

Energetics of biological macromolecules can be explored by two major calorimetry technology platforms. Differential scanning calorimetry (DSC) allows us to study thermal transitions in the system and to directly determine enthalpy and heat changes thus characterizing the stability of the system. On the other hand, isothermal titration calorimetry (ITC) helps us to obtain a complete thermodynamic profile of the molecular interaction in a single experiment. That means that ITC doesn't just provide binding affinities but offers an insight into the mechanism of the molecular interaction.

Solution calorimetry, supported by other experimental techniques and molecular modelling, is used on a regular basis in our laboratory to understand what factors contribute to stability of biological macromolecules and to understand interaction mechanisms between biological targets and ligands or between drugs and excipients. DSC and ITC can be applied on various pharmaceutical and biopharmaceutical systems. Some of these will be presented and discussed.

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Advanced biocompatible thin films with potential in skin cancer treatment

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Self-regulating magnetic hyperthermia induced using superparamagnetic nanoparticles (NPs) is a promising method cancer treatment. This type of therapy leads to cancer cell death with minimal damage to healthy surrounding tissue. Nickel-copper (Ni_xCu_{1-x}) alloy-based NPs with a narrow size distribution were prepared by reducing a Ni, Cu-oxide mixture in a silica matrix. Using the sol-gel method, NPs with a suitable Curie temperature (the therapeutic range is 42 °C - 46 °C), were obtained. With the aim to develop novel materials for non-invasive skin cancer treatment, the as-prepared NPs were combined with a model drug and incorporated into a potential wound dressing material. The combination of two possible treatment modalities, namely hyperthermia and active pharmacotherapy, provides the basis for a synergistic therapeutic intervention, with a greater overall efficiency in cancer treatment. Magnetic nanoparticles in a silica matrix were filled with a model drug and incorporated into two different biocompatible polysaccharide host materials, namely alginate and chitosan, using the spin-coating technique. Drug release was quantified using UV-Visible Spectrophotometer (UV/Vis) and performed in special experimental setup, where magnetic stirring was provided directly in the quartz quevette (used for UV/Vis). For this purpose *in situ* magnetic stirring directly under the quevette was used (Fig. 1). As the release media, Phosphate buffered saline (PBS) was used. The temperature was maintained at room temperature (at 25 °C). At defined time intervals the amount of released drug was quantified *in situ*, via a direct UV/Vis measurement. The measured absorbance was transformed to concentration using Beer-Lambert law. Release studies were performed for 180 minutes, while samples were withdrawn at same time intervals for each parallel. All release studies were performed in at least two parallels. The characterization of the Ni_xCu_{1-x} magnetic nanoparticles was performed using X-ray powder diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectra (FTIR), scanning electron microscopy (SEM), surface area and pore size were determined by using BET analysis. Final, biocompatibility/cytotoxicity of the as-prepared samples was evaluated on human skin-derived fibroblasts (ATCC-CCL-110 (Detroit 551)).

Fig. 1: *In vitro* release experimental setup.

Interaction of curcumin with human serum albumin: calorimetric and spectroscopic studies

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The interactions of the anti-angiogenic cancer drug, Curcumin an antioxidant with human serum albumin (HSA) have been examined by the fluorescence, UV–vis, and isothermal titration calorimetry (ITC) techniques. Fluorescence results indicate that in case of HSA–drug complexes the quenching of fluorescence intensity is at 295 nm. Experimental results revealed curcumin have an ability to quench the intrinsic fluorescence of HSA tryptophan through a static quenching procedure. The binding constant is determined using Stern–Volmer modified equation and energy transfer mechanisms of quenching are discussed. ΔG, ΔH, and ΔS values are also calculated. It is found that curcumin remained bound to unfolded state of HSA and facilitates the process by pushing tryptophan moiety to more polar environment in the unfolded state. The curcumin slower down the process of denaturation of reversibly refold the sub-domain IIA, by also recovering fluorescence lifetime loss, but it was slow in the presence of curcumin. The spectroscopic and thermodynamic techniques provide a quantitative understanding of the binding of anti-angiogenic cancer drug with human serum albumin.

Kinetic Study of Thermal Decomposition of Rigid Polyurethane Foams by Artificial Multilayer Neural Network

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Rigid polyurethane foams (RPF) have a rigid highly cross-linked polymeric network. Inorganic fillers addition in their manufacture process, such as alumina industrial waste, increases the mechanical strength of the foams and besides is an economic and environmental choice [1]. Kinetic models describe the foams decomposition process. However, not always the adjustments made by the models are suitable. In order to overcome this problem, the use of Artificial Neural Multilayer Network is originally proposed in this work for kinetic investigations. The proposed Neural Network structure sets the weights in the input layer according to the rate constants determined by fitting the experimental data for each considered kinetic model. This linearization ensures the use of models as activation function of neurons in the hidden layer and the interconnection weights between this intermediate and the output layer determining the contribution of each model in the overall fit [2,3]. The proposed network is a powerful mathematical procedure, which considers the contribution of several models for the process. It presents a significant reduction in the residual error by fitting the experimental data. These fitting improvements allow detailed study of the physical process and therefore the accurate calculation of the kinetic parameters such as the activation energy, frequency factor and half-life. Two samples were used for RPF, load (Al_2O_3) and no inorganic filler, both synthesized from a polyol extracted from Ricinus communis seeds. The isotherms were obtained at a thermobalance Shimadzu TGA-50H in an alumina crucible, N_2 flow at 50mL/min and a heating rate of 20°C/min to temperatures of 220, 228, 230 and 232°C due the significant loss of mass in this temperature range in the TG curve. The adjusted results obtained by the neural network were higher than those obtained by individual model analysis. Therefore, reduced residual errors are on average 10^2 times lower for both materials. The decomposition process of RPF loaded by alumina was best described by the R3 model at all temperatures but at 220°C, the R2 model contributes 78.86% for the overall adjustment. The D4, R2 and R3 models best adjust the decomposition data for non-loaded samples, with contributions depending on the analyzed temperature.

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Effects of polycaprolactone content on mechanical properties of flax fibre-reinforced biocomposites

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In general natural fibres increase elastic modulus while often decrease impact strength of polymer biocomposites. The aim of this work was to improve and determine mechanical properties of natural fibre-reinforced biocomposites. To prepare biocomposites with improved mechanical properties polycaprolactone (PCL) was mixed and extruded with polylactide (PLA) and flax fibres. The composite varied with the content of polycaprolactone (0, 5, 10 and 15 wt%) whereas the content of flax fibres was constant (20 wt%). The extruded composite granulates were injection moulded to form the samples for testing. The samples were characterized by means of dynamic mechanical analysis (DMA), impact strength measurements and differential scanning calorimetry (DSC). The detailed discussion on the influence of structural properties of flax fibres-reinforced PLA/PCL composites on their mechanical properties was presented.

Keywords: biocomposites, natural fibres, polylactide, polycaprolactone, thermoanalysis, mechanical properties.

Thermal and spectral behaviour of some biocompatible powder particles for bone reconstruction

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It is well-known that the hydroxyapatite (HAP) is widely used for bone grafts manufacturing [1]. For the same purpose, our research uses biocomposite mixtures made of micronic (av. 100 μm) respectively submicronic (< 200 nm) HAP particles (> 60 % mass) and titanium powders (20-30 % mass) [2]. Beyond these components, the mixtures content citric acid (1-3 % mass) and foaming agents as $CaCO_3$ and NH_4HCO_3, each of (1-2) % in order to obtain the required density related to the grafted cortical respectively trabecular bone tissue.

In order to depict the thermal effects during the heating in argon, the thermal analysis was developed. The TA thermoanalytical curves from Fig. 1 a show the thermal behaviour of the biocomposite mixture. Its organic bonds are underlined by FTIR analysis in Fig.2.

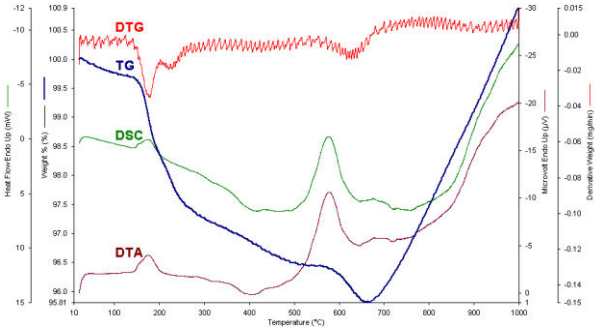

Fig. 1

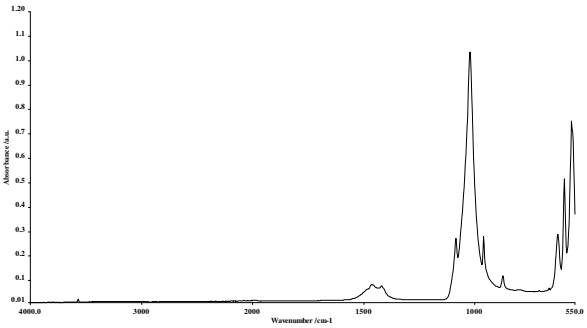

Fig. 2

Decomposition of the sample takes place in three stages to a temperature of 650 °C. In the first stage (weak endothermic), loss of mass is 2.5 %. The second step (very weak exothermic) shall be carried with mass loss of 1 %. In the third stage (strongly endothermic), loss of mass is 0.8 %. From 650 °C, the porous sample absorbs argon from the gas stream, increasing its mass by 5.1 %. This phenomenon frequently occurs in the case of porous materials located in argon.

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Dynamic mechanical analysis of silicones for podiatry applications

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The aim of this work is to analyse the viscoelastic properties and the mechanical behaviour of silicones currently used in podiatry, in orthotics' applications. Orthotics is an interdisciplinary medical speciality that combines anatomy, pathophysiology, engineering and biomechanics [1]. Nowadays, the increasing use of silicones in podiatry orthoses and removable shoe inserts justifies performing deeper dynamic mechanical studies. This study is focused on properly characterizing this type of silicones and optimizing their formulations. Taking into account this type of orthoses special applications, dynamic mechanical thermal analysis (DMTA) [2] is performed to study the viscoelastic properties of different types of commercial silicones used in podiatry. The effect of frequency in viscoelastic properties is measured in application conditions. The silicones are compared attending to type and weight percent of hardener, applying statistical tools such as design of experiments, analysis of variance and nonlinear regression modelling [3]. This work shows a methodology to test and evaluate the thermal mechanical performance of silicones before their application such as orthoses in podiatry.

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Microcalorimetry as a suitable tool for API characterization

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Microcalorimetry is a widely used method not only by chemists, but also by other technical fields including pharmaceutical industry. The object of this work is a special technique called solution calorimetry. Solution calorimetry measures the heat of solution of a material (solid, liquid) dissolving into a solvent. Typically, there is a measurable difference in the enthalpies of solution – dissolution of a crystalline material is an endothermic process and exothermic for an amorphous material. Therefore it is possible to differentiate between different morphologies of the sample – between mixtures of crystalline and amorphous material and between mixtures and polymorphs. In addition, solution calorimetry is used not only for the detection but also for the quantification the amorphous composition of materials. This ability is important, for example, for formulators of solid dosage forms for drug delivery.

The presented work focuses on the characterization of pharmaceuticals, especially of active pharmaceutical ingredients (APIs). The measurements were provided using a special solution calorimetry module which is a part of a modular microcalorimeter TAM III (TA Instruments).

The reason for amorphous APIs production in the world is mainly their better solubility when compared with the crystalline form. The precise amorphous phase content in the unknown sample is determined from the method of a calibration curve when 100% amorphous and 100% crystalline material and a known mixture of thereof are measured.

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Smart organic receptors

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A number of hosts were studied, which have unusually high selectivity and clathrate stability caused by cooperativity of clathrate formation and decomposition. Absolute selectivity of host response to guest inclusion and release was observed, which goes far beyond the capability of ordinary key-to-lock mechanism. While current concept of molecular recognition is based on the preferential binding of complementary species, the present work uses smart properties of host crystals such as their memory of previously bound guest, pseudopolymorphism of host-guest clathrates with more than one step of guest inclusion and/or guest release, favorable hydration effect on inclusion of hydrophobic guests. Thus, small guest molecules having no more than one functional group capable of H-bonding or donor-acceptor interactions can be discriminated even from their close homologues.

A true recognition was found in a two-step formation of benzene clathrate with tert-butylthiacalix[4]arene derivative both on vapor sorption isotherm and in kinetic response of mass-sensitive sensor [1]. This experiment is extremely selective being capable to detect benzene qualitatively and quantitatively in mixtures with any other compounds.

An observed ability of several calixarenes to remember evolved guests [2] does not have any precedents by selectivity. This memory can be read in simultaneous TG/DSC experiment as an exothermic effect of host collapse from loose to dense phase without mass change. The memory parameters (enthalpy and temperature of polymorphic transition) strongly depend on the guest structure. A loose metastable polymorphic phase of studied calixarene with imprinted guest image may have rather large free volume up to 6 vol.%. In some cases, such memory effect can be found only after solid-phase guest exchange in calixarene clathrates [3].

The procedure of clathrate preparation by guest exchange is rather selective itself and gives boost to guest inclusion capacity and clathrate thermal stability both for calixarenes [3, 4] and beta-cyclodextrin [5]. This may produce clathrates that cannot be formed by direct host-guest interaction. Additional surge in clathrate stability was found for calixarene capable of special anti-sieve effect, so that larger guests can be bound, while smaller ones are excluded [4]. The work was supported by RFBR (grant no. 14-03-01007-a).

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Investigation of Alkyl Chains as Entropy Reservoir in Selected Liquid Crystalline Substances

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Phase transition is a result of changes of three main factors vs temperature: 1) molecular structure, 2) molecular dynamics and 3) intermolecular interactions. Stability of a given phase is regulated by the Gibbs energy, which consists of enthaply and entropy [1]. Molecular motions have direct effect on the value of entropy and therefore Gibbs energy is modulated.

Alkyl chains are labile and can easily change they conformational state, thereby they play unique role from the viewpoint of entropy. Therefore, alkyl chains can be perceived as an entropy reservoir that determines which of two energetically close phases appears. This presentation demonstrates the important role of molecular dynamics in occurrence of a particular phase.

Our investigations were focused on the selected Schiff base compounds 4-chlorobenzylidene-4'-pentyloxyaniline (5CBAA) and 4-pentyloxybenzylidene-4'-chlorobenzene (5BACB) [2]. Those two compounds of different azomethin bridge isomerisation have similar polymorphism. In case of 5CBAA smectic A, smectic B and crystal phases were observed and for 5BACB smectic A, smectic B, crystal I and crystal II phases were found. The adiabatic calorimetric study are supported by complementary methods, i.e., X-ray diffraction, dielectric spectroscopy, infrared spectroscopy and DFT calculation.

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Effect of chain length of ionic liquids on the dissociation temperature of methane hydrate at high pressures by using a high pressure differential scanning calorimetry

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A high pressure differential scanning calorimeter (HPDSC) was applied to determine the dissociation temperature of methane hydrate in the presence of an ionic liquid 1–carbonyl–3–methylimidazolium chloride at a constant pressure ranging from 5.0 to 35.0 MPa. A homologous series of the ionic liquid with different side chain lengths, 1-*ethyl*-3-methylimidazolium chloride, 1-*hexyl*-3-methylimidazolium chloride and 1-*decyl*-3-methylimidazolium chloride, were used as additives to form the methane hydrate. All these ionic liquids were found to act as inhibitors on methane hydrate formation, i.e., occurrence of methane hydrate formation at higher pressures and lower temperatures. In addition, it is found that the shorter the side chain length is, the stronger the inhibition effect is. In other words, the order of inhibition capability of these ionic liquids is as following: 1-ethyl-3-methylimidazolium chloride > 1-hexyl-3-methylimidazolium chloride > 1-decyl-3-methylimidazolium chloride. The experimental results of dissociation temperature of methane hydrate in the presence of 1–carbonyl–3–methylimidazolium chloride at pressures ranging from 5.0 to 35.0 MPa were further compared with the predictions resulting from a predictive model [1]. The Peng-Robinson-Stryjek-Vera equation of state incorporated with COSMO-SAC activity coefficient model and the first order modified Huron-Vidal mixing rule were applied to evaluate the fugacity of vapor and liquid phase. A modified van der Waals and Platteeuw model was applied to determine the fugacity of hydrate phase. This predictive model can successfully describe the phase behaviour of methane hydrate in the presence of the ionic liquid.

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Natural aluminosilicates for catalytic depolymerization of waste plastics to olefins

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Global annual polyethylene (PE) production accumulates to about 80 million ton and the majority is used for short-lived products, such as packaging, which represent an enormous environmental burden. Due to its easy availability, high energy density and defined chemical composition, thermocatalytic pathways offer attractive means for depolymerization of waste plastics to olefins, which can be used as liquid fuels or added value chemicals. Natural aluminosilicates are abundant and cheap, exhibit moderate acidity and have been extensively used before the discovery of synthetic zeolites as catalytic cracking catalysts for hydrocarbons [1]. Chemical and morphological modifications to improve their activity and selectivity provide an attractive approach to liquid hydrocarbon production from PE depolymerization.

Natural aluminosilicate containing primarily clinoptilolite and heulandite (Montanit300®, M) was subjected to H_2SO_4 acid treatments in order to increase specific surface area, create mesoporosity and acidity by substitution of charge compensating ions. Catalytic tests were performed in a TG/DSC apparatus (Perkin Elmer) by thoroughly mixing PE and catalyst powders in various ratios. In this study reaction kinetics was investigated in detail, too.

Acid treatment of M sample (initially containing 6.3 wt. % Al) with H_2SO_4 was successfully employed to increase the BET specific surface area for about 5 times (from 36 to 130-150 m^2/g, depending on acid concentration). By prolonging the acid treatment, progressive sample dealumination was observed. Loss of Al reflects itself also in the FTIR spectra, which show disappearance of Si-O-Al bending and a progressive shift to higher wavenumbers of the absorption band belonging to asymmetric stretching of SiO_4 tetrahedron units. Observed activity in PE depolymerization correlates with the abundance of surface acid sites. Various acid treatments resulted in improved catalytic performance at lower temperatures; compared to M sample, inferior activity was measured at higher temperatures, which is due to a considerable loss of tetrahedrally coordinated aluminum. The presence of the latter is the prerequisite for activity, as it enables the formation of highly acidic bridging hydroxyl or sulfonic surface functional groups. The pyrolysis of pure PE is well described by the variable order kinetics, while in the presence of solid catalysts the reaction mechanism changes. For example, pyrolysis of PE/M mixture follows the contracting sphere reaction model, while the pyrolysis of a mixture consisting of PE and H_2SO_4 treated catalyst could be predicted by zero order kinetics. Gas phase evolved during PE depolymerization was continuously monitored by means of FTIR spectroscopy to identify the products; alkanes and alkenes were formed, the presence of aromatics could not be confirmed. Isomerization occurred as well, resulting in a wide distribution of alkene structures [2]. Over the M catalyst, exclusively alkanes with chain length up to 21 C atoms were present in the condensed liquid phase (53 % yield). Coke yield was very low (0.4 %), while lower C2-C4 alkenes and alkanes constituted the remaining part.

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The influence of photoluminescent dopant on thermal and spectroscopic properties of poly(methy methacrylate) – material used in polymer optical fibres technology

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Photoluminescence monomers and polymers are modern, gaining more importance materials that are apply in optoelectronics, among others, as organic projectors (O-LED) and for construction of energy saving light source [1]. Therefore, demand for new and more resistant materials is still increasing becoming a challenge for researchers. Materials so far used in photoluminescence, among others, zinc sulfide with copper and cobalt admixture are inorganic aluminum compounds with admixtures of mainly rare earth elements are replaced with accessible organic compounds particularly naphthalene derivatives.

Based on our previous work, we are able to obtain PMMA, useful in polymer optical fibers technology [2]. In this work, we will show studies made on poly(methyl methacrylate), used as a polymer matrix and dimethacrylate derivative of naphthalate-2,7-diol, used as a photoluminescent dopant. Thereby doped material is suitable as the active coating on the optical fibers, and as the active core material for the polymer optical fibers.

The degree of usefulness of the received materials as optical materials has been studied using the coupled thermal and spectroscopic methods (TG/DTG/DSC/QMS). Using these methods we can get, in addition to quantitative information (weight change, process heat), the qualitative information regarding the chemical composition of the gas products. The spectral characteristics will also be shown, made by supercontinuum as a light source and optical spectral analyzer as the detector.

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Thermal degradation of cellulose from different sources

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Cellulose is the most abundant homopolysaccharide available worldwide and its molecular structure consists of repeating β-D-glucopyranose units, which are covalently linked by glycosidic bonds [1]. Cellulose (nano)fibrils (CNF) can be extracted from various cellulosic resources such as wood pulp, cotton, algae, jute and many others [2, 3].

The aim of this work was to characterise thermal degradation of various materials based on CNF from different sources, to compare their properties before and after pyrolysis under inert atmosphere and to evaluate their ability as new sorbents for non-polar solvents.

The samples used in this work were bacterial cellulose, CNF obtained from wood pulp by mechanical disintegration and algae CNF prepared by chemical treatment. All cellulose materials were prepared as a foam or film.

The pyrolysis process was investigated via thermal analysis interconnected with a mass spectrometer for analysis of evolved gases. The temperature programme comprised a heating step from 15 °C to 100 °C (10 K min^{-1}), an isothermal step at 100 °C (1 hour) and heating to 1000 °C (10 K min^{-1}) in argon flow. Non-pyrolysed and pyrolysed materials were investigated by several techniques such as scanning electron microscopy, X-ray diffraction or dynamic vapour sorption analysis.

The main step of thermal decomposition occurred in the range from 200 to 400 °C and selected signals related to water, carbon mono- and dioxide, hydrocarbons, levoglucosan, furan, acetaldehyde, acetone and other pyrolysis products were detected. The mass losses were in the range from 77 to 91 % depending on the source of cellulose and its form.

It was found by SEM that the structure of the samples after pyrolysis was different, the inner net of fibrils changed and fibrils stuck together. The results from XRD confirmed that cellulose materials include crystalline and amorphous regions and the ratio between them depends on the source of cellulose. After pyrolysis, the samples were amorphous, which was independent from the cellulose origin. DVS results indicated that cellulose-based carbon materials exhibited higher hydrophobicity then non-pyrolysed precursors and they are ideal candidates for adsorption of non-polar solvents.

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Thermal analysis of chimney deposits

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A growing application of wood and wood products as a fuel has been observed in Slovenian households and smaller industrial plants or hotels in the last decade due to economic crisis and low costs of energy produced in new wood burning appliances. The intensive usage of wood burning is accompanied by heating-related home fires. Slovene statistical reports indicate approximately 500 chimney fires annually, most of them due to old wood-fired equipment, unsuitable operation and inadequate maintenance of chimneys and stove pipes.

We were interested in the fuel involved in chimney fires, these are deposits in chimneys mostly known as soot, but more correctly described as creosote. 30 chimney deposits were collected in residential type chimneys and analyzed to evaluate their fire hazard. Origins of samples with fuel type (logs, pellets, wood chips), type of equipment and air introduction were carefully evidenced. Color, hardness, particle size and homogeneity of samples from different sources varied greatly.

TG, DSC and EGA/MS analyses were performed in air in a temperature range from 25 to 1000°C using Mettler Toledo TG/DSC 1 instrument coupled with MS Balzers Thermostar. Elemental analyses were performed with a field emission scanning electron microscope (FE-SEM, Jeol, 7600F) equipped with electron dispersive X-ray spectrometer (EDX).

Results of all analyses proved a low total mass loss and a low combustion enthalpy for samples containing mostly carbon (soot) and mineral ashes whereas a higher total mass loss and a higher combustion enthalpy were observed for samples containing partly oxidized organic compounds. Samples were classified into four groups according to total mass loss, which was approximately 20%, 40%, 80% and almost 100%. Sulphur dioxide evolved at 350°C during heating of most samples, while evolution of hydrogen chloride was detected above 900°C only in one sample.

Poster Session 1

Theory & Methods, Kinetics & Catalysis, Fuels & Biofuels and Applied Thermal Engineering

Multistep Thermal Decomposition of Granular Sodium Percarbonate

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Thermal decomposition of granular sodium percarbonate (SPC : $Na_2CO_3 \cdot 1.5H_2O_2$) is regulated by the physico-geometrical reaction mechanisms and chemical restrictions of the successive processes; endothermic dissociation of SPC to Na_2CO_3 and H_2O_2 and exothermic decomposition of H_2O_2. Herein, kinetic features of the thermal decomposition of granular SPC are discussed on the basis of the experimental approaches using thermoanalytical measurements and morphological observations.

The mass-loss process due to the thermal decomposition of SPC proceeds via overlapping two reaction steps [1,2]. The multistep behaviour results from the impedance of the gaseous diffusion by the surface product layer and the gradual increase in the internal pressure of H_2O that accelerates the latter-half reaction. The DSC curves for the thermal decomposition indicate apparently different shape from the DTG curves as the result of the successive endothermic and exothermic processes. With reference to the decomposition enthalpy of H_2O_2, the DSC curves can be deconvoluted into the endothermic and exothermic processes (Figure (a)) [3]. As is expected from the reaction sequence, the exothermic peak is observed at the temperatures slightly higher than the endothermic peak.

Considering both the physico-geometrical mechanism and the successive reaction scheme, the DSC curves are further deconvoluted into two endothermic and two exothermic processes (Figure (b)). The kinetic features of the thermal decomposition of granular SPC are discussed on the basis of the results of kinetic deconvolution analysis. At the same time, practical usefulness of the empirical kinetic deconvolution analysis for applying to overlapping multistep reactions is evaluated.

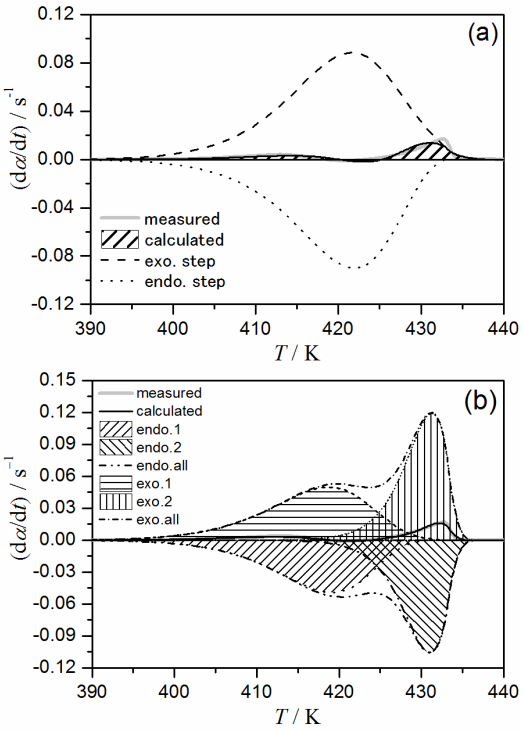

Figure. Typical results of kinetic deconvolution of DSC curve: (a) based on the successive reaction scheme and (b) that based on the physico-geometrical mechanism and successive reaction scheme.

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Doubts on Kissinger´s method of kinetic evaluation based on several conceptual models showing the difference between the maximum of reaction rate and extreme of DTA peak

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The famous Kissinger´s kinetic evaluation method (Anal. Chem. 1957) is examined with respect to the feasible impact of the individual quantities and assumptions involved, namely the model of reaction mechanism, $f(\alpha)$ (with the iso- and noniso-thermal degrees of conversion, α and λ) the rate constant, $k(T)$ (and associated activation energy, E), heating/cooling rate, β (supplementing additional thermodynamic term for the melt undercooling, ΔT) , e.g., $(3\beta)/[T^2_m\ (\Delta T)^2] = df(\alpha)/d\alpha\ (A/B)\ \exp\{-B/T_m\ (\Delta T)\}$, and above all, the association of the characteristic temperature with the DTA peak apex. It is shown that the Kissinger´s equation, in contrary to the results of Vold (Anal. Chem. 1949), is omitting the term of heat inertia arising from the true balance of heat fluxes, e.g., $d^2\alpha/dt^2 = (K/H)\ (d\theta/dt)$, (where θ, is the difference in temperature of the centers of the two samples) explicitly showing the misfit between, T_m and broadly implemented value of the DTA apex, T_p. The absence of this term skews the evaluated values of activation energies. Despite a long lasting history of kinetic evaluation it is clear that such an important part of DTA peak analysis has been overlooked at everyday applications. It is possibly caused by the obvious methods simplicity, which provides easy publishable values of activation energies. It is surprising that anybody who evolved various alternatives of the Kissinger method did not find any reasons for its criticism.

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A Novel STA Furnace with Tungsten Heating Element for Measurements under High-Purity Inert Gas Atmospheres and High Vacuum

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Many high-melting metals form metal carbides or also eutectic systems with carbon. By trying to determine the melting point of such metals by means of the DTA technique in a furnace with carbon heating elements, this value is often false, mostly too low. This is generally due to the carbon-containing atmosphere in these furnaces which can be explained by the considerable vapor pressure of the carbon at such high temperatures.

This can also cause problems during melting of high-melting oxide ceramics/compounds such as alumina or garnet crystals. Here, premature decomposition can occur.

A tungsten furnace, however, allows for an oxygen- and carbon-free atmosphere during DTA measurements and therefore yields the true values for the melting point and melting enthalpy. This poster illustrates the design of the furnace and STA, respectively. With examplary measurement results on metals/ceramics, differences in the results obtained with a graphite furnace and a tungsten furnace are presented.

Combined calorimetric and manometric measurements for the study of sorption properties of porous materials

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The gas sorption Sievert's technique has proven to have many advantages for the evaluation of the ad- or ab- sorbed amount of gas by porous materials in a wide range of temperature and pressure. In addition, there is a total freedom in the size and shape of the sample holder in the volumetric technique, enabling the coupling of techniques and in-situ measurements of various chemical and physical parameters. X-rays and neutrons diffractomers, gas chromatographs or mass spectrometers have already been successfully tested and allow having simultaneous PCT isotherms and kinetic measurement with structural or gas composition data.

The thermodynamics of the adsorption are essential for the practical application and among all the heat of adsorption (or desorption) is a key parameter. Practically there are two ways to determine it. The first one is an indirect method, where it is derived from adsorption isotherms at different temperatures. The second one is a direct method, where the enthalpy is measured via calorimetric techniques. When used on its own, the biggest disadvantage of calorimetry is that it gives a heat output per mole of solid sample and not per mole of gas. The combination of manometric technique (to quantify the amount of gas absorbed/released) and calorimetry was successfully applied to overcome this issue and the direct measurement of enthalpy of formation per mole of gas was reported [1-3].

The presentation will give some new results on combinations of calorimetric and volumetric technique, especially on MOF-5, selected as an example of Metal Organic Framework that is commercially available. But also on different other porous materials such as amine modified mesoporous silica. It will give an overview of the state-of-the art possibility of combined calorimetric analysis together with the Sievert's technique.

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Flash DSC – A Quantum Leap in DSC Performance

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Conventional DSC instruments allow measurements to be performed at heating rates of up to 500 K/min and cooling rates of 200 K/min. The signal time constant is about 1 to 2 seconds. This level of performance is however not adequate for a number of important applications such as the investigation of the structure and morphology of polymers and polymorphic substances or of metastable materials in general. In addition, kinetic analysis of processes that occur on a time scale shorter than the signal time constant is not possible.

The morphology of a semicrystalline polymer depends on the cooling conditions experienced by the material as it was cooled from the melt. Furthermore, when a semicrystalline polymer is heated, crystallites may melt and recrystallize to form larger and more stable crystals. The material in fact undergoes continuous reorganization. This process can only be suppressed if the heating rate used is sufficiently high. Depending on the particular material under study, heating rates of several thousand Kelvins per second are in fact necessary to suppress reorganization.

In isothermal crystallization experiments, the sample has to be cooled rapidly from the melt to the desired crystallization temperature to prevent the formation of crystals or crystallization nuclei. For many materials, this requires cooling rates that are far higher than those achievable using a conventional DSC.

The Flash DSC 1 from METTLER TOLEDO provides heating rates of up to 40,000 K/s and cooling rates of 4,000 K/s. The signal time constant is 1000 times shorter than that of a conventional DSC. This allows processes to be studied that occur on a time scale of a just a few milliseconds, for example fast chemical reactions or the crystallization of certain materials. In particular, production processes such as injection molding can be simulated.

To achieve these performance parameters, the Flash DSC 1 utilizes a technology known as chip calorimetry. Here, the sample is no longer enclosed in a crucible and heated in a furnace. Instead, a tiny sample (in the submicrogram range) is measured directly on the chip sensor. The chip sensor is in fact a complete, miniaturized DSC furnace for sample and reference.

In this contribution, we will describe the technology and working principles of the Flash DSC 1. The performance of this new instrument is demonstrated with the aid of several application examples.

Swine manure combustion and oxy-combustion processes: kinetic analysis

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The utilization of manure as bioenergy for thermochemical processes may be a sustainable development choice rather than its traditional use as fertilizer [1]. Combustion is the most ancient and widely process used for burning a biomass for power generation at industrial scale, usually carried out in an air atmosphere. Oxy-combustion is the process that involves the combustion of biomass to obtain energy source in the presence of pure oxygen and carbon dioxide. Combustion and oxy-combustion processes of swine manure were performed through thermogravimetric-mass spectrometric analysis. The combustion was performed in Ar/O_2 atmosphere whereas the oxy-combustion was performed by replacing argon with CO_2. To evaluate the effect of the O_2 concentration, the following volume proportions were tested for both atmospheres: 20, 40, 50, 60 and 80 vol.% O_2. To assess the kinetic parameters three different heating rates was used (10, 20 and 30 ºC/min). The decomposition profiles followed a two-step reaction process, starting by the devolatilization of the sample and ending with the oxidation of the in situ formed char.

Kinetic analysis was performed for combustion and oxy-combustion processes. Activation energy was obtained by means of model-free methods. Friedman is the most common differential isoconversional method. Ozawa–Flynn–Wall method and Kissinger–Akahira–Sunose method are integral isoconversional methods [2]. Therefore, the latter methods were selected to obtain kinetic parameters.

For these methods, it was shown the activation energy ($E\alpha$) to be dependent on the degree of conversion (α). This way, two regions were considered regardless the atmosphere used. The first region, corresponding to $0.1 < \alpha < 0.5$ conversion, was related to the devolatilization stage where the activation energy was practically kept constant (combustion: $E\alpha \sim 180$ kJ/mol; oxy-combustion: $E\alpha \sim 140$ kJ/mol). The second region corresponded to sample oxidation ($0.6 < \alpha < 0.8$ conversion). The values of the constant activation energies obtained in this case were lower than those observed for the first region, (combustion: $E\alpha \sim 80$ kJ/mol; oxy-combustion: $E\alpha \sim 60$ kJ/mol). In addition, the apparent activation energies computed for both processes did not seem to be dependent on the amount of O_2.

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Studying the kinetics of walnut shells pyrolysis and combustion in various atmospheres using thermogravimetric analysis

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Thermochemical conversion of biomass has been the subject of increasing attention. Combustion, gasification and liquefaction are particularly employed for power generation and production of liquid biofuels, chemicals and charcoal, the latter being used in production of activated carbon. Thermogravimetric analysis (TGA) is a traditional method to investigate thermal degradation by determining the characteristics of weight loss at different heating rates and atmosphere conditions.

Biomass is mainly composed of hemicellulose, cellulose and lignin, along with small amounts of extractives and inorganic matter. Variation of the components ratio in biomass gives different thermal behaviour and the products can generally be classified into three categories: non-condensable gases, heavy volatiles and char.

Processes of wood pyrolysis and combustion are widely studied, while there are only a few works describing these processes for biomass with high lignin content, such as walnut shells, in which lignin constitutes about 50%. The high content of lignin that is the most thermally stable component of wood, leads to modification of the ratio between resulted after decomposition volatiles and coal.

Thus, this work is aimed at determining the kinetics of walnut shells combustion and pyrolysis, by using thermogravimetric analysis method. The experiments were carried out in the temperature range of 20-1000 ^{o}C for heating rates of 5, 10 and 20 °C/min under air (dynamic and static), nitrogen and CO_2 atmospheres. The use of carbon dioxide has allowed modelling the processes occurring at coal activation. The results of experimental investigations are used to develop a mechanism of thermal degradation of walnut shells; the further investigations on kinetics of walnut shells pyrolysis and combustion of biomass are in progress.

Kinetics analysis of condensed phase decomposition of ammonium dinitramide (ADN)

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Ammonium dinitramide (ADN: $NH_4N(NO_2)_2$) is a promising new oxidizer for solid propellants because of high oxygen balance, high energy, and halogen-free material [1]. In the design of new solid rocket propellants, considerable attention has been given to investigation of the mechanism and kinetics of thermal decomposition of propellant components because the thermal decomposition is the first and major stage of the combustion process. Thakre et al reported that combustion velocity is characterized by condensed phase decomposition below less than 2 MPa [2]. There are some studies about decomposition and combustion mechanisms of ADN [3-6]. In general, they assumed that ADN decompose to N_2O and ammonium nitrate in condensed phase. However, condensed phase decomposition mechanism and their kinetics are not well known. The purpose of this study is to examine condensed phase decomposition of ADN experimentally and theoretically. We carried out evolved gas analysis and kinetics analysis using Thermal gravimeter-differential thermal analysis coupled with mass spectrometry and infrared spectrometry (TG-DTA-MS-IR). We also calculated energy change of condensed phase decomposition using quantum chemistry calculation (CBS-QB3//ωB97XD/6-311++G(d,p) level). The activation energy for producing N_2O of approximately 183 kJ/mol obtained from TG-DTA-MS-IR is good agreement with energy barrier of 165-172 kJ/mol obtained from quantum chemistry calculation.

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Kinetics analysis of thermal decomposition of dimethyl sulfoxide (DMSO) under acidic condition

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The purpose of this study is to understand hazardous decomposition of dimethyl sulfoxide (DMSO) under acidic condition. DMSO has been extensively used as solvent because of its high solubility. However, there are accidents at the chemical processes where DMSO is used. The explosion mechanism has not been cleared. Although the decomposition mechanism of DMSO under acidic conditions is known [1], the number of studies about thermal behaviour of DMSO under acidic condition is not large [2]. We carried out kinetic analysis and quantum chemistry calculation. Thermal analysis using an accelerating rate calorimeter (ARC) was carried out with acids chosen for their acid dissociation degree constant (pKa), which is a typical parameter of acid strength. ARC data show that the self-heat rate increased and the exothermic onset temperature decreased with decreasing pKa. Additionally, the exothermic onset temperature and pKa had good linear correlation [2]. To verify the initial exothermic reaction, differential scanning calorimetry (DSC) analysis was carried out. DSC results showed that the exothermic onset temperature was due to decomposition of DMSO. The activation energy of the decomposition reaction was calculated from the ARC results (self-heat rate). Our data indicate that the activation energy of the decomposition reaction decreased with decreasing energy barrier obtained from quantum chemistry calculation. Therefore, thermal hazards of DMSO increase with the decrease in energy barrier, with good linear correlation.

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Influence of the mixed solvent on the thermal hazard of cellulose dissolving process using ionic liquids

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Ionic liquids (ILs) are used as effective solvent because of their high flame retarder properties, high thermal stability, low volatility and low impact to environment. In a chemical process of cellulose dissolving such as in biomass manufacturing plant solvents system of ILs mixed with conventional solvent are expected for higher performance and effective ones.

In this paper thermal hazard of IL, acetate salt of 1-butyl-3-methylimidazolium (BmimAc), mixed with three types of non-proton solvent; dimethylsulfoxide (DMSO), dimethylacetoamide (DMAc) and N,N-dimethylformamide (DMF) are analyzed with differential scanning calorimety (DSC).

The experimental results showed that thermal hazard of BmimAc/DMSO is classified as medium class and that of BmimAc/DMAc and BmimAc/DMF were classified as low level. Further the reaction mechanism and kinetics of BmimAc/DMSO was analyzed. It was found that the temperature control is a key factor for safer process of BmimAc/DMSO solvent system.

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Thermal hazard analysis of ionic liquid 1-butyl-3-methylimidazolium chloride and cellulose mixtures

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Ionic liquids (ILs) are used as effective solvent because of their high flame retarder properties, high thermal stability, low volatility and low impact to environment, and they are expected as suitable solvent used in a chemical process of cellulose dissolving such as in biomass manufacturing plant [1-3].

In this paper thermal hazard of IL, 1-butyl-3-methylimidazolium chloride (BmimCl) and cellulose composition was analyzed with TG-DTA. Further to investigate the influence of impurities which were thought to exist in processes, BmimCl/cellulose mixed with ferric oxide (Fe_2O_3), acetic acid (CH_3COOH) and copper(II) oxide (CuO) were analyzed with TG-DTA, DSC and TG-DTA-IR for evolved gas analysis.

The experimental results showed that copper(II) oxide had a influence on the thermal hazard of BmimCl/cellulose in a manner of catalytic reaction, and it had a possibility of spontaneous ignition in case if they are in adiabatic conditions.

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Thermal properties of ionic liquids based on ammonium dinitramide and acetamide mixtures

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Ammonium dinitramide (ADN) is a promising high energy oxidizer for rocket propellant because of high oxygen balance and high energy content. It has been studied as ADN-based ionic liquid propellants [1]. In this paper, solvent-free liquid propellants are called as ionic liquid propellants. Ionic liquid is defined as salt whose freezing point is below 100 °C [2]. It was known that melting point of ADN and acetamide (AA) mixture prepared with powder mixing was below 25 °C [3]. To obtain better understanding of thermal properties of ionic liquids based on ADN, we prepared ADN and AA mixtures. Thermal behaviors of ADN/AA mixtures were measured using differential scanning calorimetry (DSC) and evolved gases of samples were analysed using thermogravimetry–differential thermal analysis with mass spectrometry (TG-DTA-MS). DSC results showed similar exothermic onset temperatures regardless of changing mixing ratio. The results of TG-DTA-MS indicated that ADN/AA mixture decomposed through two-steps. The first step was vaporization of AA and second one was thermal decomposition and reaction with each sample.

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Thermal decomposition characteristics of cesium captured potassium cobalt cyanoferrate

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The study of cyanocomplexes has received much attention over a long period because these compounds have a variety industrial application [1]. The nuclear industry utilizes metal cyanoferrate as an ion-exchanging precipitator to remove radioactive and hazardous metal ions from waste water. Precipitated cyanoferrate containing hazardous metals should be properly treated and stabilized so that it can be disposed of. High-temperature waste thermal processes such as vitrification have been developed for such radioactive and hazardous wastes. The emission of semi-volatile radioactive metals such as cesium as well as hydrogen cyanide (HCN) during thermal stabilization treatment of ferrocyanide sludge have been studied.

First part of this study investigated thermal decomposition characteristics of cesium-captured potassium cobalt ferrocyanide hydrate ($K_{2-a}Co_{2/(1+a)}Fe(CN)_6 \cdot yH_2O$) in air. Following reactions occur, in order, as the sample is heated to 1600 K.

$$K_{2-(a+b)}Cs_bCo_{2/(1+a)}Fe(CN)_6 \cdot yH_2O \rightarrow K_{2-(a+b)}Cs_bCo_{2/(1+a)}Fe(CN)_6 + yH_2O(g) \quad (1)$$

$$K_{2-(a+b)}Cs_bCo_{2/(1+a)}Fe(CN)_6 + zO_2 \rightarrow K_2CO_3 + Cs_2CO_3 + Fe + CO_{2\,(g)} + N2\ (g) \quad (2)$$

$$Fe \rightarrow FeO \rightarrow Fe_2O_3 \quad (3)$$

$$Cs_2CO_3 \rightarrow Cs_2O(g) + CO_2(g) \quad (4)$$

$$K_2CO_3 \rightarrow K_2O(g) + CO_2(g) \quad (5)$$

The second part of this study investigated the volatility characteristics of cesium species in the presence of various mineral sorbents. Isothermal TG analysis of cesium-captured potassium cobalt ferrocyanide hydrate with various kinds of mineral sorbents at several temperatures were performed to know the relative effectiveness of tested mineral sorbents. Among tested sorbents, kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot xH_2O$) appeared to be the most appropriate sorbent to capture vaporizing cesium species. Two kinds of non-volatile cesium compounds such as $Cs_2O \cdot Al_2O_3 \cdot 2SiO_2$ and $Cs_2O \cdot SiO_2$ were identified as remaining cesium species in TG analysis residue by the XRD pattern analysis.

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Assessing the thermal stability of two azo compounds by thermal analysis with kinetic calculation method

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Azo compounds are always used as initiators and blowing agents. However, they are also typical self-reactive materials which are capable of undergoing runaway reaction during storage or transportation, which can cause serious fire and explosion accidents [1].

To ensure thermal safety of azo compounds in processing, transportation, and storage, two common azo initiators, 2,2′-Azobis(2-methylpropionitrile) (AIBN) and 2,2'-Azobis(2,4-dimethyl)valeronitrile (ABVN), are selected to be investigated. First, their thermal decomposition characteristics under non-isothermal and adiabatic conditions were obtained by using differential scanning calorimeter (DSC) and vent sizing package 2 (VSP2) from the literature. Second, the collected data can be input into thermal safety software (TSS) to evaluate the basic thermal hazard for both azoes [2–3].

In addition, based on Semenov and Frank-Kamenetskii theoretical models, as well as thermokinetic parameters, the self-accelerating decomposition temperatures (*SADT*) were extrapolated for consideration and non-consideration of consumption of chemicals. The results show that the *SADT* are all less than 80 oC. Therefore, it is essential to avoid a temperature beyond *SADT* or cooling system failure. Moreover, the influence of consumption is also a concern for *SADT* in this study.

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Determination of the thermal and decomposition behaviours for tert-butyl peroxy-2-ethylhexanoate

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Organic peroxides (OPs), which are commonly used in radical polymerization, easily show their self-reactive properties. Due to sensitive thermal decomposable features, they have triggered several accidents in the past. To avoid unexpected thermal decomposition, the thermal stability OPs and the reliable technical parameters of OPs should be provided to the on-site staff [1].

In this study, the target substance, *tert*-butyl peroxy-2-ethylhexanoate (TBPO), has higher activity compared with other OPs, and its thermal decomposition characteristics are discussed based on a review of the literature by results of differential scanning calorimetry (DSC). The thermal dynamics analysis of TBPO is conducted by advanced thermal analysis software (AKTS) using DSC data.

The results provide process control data and the consequences of thermal runway for TBPO. In addition, based on related numerical methods, critical runaway temperatures, stable temperatures, self-accelerating decomposition temperature (*SADT*), and required heat removal rate for prevention of thermal runaway reaction can be calculated during process deviation. Therefore, the assessment results also show that measures and process parameters must be controlled strictly under desired reaction [2–3].

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Explosion properties of two environmental refrigerants with high pressure

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Rudimentary properties of environmental refrigerants contain hydrofluorocarbons (HFCs), which have advantages of lower ozone depletion potential (ODP) and global warming potential (GWP) compared with CFCs [1].

However, HFCs are stable at normal temperature and pressure, whereas they may have potential explosion hazards, because of having atoms of C, H, and F or Cl on molecular structure [2]. We explored the explosion properties of R-22 (HFCs) and R-600a (HCs), considered with the effects of different pressures (1, 1.5, and 2 bara) by using 20-L-apparatus.

The experimental results indicated that environmental refrigerants of R-600a have explosion properties at normal pressure. The explosion limits of R-600a were 1.5–9 vol.% at room temperature. When the explosion limits of R-600a rose with increasing pressure from initial pressure 1 bara raised to 2 bara, the lower explosion limits of R-600a rose from 1.5 to 2 vol.%, and the upper explosion limits rose from 9 to 10 vol.%. In addition, R-22 did not present an explosion phenomenon at normal pressure. However, R-22 has explosion phenomenon with increasing pressure condition, and the explosion limits were 20–35 vol.% and 1–50 vol.% at 1.5 and 2 bara, respectively.

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A kinetics study of coffee bean roasting conditions under non-isothermal simulation

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Coffee has been one of the most popular beverages all over the world, and its consumption continues to increase, due to its physiological effects as well as its pleasant taste and aroma. Roasting is an important step in the production of coffee because it enables the development of flavour, aroma and colour [1-3]. Most coffee beans are large-scale commercially roasted, but some coffee drinkers prefer to precisely control the freshness and the special flavor by their own roasting method. This study was conducted to develop a novel approach to thermal decomposition that includes the heat reactivity properties of coffee beans, such as the kinetics of reaction, pre-exponential factor (lnk0), reaction order (n), activation energy (Ea), heat of decomposition (ΔHd), isothermal condition for time to maximum rate (TMR), total energy release (TER), and time until 10% conversion limited (TCL) [4]. From roasting conditions vs. thermal decomposition characteristics, we found the roasting conditions and thermal decomposition characteristics, and learned the control conditions. The parameters and reactivity properties could be applied to design during roasting and storage conditions. Differential scanning calorimetric (DSC) experimental data were processed and then the kinetics was evaluated by simulation. Overall, we applied the non-isothermal kinetic model for the evaluation of thermokinetic parameters and storage conditions, compared the results to simulated thermal analysis, and then did a sensory evaluation to determine the suitable roasting condition.

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A new experimental set up of EPE technique

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In the past few years, the Electro-pyroelectric technique (E.P.E) has been proposed and described in detail elsewhere [1-3]. This work presents a new set-up of EPE technique based on defect detection, in order to provide faster and low cost protection of the Lock-in amplifier. Sample material is warmed up by an electrical power with impulsion electrical generator. Then, pyroelectric experimental data is fed into defect detection. Next, the latter output was acquired by a lock-in amplifier arrangement (model EG & G 5210). Thereby, the Lock-in-amplifier is well-protected.

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A thermo-electrical parameters investigation of Mylar using photopyroelectric and electropyroelectric calorimetric techniques

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The present paper deals with the determination of thermal and electrical properties of thermoplastic composite materials whose application are increasingly used in various technical applications using two complementary photothermal techniques; the Photopyroelectric (PPE) and Electropyroectric (EPE) methods which have been used due to their simplicity, sensibility and non destructive advantages. The operating functional between these techniques is the same even though only the heating mode differs. So, a generalized one-dimensional theoretical model for a photopyroelectric (PPE) and an electropyroelectric (EPE) calorimetric technique has been developed to investigate thermal and electrical parameters of polyethylene terephthalate film (Mylar - Trade name). The coincidence between experimental curves giving the pyroelectric amplitude and phase variations versus modulation frequency and the corresponding theoretical curves makes possible to deduce thermal diffusivity, conductivity and electrical impedance of Mylar sample. The experimental results were found to be in good agreement with the literature and the impedance analyzer values.

Kinetic studies of a complex polymerization behaviour of guaiacol based benzoxazine

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Recently, due to the growing environmental and sustainability concerns, much attention has been given to replacing synthetic polymeric materials with materials from renewable resources. This is why the focus in the field of polybenzoxazines, which possess various outstanding characteristics, shifted towards the synthesis of fully bio-based polybenzoxazines. In present research benzoxazine was synthesized using bio-based guaiacol, furfurylamine and formaldehyde [1] and the main emphasis was on the kinetic study of the derived bio-benzoxazine curing process.

The sample was cured in DSC under non-isothermal conditions at heating rates of 5, 10, 15 and 20 °C/min. Curing of guaiacol based benzoxazine showed complex polymerization behaviour, since the exothermal signal of the curing consisted of several overlapped peaks. This suggests that the polymerization of benzoxazine has a least two polymerization stages: the polymerization at lower temperatures associated to reaction 1 and the polymerization at higher temperatures associated to reaction 2. In order to differentiate and study each overlapped peak, peaks fitting and deconvolution was performed using the Pearson VII distribution, since it caused the best DSC peaks fitting and deconvolution results.

Further on, each deconvoluted peak was studied individually by performing Kissinger and Flynn-Wall-Ozawa method in order to study the apparent activation energy. Friedman and Malék statistical analysis was used to determine the order of the reaction [2, 3]. The results of the kinetic analysis showed that the first peak could be associated to the autocatalytic nature of benzoxazine resin, when phenol groups are generated while the benzoxazine ring starts to open (reaction 1), and electrophilic attack. As a result the Šesták–Berggren autocatalytic equation [2] was successfully applied in the mathematical modelling of non-isothermal curing process and a complete set of kinetic parameters were calculated. On the contrary, deconvoluted peak at the higher temperature (reaction 2), applying Friedman statistical analysis, showed typical n-th order of the reaction, which was also successfully applied in the mathematical modelling deriving appropriate kinetic parameters. The second reaction can be explained by the transformation of phenoxy structure into phenolic structure by rearrangement and to the diffusion-controlled step [1]. On the basis of the comparison of the results between experimental and calculated data, we can conclude that the present work provides a clear image of non-isothermal reaction kinetics characteristics of guaiacal based benzoxazine consisting at a least two polymerization stages.

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Kinetics of reduction of cupric oxide pre-treated isothermally at different temperatures

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Copper(II) oxide is widely used as a selective catalyst in many oxidation and reduction reactions. Its catalytic activity can be modified by the reductive thermal pre-treatment [1-4].

In this study we synthesised CuO by citrate gel combustion technique [5]. Upon an isothermal pre-treatment at 400, 600 and 800 °C, the morphology was examined by SEM, and particle growth commensurate to the pre-treatment temperature was evidenced. The reduction of the samples by hydrogen was investigated thermogravimetrically under non-isothermal conditions, at heating rates of 5,10, 20 and 30 °C min^{-1}.

A detailed kinetics analysis of theromogravimetric data was performed by Kinetics05 software. The Friedman, Coats-Redfern and Kissinger isoconversional methods were used to assess the variation of energy of activation in dependence of conversion degree. The nucleation and growth model gave the best agreement between the experimental and calculated data for all samples. The following parameters provided the best fit: 400 °C : n = 0.764, m = 0.966, Ea = 64.45 kJ mol^{-1} and $A = 4.60 \cdot 10^4$ s^{-1}; 600 °C: n = 1.131, m = 1.045, Ea = 59.93 kJ mol^{-1} and $A = 2.19 \cdot 10^4$ s^{-1}; 800 °C: n = 1.063, m = 1.094 Ea = 67.92 kJ mol^{-1} and $A = 7.914 \cdot 10^4$ s^{-1}.

The temperature induced changes in morphology and particle size, although notable, caused relatively small variances of kinetics parameters, and left the possibility of use of an unique reaction model.

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Kinetic analysis of poly(ethylene oxide)/lithium montmorillonite nanocomposites

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Poly(ethylene oxide)/lithium montmorillonite (PEO/LiMMT) nanocomposites have been prepared by melt intercalation and non-isothermally degraded in nitrogen atmosphere [1]. The obtained non-isothermal data have been used in this work for the kinetic analysis of the degradation process. Kinetic analysis was performed using isoconversional Friedman (FR) method in combination with the multivariate non-linear regression method incorporated in Netzsch Thermokinetics Professional software.

Our earlier investigations have shown that thermal degradation of PEO is simple (one-step) process [1] while thermal degradation of PEO/LiMMT nanocomposites is complex (multi-step) process that may involve several overlapping or consecutive processes [2].

Kinetic analysis performed for the purpose of this work revealed the complexity of the thermal degradation process for both pure PEO and all PEO/LiMMT nanocomposites. The contribution of the each individual process has been determined and each of them was independently analyzed. Kinetic parameters (activation energy, pre-exponential factor and kinetic model) have also been calculated for each degradation stage of all investigated samples.

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The influence of poly(ethylene glycol) on thermal properties and kinetics of poly(vinyl chloride)/poly(ethylene oxide) blends

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The influence of poly(ethylene glycol) (PEG) addition on thermal characteristics and thermal degradation of poly(vinyl chloride)/poly(ethylene oxide) (PVC/PEO) blends was investigated by differential scanning calorimetry and thermogravimetry. Thermal degradation of PVC/PEO blends has already been investigated [1]. Results show that addition of PEG decreases melting temperature and lowers thermal stability of PVC/PEO blends.

Kinetic analysis of the non-isothermal degradation of PVC/PEO/PEG blends in the entire conversion range was performed using the isoconversional Friedman (FR) method in combination with the multivariate non-linear regression method incorporated in the Netzsch Thermokinetics Professional software. Kinetic analysis revealed four-stage degradation mechanism for all PVC/PEO/PEG blends. Kinetic model, activation energy and pre-exponential factor for each degradation stage of all PVC/PEO/PEG blends were calculated. It was found that the addition of PEG lowers the activation energy and changes degradation kinetics in the majority of degradation steps.

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Kinetics of epoxy-amine reaction of pre-hydrolysed 3-glycidyloxypropyltrimethoxysilane

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Hydrolysis of 3-glycidyloxypropyltrimethoxysilane (GLYMO), an organically modified methoxysilane with a reactive epoxy group linked to a silicon atom through a stable Si-C covalent bond, was studied by Fourier-transform infrared spectroscopy (FTIR). Stoichiometric molar ratio for full condensation of GLYMO, of 1.5 mol of water per 1 mol of GLYMO, was used. Hydrolysis was catalysed by addition of varying concentration of hydrochloric acid, HCl.

Kinetics of subsequent reaction of hydrolysed GLYMO with poly(oxypropylene)diamine was studied by differential scanning calorimetry (DSC), using varying heating rates to obtain isoconversional kinetics data. Glass transition, of hybrid materials obtained in this manner was characterised by DSC, thermal stability by thermogravimetric analysis (TGA) and hardness by ball-indentation method.

FTIR and DSC results have shown that epoxy groups remain stable during hydrolysis. Activation energy of the epoxy-amine reaction was determined by Kissinger and Friedman isoconversional methods from dynamic DSC scans. Obtained plots of E_a vs α indicate a complex reaction mechanism, and the influence of hydrolysis conditions. In all conditions, silanol groups formed by hydrolysis can act as catalysts for the epoxy-amine reaction.

Residual chloride ions from acid-catalysed hydrolysis act as scission centers and decrease thermal stability of hybrid materials as determined by TGA. Hardness of hybrid materials was not improved when compared with ones obtained from non-hydrolysed GLYMO.

Influence of Microwave Heating on the Kinetics of Isothermal Dehydration of Equilibrium Swollen PAAG Hydrogel

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The kinetics of isothermal dehydration of the equilibrium swollen newly synthesized poly(acrylic acid)-g-gelatin hydrogel (PAAG) under the microwave heating was evaluated. The PAAG hydrogel was synthesized via crosslinking free-radical graft polymerization of AA and gelatin in aqueous media [1]. The primary structural properties of the synthesized xerogel have been determined. Dehydration kinetics curves (isothermal dependence of dehydrated water percentage on time) have been measured by using a newly, originally constructed device, the so called microwave–thermo–gravimetric analyzer within the temperature range from 323 K to 353 K.

The dependence of activation energy ($E_{a,\alpha}$) under the microwave heating on the degree of dehydration (α) was assessed by application the methods of Friedman and Vyazovkin. [2,3] We established that the investigated dehydration was an elementary kinetics process. By employing the model-fitting method it was found that the kinetics of isothermal dehydration under the microwave heating can be mathematically best described by the Polang-Wingers equation.

The values of model's constant rates of the isothermal microwave dehydration of the PAAG hydrogel have been calculated. In accordance with the Arrhenius equation the values of kinetics parameters have been calculated: E_a =52.0 kJ/mol and ln(A/min^{-1}=12.1).
The obtained results were compared with the ones obtained for the isothermal dehydration of the PAAG hydrogel under conventional thermal heating.

A novel model, called the nucleation model, was suggested to describe the investigated kinetics isothermal dehydration under MW heating. By application the presented model we are able to describe the model of the mechanism of the isothermal dehydration of the PAAG hydrogel under the MW heating and the effects of microwave heating on the kinetics of isothermal hydrogel dehydration.

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Non-isothermal Kinetics of Fulerol Dehydroxylation

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The kinetics of non isothermal dehydroxylation of a fullerol was investigated. Fullerol was prepared by synthesis in toluene solution of fullerene in the presence of interface catalyst CTABr and sodium hydroxide [1]. The basic physic-chemical properties of the synthesized fullerol have been determined. The kinetics of non isothermal thermogravimetric curves of the fullerol dehydroxylation have been recorded using a TG Analyser, TA Instruments, in the temperature range from 423K to 853 K at different heating rates from 5 to 20 K/min.

The dependence of activation energy ($E_{a,\alpha}$) degrees of dehydroxylation (α) was investigated applying the KAS method [2]. Performed analyses of the shape of the dependence of $E_{a,\alpha}$ on α leaded to the conclusion that the investigated dehydroxylation was a complex kinetics reaction. The complex thermogravimetric dehydroxylation curves have been found that are mathematically best described as a combination of the two logistic functions.

By the analyses of the effects of heating rate on the parameters of the logistic functions it was found that the increase in the heating rate leads to the increase in the values of parameters *w* and *a*, whereas the value of parameter *b* decreases.

Based on the shape of the thermogravimetric curves of the particular components of the fullerol dehydroxylation curves we conclude that the fullerol dehydroxylation reaction takes place through the two different, well separated stages. During the first stage, within the temperature range 420 K≤T ≥560, happens the release of the 10-11(OH) groups with the energy of activation E_a =50.0 kJ/mol whereas for the second stage, the temperature range 560 K≤T ≥830, the 14-15(OH) groups are released with the energy of activation E_a =100.0 kJ/mol A model able to describe mechanism and kinetics of fullerol dehydroxylation is was suggested and discussed. Physical meaning of the parameters of the logistic function is presented.

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Non-isothermal kinetic behavior for crystallization process of $Lu_2Ti_2O_7$ precursor powder prepared by Pechini method

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The crystallization process of $Lu_2Ti_2O_7$ precursor powders prepared by Pechini-type polymerized complex route has been studied under non-isothermal conditions. In order to characterize the precursor's powders and final product of the crystallization, a variety of experimental techniques, such as simultaneous thermogravimetric (TG) and differential thermal analysis (DTA), Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) analysis, the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses were used. Samples were characterized with differential thermal analysis (DTA) using different heating rates (5, 10, 20, 40 ^{o}C /min) to study the kinetics of crystallization process. Kinetic parameters were calculated with two non-isothermal methods based on the Arrhenius equation: Kissinger and Ozawa peak methods.

The mechanistic scheme of crystallization process for **pyrochlore ceramics originated from precursor's system** was presented in detail. It was found that all curves are shifted to a higher temperature with an increase of heating rate, verifying that thermal activation steps occur during the crystallization process. The crystallization peaks appeared in the temperature range of 1045-1100 K. Apparent activation energy of crystallization under linear heating condition were obtained from the temperature dependence of the exothermic peak on the heating rate: (770 ± 50) kJ/mol and (750 ± 50) kJ/mol, for Kissinger and Ozawa method, respectively.

Thermogravimetric investigation of oxidation resistance of some commercial carbons

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Oxidation resistance of carbon materials is extraordinary important property in many applications. Low oxidation resistance is desirable in exhaust gases of automobiles, while high oxidation resistance is desirable in fuel cells [1]. Numerous factors may influence this prperty, such as degree of carbonisation, preseence of catalytic or inhibiting impurities, specific surface area, composition of oxidiying atmosphere, etc.

In this work, we compared the oxidation resistance of four commercial carbons with various specific surface areas: Timrex KS44 (9 $m^2 g^{-1}$), Flammruss 101 (30 $m^2 g^{-1}$), Vulcan XC 72 (220 $m^2 g^{-1}$) and Printex XE-2B (1170 $m^2 g^{-1}$). The TG curves for Timrex KX44 and Vulcan XC 72 vere measured, while the others two were taken from the literature [2]. High purity of these carbon eliminated all other influencing factors but specific surface area. The TG curves of oxidation were recored in synthetic air. Taking, for common heating rate of 5 $^oC\ min^{-1}$, the temperature at which the combustion degree achieves 0.5 as a criterion of oxidation resistance, the following stability order was found: Timrex KS44 (766 ^oC), Flammruss 101 (717 ^oC), Vulcan XC72 (647 ^oC) and Printex XE-2B (567 ^oC), identical to the order of reciprocal values of specific surface areas.*

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Reaction kinetics of mechanically activated cordierite based ceramics studied via DTA

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Cordierite, $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ (MAS), is a very attractive high-temperature ceramic material. In order to accelerate the process of sintering, 5.00 mass% MoO_3 was added to the starting mixtures. The mechanical activation of the starting mixtures was performed in a high energy ball mill in time intervals from 0 to 160 minutes. In following, starting mixtures were sintered at 1300 ^oC for 2h. In order to determine the changes in the particle size distribution, the mechanically treated powders were characterized by a laser light-scattering particle size analyzer. The phase composition of the starting mixtures and sintered samples was analyzed by the X-ray diffraction method. Differential thermal analyses (DTA) and thermo-gravimetric (TG) analysis were used in order to determine characteristic temperatures. Kissinger's equation was employed to calculate apparent activation energies of various processes that occur within the system while heating. Based on the obtained DTA results, it was established that mechanical activation along with MoO_3 additive, has influence on sintering temperature which was decreased for about 150 ^oC.

Temperature analysis of thermoplastic machining for optimization of turning process

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In production of modern industrial products one of the increasingly used material is plastic. Variety of different plastics with a favorable technical characteristics is extremely wide. Good mechanical, thermal, friction, electrical and other properties enable the use of these materials for making different mechanical parts (elements). During machining of these parts (elements), development of high temperature in the cutting zone would have a harmful effect on mechanical properties of the workpiece material and on durability of cutting tool.

In this study the temperature in the cutting zone was analyzed during production of engine gaskets made of polypropylene. Based on test results, optimal machining parameters was determined for machining parts made of polypropylene.

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Thermal transport characteristics of directionally oriented polymer fibrous materials

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Nature and man-made polymer fibre materials are widely applied in practice and they are available with a great range of properties. Fibres can be easily assembled in a number of different two- or three-dimensional structures using highly automated techniques such as stitching, weaving, braiding and knitting. These highly anisotropic fibrous assemblies afford opportunities for property control along more than one direction. The heat transfer mechanism in porous fibrous materials is a very complex phenomenon which generally involves conduction, convection and radiation. The complexity of the phenomenon comes from the fact that the heat transfer in porous fibrous material is closely related to the material's thickness, air volume fraction and bulk density. Starting from the fact that these parameters are dependent on the way in which fibres are packed into a yarn, the aim of this study was to investigate the effect of yarn structure on thermal transport properties in both transient and stationary heat flow through the materials.

The rib knitted fabrics were produced by combining one of the two cotton plied yarns (differing in folding twist) with one of the two complex hemp yarns (plied or two-assembled). The parameters describing thermal transport properties of the knits in steady-state (thermal conductivity) and transient (thermal diffusivity, thermal absorptivity) conditions were determined according to the procedure described elsewhere [1-2]. Although the knits were produced under the same processing conditions, they differed to some extent in construction characteristics as a consequence of differences in the core and surface geometry of the yarns. The lowest porosity of the knitted fabrics composed, in part, of two-assembled hemp yarn caused their thermal conductivity to be higher than that of their counterparts. Their higher thermal conductivity resulted in higher thermal absorptivity which indicated their cooler thermal sensation. The values of thermal diffusivity were higher for the knits having the highly twisted cotton yarn as a component which indicated higher speed of the heat propagation through these knits. Although the results obtained cannot be explicitly extrapolated to fibrous materials other than those tested in the study, it is confirmed that the arrangement and packing density of fibres can be a designing factor in heat transfer (in steady-state and transient stage) through fibrous materials.

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Thermal contact properties of textile materials exposed to repeated wash and wear cycles

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The human skin acts as the interface between the human body and its environment. Being richly innervated and having specialized sensory receptors, the skin is able to detect various external stimuli such as temperature changes due to heat flow to or from the body surface. As a respond to these stimuli, the skin receptors produce warmness sensations. The warm/cool feeling is believed to result from the rapid heat transfer from the skin to the surface of clothing material immediately after making contact between the material and skin. A parameter termed the thermal absorptivity, defined as the square root of the product between thermal conductivity and the volumetric heat capacity of a material, is used for assessment of the tactile warm/cool feeling of textile materials. The higher the thermal absorptivity of a fabric, the cooler it seems at the initial contact.

In this study, the warm/cool feeling of the knitted fabrics produced from the two-assembled hemp and acrylic (PAC) yarns so as to obtain three different fibre contents: pure hemp, pure PAC and 50%/50% hemp/PAC knitted fabrics. In order to indicate the changes in thermal contact properties of the knitted fabrics exposed to repeated wash and wear cycles, the clothing items made from the knits were subjected to wear trial test including care of the knits. The thermal conductivity and specific heat of the knitted fabrics before and after wear cycles were experimentally determined according to the procedures described elsewhere [1-2], which made it possible to calculate their thermal absorptivity. The results obtained indicated some differences in thermal absorptivity among the knitted fabrics coming from the differences in volume heat capacity and thermal conductivity. Although having the highest thermal conductivity, the PAC knit was characterized by the lowest thermal absorptivity due to the lowest volume heat capacity. Thanks to the significantly higher volume heat capacity, the hemp knit exhibited the highest thermal absorptivity, and therefore the coolest thermal sensation. Relaxation and shrinkage of the knitted fabrics after undergoing wash and wear cycles caused the changes in their construction and thermal properties, thus changing their thermal contact properties. Specific heat of the knits was reduced by washing and wearing, and even though their bulk density was increased, volume heat capacity of the knitted fabrics was mainly reduced. Thermal conductivity was increased. As a result, the thermal absorptivity of the pure hemp and blended knits was increased giving cooler sensation after “using the knit”, whereas the pure PAC knit exhibited warmer thermal sensation after wear and care cycles.

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Determination of combustion behaviour of dried sewage sludge with usage of advanced thermogravimetric technics

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Dried anaerobically stabilized sewage sludge is due to its physico-chemical properties and hygienisation suitable for energy utilization and thus an appropriate substitute for fossil fuels. For the purpose of achieving the desired energy efficiency in the energy recovery process the stakeholder should be familiar with the characteristics of alternative solid fuel used at existing incineration devices. In addition, the design of new incinerators for energy recovery, is much easier and more successful because of the known kinetic properties of the alternative fuel.

Tests for thermal decomposition of sewage sludge with simultaneous thermal analysis (TG/DTG/DTA/QMS) were made using a variety of combustion atmospheres: i) an oxidizing atmosphere (A: $Ar:O_2 = 80_{Vol\%}: 20_{Vol\%}$; B: $Ar:O_2 = 90_{Vol\%}: 10_{Vol\%}$), ii) combination of inert and oxidizing atmosphere - aiming to C_{fix} determination [1], iii) an inert atmosphere (Ar), iv) different temperature regimes (dynamic and isothermal regime) and v) different heating rate in the dynamic temperature regime [2-3].

To determine the kinetic parameters we used the isoconversional method with multi – heating rate and we calculated them without knowing reaction model. For these measurements, the conversion rate α is defined as the quotient of the current pattern of weight loss and total weight loss of the sample during the experiment. The basic assumption of the isoconversional method is only temperature dependence of the reaction rate at the same conversion rate. Advanced isoconversional method takes into account the change in activation energy (E) at various stages of conversion (α). Under the proposed method, we carried out a series of non-isothermal measurements of weight loss of the sample at selected different speeds heated (2,4,6,8,10,15,20 Kmin-1). The E_α for each α value was calculated as minimum of the Φ (E_α) function. The integral value in the function was calculated numerically, using the trapezoidal rule for a series of different elevation temperature steps [4-5].

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Temperature stability and characterization of mercury compounds present in gypsum samples from various thermal power plants

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Gypsum is a by-product of wet flue gas desulphurization (WFGD) system and contains trace amounts of different minerals, trace elements that mostly originate from the coal burning process, and the impurities present in $CaCO_3$. Thermal desorption technique is useful method for identification of mercury compounds present in solid substrates and to determine the temperature stability of those compounds present in different samples.

Two different experimental approaches were used in our experiments. The first is based on controlled heating from room T to 750 ^{0}C and detection of the released elemental Hg by AAS with Zeeman background correction (Lumex). The second approach differ in the detection system which is based on a Nier-type mass spectrometer, initially designed for Knudsen Effusion Mass Spectrometric (MS) measurements. Gypsum samples from two different WFGDs systems burning the same coal from Slovenia and 9 different gypsum samples from different Chinese TPP were tested. Temperature desorption curves of Hg from different gypsums obtained by AAS slightly differ from those obtained by MS. Additionally, multi-elemental analysis was done by k_0-INAA resulting in determination of 44 chemical elements.

Mercury content in Slovenian gypsum was much higher (> 10 mg/kg) compared to the Chinese gypsums (< 1.8 mg/kg) indicating better efficiency of Hg removal in WFGD with forced oxidation in Slovenian TPP. In Slovenian WFGD gypsums the concentrations of trace elements are largely dependent on the size fraction. Besides Hg, significantly higher concentrations of other trace elements were also found in fine fractions. In the case of Chinese gypsum samples information on coal composition was not available and the size fraction taken from the WFGD was also unknown.
Significantly different temperature desorption curves were observed for Chinese and Slovenian gypsum samples. Hg-species present in gypsums might be attributed to the presence of Hg(0), Hg-Cl species, Hg-compounds adsorbed onto Al or Fe oxides/hydroxides or simply to desorption of mercury compounds such as Hg oxides or sulphates. The methodology tested is suitable to determine temperature stability of Hg present in gypsum, while the determination of the exact Hg species composition is still a subject of further research.

Thermal investigation of different modified cement mortars

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The self-compacting cement mortars and concretes are characterized by excellent workability and high early strengths, which makes them suitable for elements in ***pre-cast*** concrete. Both of the dense structure and the non-defect surface of self-compacting mixes are achieved by the incorporation of relatively large amounts of fine mineral additives – Marble and Zeolite. This determines the great potential for manufacturing of architectural elements and details with use of white cement self-compacting mortars. But there should also expect the existence of large differences in the structure formation and hardening of these systems.

Clinoptilolite is a zeolitic material which behaves excellent pozzolanic activity - reaction with calcium hydroxide to form insoluble calcium silicates (cementitious phases). Its incorporation to the cement mortars behaves economic, engineering and durable effects typical for natural pozzolans. In comparison with light in color pozzolans – silica fume, metakaolin, etc. the clinoptilolite is soft and ductile mineral. Moreover it modifies the rheological behavior of fresh mixes and takes an active part in the process of cement hydration. This predetermines the possibility of incorporation of clinoptilolite in white cement mortars and concretes to produce architectural elements and details. Free of any additional pigments the hardened white mortars behave an ancient view, due to the characteristic color of clinoptilolite.

In this study are investigated the different type of cementitious composites based on White Portland cement, Clinoptilolite and Marble as filler. The density of their structure at 28 and 120 days of water curing were evaluated by measurement of some physical-mechanical properties such as density, compressive strength and porosity. Differences in thermal behavior of self-compacting mortars are complemented with powder X-ray diffraction, IR spectroscopy and scanning electron microscope techniques

This study reports the investigation of the influence of zeolite incorporation and of marble as filler on the microstructure of self-compacting white mortars. Attention was focused on the general microstructural development during curing with a special attention on the evolution and morphology of pore space and observed calcium silicate hydrates (C–S–H), portlandite and carbonate-containing phases.

Crystallization of GeS_2 in Ge-Sb-S glasses

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Chalcogenide glasses exhibit unique physical properties, such as transmission from the far visible to the far - infrared (IR) wavelength range, a strong photosensitivity and have high linear and nonlinear refractive indices. Based on these properties there are many potential applications involving near- and mid- infrared light such as laser delivery, optical data storage and all-optical switching etc. The crystallization process plays a key role in many of these applications [1].

Crystal growth kinetic of chosen compositions from Ge-Sb-S glassy system was studied under isothermal conditions by optical microscopy. Study is targeted on GeS_2 rich part of $(GeS_2)_x(Sb_2S_3)_{1-x}$ system where predominantly growth of GeS_2 crystals were identified. The linear growth kinetics of GeS_2 in $(GeS_2)_x(Sb_2S_3)_{1-x}$ for x=0.9 has been observed in the temperature range 428 °C ≤ T ≤ 472 °C in bulk and 390 °C ≤ T ≤ 429 °C in thin film samples. The crystal growth takes place between 378 °C ≤ T ≤ 398 °C in bulk and 381 °C ≤ T ≤ 415 °C in $(GeS_2)_{0.8}(Sb_2S_3)_{0.2}$ thin film. The linear crystal length-time dependence indicates that the crystal growth is controlled by liquid–crystal interface kinetics. Activation energies of crystal growth were estimated of optical microscopy measurements and crystal growth kinetics were described in terms of the 2-D nucleated growth model.

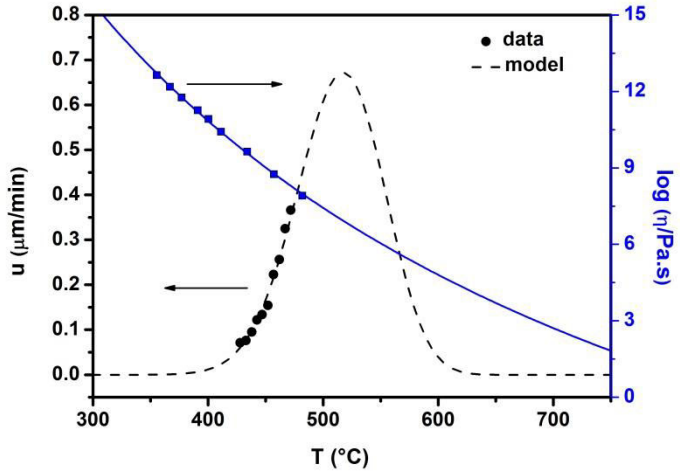

Fig. 1 Temperature dependence of crystal growth rate and viscosity in $(GeS_2)_{0.9}(Sb_2S_3)_{0.1}$ undercooled melt.

All results obtained by optical measurements of compositions with x = 0.9; 0.8 prepared in thin film and bulk form will be demonstrated in this contribution.

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Crystallization behaviour of $Ge_{20}Te_{(80-x)}Se_x$ infrared glasses

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Non-isothermal crystallization kinetics of the $Ge_{20}Te_{(80-x)}Se_x$ infrared glasses was studied by means of differential scanning calorimetry in dependence on particle size. The compositions with x = 0, 2, 4, 6 and 8 were investigated. For each particle size and each composition a full-scale kinetic analysis was performed based on a set of heating scans obtained at rates from 0.5 to 30 °C·min^{-1}. Activation energies of the crystallization processes were evaluated by nowadays top three methodologies (original Kissinger [1], Kissinger-Akahira-Sunose [2], Friedman [3]) – their pros and cons will be discussed.

Complexity of the DSC data obtained for powders was treated by means of the Fraser-Suzuki deconvolution and the particular crystallization sub-processes were identified and described in terms of the nucleation-growth Johnson-Mehl-Avrami [4, 5] and autocatalytic Šesták-Berggren [6] kinetic models. The bulk as-prepared $Ge_{20}Te_{80}$ samples, on the other hand, exhibited simple zero-order crystallization kinetics. The marked difference between the powder and bulk crystallization mechanisms was explained based on the mechanically induced defects and heterogeneities, which surrogate/accelerate the primary nucleation process.

Regarding the compositional evolution of the crystallization kinetics, the addition of Se led to domination of the slower nucleation-growth crystallisation mechanism over the fast autocatalytic growth from mechanically-induced defects. The nature of the proposed crystallisation mechanisms was confirmed by infrared microscopy and XRD. The addition of selenium into the $Ge_{20}Te_{80}$ matrix caused an enlargement of the identified crystallites; this, together with the overall deceleration of the crystallisation processes, indicates the suppression of nucleation processes. The presence of Se also greatly enhances domination of the CNT-based three-dimensional growth of volume-located crystallites. These findings provide explanation for the markedly increased thermal stability of Se-doped Ge-Te infrared glasses.

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CENTEM: Thermonanalytical center at the Czech West Bohemian University and its international cooperative program

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Specified research in the spheres of polymeric membranes, hydrogels, polysialates and geopolymers, composites (and their profiles drawn by new pultrusion technology), photovoltaic cells and panels, fuel cells, batteries and solid electrolytes, biomaterials and biomedical application, car exhaust catalyses, nanomaterials and noncrystallites, foams heat isolators, etc., is concerned.

Instrumentation comprise MTGA – Thermogravimetric analyzer Q500, MDSC – Differential scanning calorimeter Q200, DMA – Dynamical mechanical analyzer Q800, MTMA – thermo mechanical analyzer – Q400, Rotary rheometer – ARES G2, Electrochemical impedance spectrometer – AIS, Dynamic thermogravimetry of vapor sorption – DVS, Inverse gas chromatography – IGS-SEA, Fuel cell testing with polymer membrane – PEMFC-TS, Laser deposition of thin layers, Dispersive fluorescence RTG spectrometer – AXS Bruker S4, Capillary electrophoresis with UV detection, Low angle RTG diffraction – SAXS Anton Paar, 3-D light microscopy, electron microscopy, etc.

The Centre is prepared to serve as an international reference laboratory ready to cooperate on the explication of variety methodical, scientific and industrial problems, providing material analysis and allied data evaluation, eventual explanation of whole problematic including the selection and association of individual types of measurements, analysis and material´s option.
Beside international assignments, domestic projects and cooperation with industry, the Centre provides education service in both the material science and a wider range of interdisciplinary learning; recently is subordinating the international program "Excellence of human resources as basis for the competition ability" granting postdoctoral studies. Research includes powerful state of theoretical basis on thermophysical measurements, thermal analysis and calorimetry, material thermodynamics and technology, mechanical dynamics, reaction kinetics, data evaluation, computer data processing and analysis. It encompasses links to various interna-tional boards as well as wider publication activities, including special book (now exhibited):

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Dilatometric measurement and calculation of thermal expansion coefficient of real steel grades

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This paper deals with the study of thermal expansion coefficient of real steel grades. Two real steel grades were investigated and their thermal expansion coefficient and density were obtained. The dilatometric measurements [1] were performed on the NETZSCH Dilatometer DIL 402C/7 device. Both quantities were also computed using Thermo-Calc software with TCFE7 [2] database. Comparison and discussion of experimental and computed data was performed.

Investigated quantities are valuable for many SWs used for technological processes modelling. These data are also very useful for thermodynamic and kinetic modelling. Obtained data can serve for addition and enhancement of many thermodynamic databases [3].

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Study of equilibrium and nonequilibrium phase transformations temperatures of steel by thermal analysis methods

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Phase transformations temperatures of steels are one of the crucial thermophysical parameters used for process behaviour prediction in many applications (thermal treatment of steels). Phase transformations temperatures are an input variables for many thermodynamical and kinetic programs. Experimental data of phase transformations temperatures can be found in literature, but it is difficult to find data for concrete steel (with exact chemical composition).

The paper deals with the study of phase transformations temperatures of steel in the low temperature region. Phase transformations temperatures were obtained using two different methods - Differential Thermal Analysis (DTA) and Dilatometry. Measurements by both methods were performed at the same experimental conditions (heating/cooling rate, isothermal holding, atmosphere). Obtained phase transformation temperatures were compared and discussed.

Micro-structural characterizations of investigated steels were carried out after differential thermal analysis and dilatometry. Micro-structural characterization using optical microscopy was performed.

Thermoanalytically determined phase transformations temperatures were then compared with values obtained by calculations (Thermocalc, IDS and QTSteel software).

The phase transformations temperature obtained for the low temperature region may be used in the field of thermal and mechanical treatment of materials.

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Determination of phase transformations temperatures of real steel grade in the low and high temperature region

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Steels are one of the most frequently used materials. The demands made on them at present are still higher. That's why behaviour of steels under precisely defined conditions of heating and cooling are still the object of extensive research. Differential Thermal analysis (DTA) is one of the suitable experimental methods for description of thermal behaviour of steels.

The paper deals with the study of phase transformations temperatures of real steel grade. Phase transformations temperatures were obtained using Differential Thermal Analysis (DTA) and Setaram Setsys 18_{TM} laboratory system. There are presented results from the low temperature region (below 1000 °C) and high temperature region (above 1000 °C). The extrapolation of obtained phase transformation temperatures to zero mass and heating rate was performed. The obtained phase transformations temperatures are discussed. Phase transformations temperatures are calculated using thermodynamic and kinetic software Thermocalc and IDS also. Experimentally obtained data of phase transformations temperatures were compared with calculated data and discussed.

The data obtained for the low-temperature area may be used in the field of thermal and mechanical treatment of materials. The data obtained for the high-temperature area may be used for an optimum setting of conditions for casting of steels.

The obtained phase transformation temperatures may be used also as input data for mathematical and physical models and they can contribute to improve precision of calculations with use of thermo-dynamic software packages.

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Thermal analysis of new Al10Ti10Co25Ni35Fe20 High-Entropy Alloy

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High-Entropy alloys are relatively young branch of Materials Science and still are not well described as applied materials. These alloys are composed of the individual elements in the range of 5-35 atomic%. Their name comes from the entropy configuration $\Delta S_{conf} \geq 1{,}5R$ (R - gas constant). This condition is true for systems containing minimum 5 constituent elements. In these alloys the crystal lattice can be predicted due to parameter of average valence electron concentration (VEC) [1-5].

Al10Ti10Co25Ni35Fe20 High-Entropy Alloy was obtained by an arc melting from pure elements. As-cast material was subjected to thermal investigations: Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and High Resolution Dilatometry (HRD). The obtained results allowed to determine the thermal effects, weight gain, liquidus and solidus temperature, linear expansion coefficient, which in turn allowed to study phase transformations occurring in the material. In addition, the effect of cooling rate on the microstructure alloy was observed (microscopic observation).

The study was conducted for the use of the Al10Ti10Co25Ni35Fe20 alloy as a material capable of working at high temperatures.

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Thermodynamic analysis of the equilibrium precipitation of carbonitrides in low-Si multiphase steel

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Strengthening of ferrous alloys can be achieved in many ways including solid solution strengthening, grain refinement, cold deformation, precipitation phenomena, phase transformations etc. One of the special groups of advanced ferrous alloys for the automotive industry are multiphase TRIP-aided steels consisting of ferrite, bainite and retained austenite. These steels utilize different strengthening mechanisms to improve a strength level but the most important is the strain-induced transformation of retained austenite into martensite. This transformation takes place during cold forming of steel and results both in improving strength and plasticity. This phenomenon is called the transformation-induced plasticity effect [1, 2].

The TRIP steels contain Si and Al additions to prevent carbide precipitation under conditions of isothermal bainitic transformation. Hence, the carbon enriches a γ phase and allows to stabilize retained austenite at room temperature. The typical addition of silicon to the steel is approximately 1.5%. Unfortunately, such amount of this element deteriorates the sheet wettability by liquid zinc during hot-dip galvanizing process [3]. Thus, the industrial requirements prefer low-Si grades of TRIP-aided steels. The decrease of solid solution potential and as a result of the strength level related to the Si content decrease is compensated by Nb, Ti and V microalloyed additions. These elements form stable carbonitrides during hot deformation of steel in the austenite region. The increase of strength properties is due to grain refinement and precipitation strengthening by disperse particles of MX-type phases [4].

The final austenite microstructure depends on the interactions between recrystallization and precipitation phenomena, which are different than in concentional C-Mn and high-strength low-alloyed steels. The reason of that is the increased content of Si, Al and Mn in multiphase steels, which affects the precipitation kinetics. Therefore, the aim of the present study is to analyse the equilibrium precipitation of carbides and nitrides under various deformation conditions. The 0.2C-1.5Mn-0.5Si steel with Nb and Ti microadditions was investigated. The Dutta-Sellars model has been applied for determination of non-recrystallization austenite temperature. Thermodynamic calculations of the volume fractions of individual phases as a function of temperature were performed with the use of JMatPro software. The research included the identification of disperse precipitations using the transmission electron microscopy analysis.

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Phase equilibrium and dilatometric analysis of austenite decomposition in advanced high-strength medium-Mn steels

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Medium-Mn steels belong to third generation of advanced high-strength steels (AHSS) predicted to use in the automotive industry for elements which combine successfully high strength and formability levels. Their tensile strength can reach 1200 MPa at the elongation levels of approximately 20-30% [1-3]. It is possible due to their multiphase microstructure consisting of fine-grained ferrite and/or carbide-free bainite and 15-40% amount of retained austenite. The martensitic transformation of retained austenite into martensite upon cold deformation results in TRIP phenomenon (TRansformation Induced plasticity) related to the increase of steel's plasticity as a result of the high work hardening rate accompanying the strain-induced martensitic transformation [3, 4].

The present work addresses the phase equilibrium analysis and dilatometric studies of two Nb-microalloyed medium-Mn steels. The steels contain 3 and 5% Mn to stabilize retained austenite and 1.5% to prevent carbide precipitation during their thermal processing including the isothermal bainitic transformation step to enrich austenite in carbon. The different Mn content influences the hardenability of the steels and hence the austenite decomposition upon cooling. The pseudo-binary Fe-C diagrams of the steels were calculated using Thermo-Calc. Thermodynamic calculations of the volume fraction changes of structural constituents as a function of temperature were carried out. The study included the determination of the time-temperature-transformation (TTT) diagrams and continuous-cooling-transformation (CCT) diagrams of the investigated steels at equilibrium conditions. The calculated diagrams were compared with the experimental ones determined using dilatometric tests. The knowledge of continuous cooling transformation diagrams is of primary importance for design of bainite-austenite microstructures with an optimal morphology of retained austenite. Light microscopy and scanning electron microscopy were used to assess the effect of heat treatment on the morphological details of the microstructure.

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Research on reduction reaction kinetics for alternative oxygen carrier material containing Fe-oxides for practical application in Chemical Looping Combustion

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The paper shows results on alternative fuel combustion method named Chemical Looping Combustion (CLC). Nowadays, CLC is thought to be one of the most promising combustion technologies. The reason for that is that the concentrated carbon dioxide (CO_2) stream is produced without any energy penalty for its separation from fuel combustion processes. Additionally NO_x emissions are greatly reduced. In CLC the direct contact between air and fuel is avoided, while oxygen is delivered by an oxygen carrier (OC) material, typically metal oxide (MeO; usually NiO, CuO, CoO, Mn_2O_3 etc.).

At the Institute for Chemical Processing of Coal the new alternative OC materials are widely investigated. For purpose of that work pigment based materials containing both Fe_2O_3 (active metal oxide) and TiO_2 oxides (inert oxide) were produced. The chemical composition was chosen based on previously gained experience. For comparison of reactivity performance, OC was also prepared from pure chemicals. Reactivity tests were performed at isothermal conditions, by means of thermo – gravimetry (TG). The aim of the work was to study kinetics of reduction reactions for Fe–based OC. Redox reactions of OC were completed by 3% H_2 and synthetic air. MathCad software was used for the kinetic parameters determination such as an activation energy (Ea), the pre – exponential factor (A_0), a kinetic constant (k). The models of the reduction reactions f(x) were selected by the model fitting method.

Reactivity study results supported that the possibly benefits coming from operation on low cost OC materials. Furthermore, it is concluded that Fe– and Ti– oxides substitutes might be a substantial alternative for synthetic OCs since they significantly decrease an overall CLC process cost.

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Thermal behavior of sodium alendronate, a kinetic study under non-isothermal conditions

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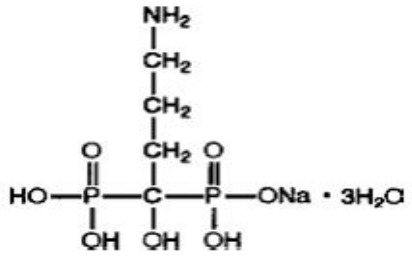
Sodium alendronate (see Scheme I) is a bisphosphonate which can be considered as a synthetic analog of pyrophosphate that bind to the hydroxyapatite found in bone. This explains the ability of interactions with the bone matrix by inhibiting bone remodeling activity and resorbtion [1]. Sodium alendronate (ALE) has strong bone-implant osseointegration and implant fixation properties [2] and also it is used to treat osteoporosis and other osteolytic bone diseases [3].



Scheme I. Sodium alendronate

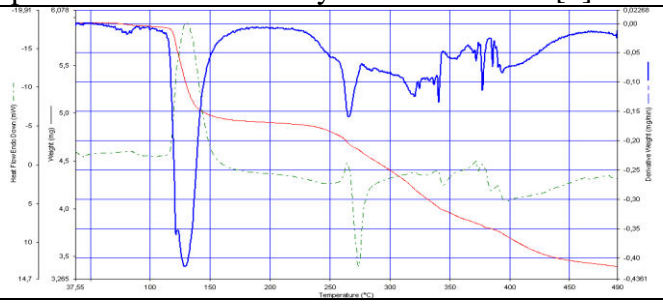


Fig. 1. TG/DTG/DTA curves of Sodium alendronate obtained at 10°C·min^{-1}

The thermal-induced destruction of the ALE molecular architecture was studied in air atmosphere at five heating rates: 5, 7, 10, 12 and 15°C· min^{-1} respectively. An example of thermoanalytical curves by 10°C·min^{-1} in presented in Fig. 1.

The TG/DTG data were processed by three different kinetic methods: Friedman, Flynn-Wall-Ozawa and Non Parametric Kinetic. The kinetic analysis had similar strategy with that presented in previous paper [4-6].

By comparison of the activation energy values, the differences are due to the differential or integral character of the data processing.

As in many previous studied cases, the NPK method reveals its two major advantages: a non-speculative and complete description of the reaction rate in respect of temperature, respective conversion degree, and the identification of the individual reaction steps of a complex process.

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The influence of temperature changes on the eigen-frequencies and mode shapes for rectangular plates clamped on the contour

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The analysis of free vibrations on rectangular plates with mixed conditions of buckling in the thermal environment is carried out by means of the 3D elasticity theory [1]. In this paper there has been analyzed by the finite element method (FEM) [2], the mode shape and the eigen frequencies for a rectangular plate clamped on the contour for different temperatures. In this analysis successive heat degrees have been used, this fact helping to find the critical values in which the frequencies were at zero and to correlate these temperatures with the values obtained from the static analysis. The temperature rise, the material graded index and the geometrical parameters on the eigen-frequencies were studied [3].

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The determination of the hydro-generator efficiency through the calorimetric method

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It is known that not always the functioning of a hydro-generator takes place in optimal conditions regarding the yield. The exploitation of a high power hydro- generator in low yield conditions can lead to high energy losses with the consequences streaming from this fact. The present paper proposes to present a simple determining method of the synchronous vertical hydro-generator yield by an indirect method, the calorimetric method for evaluating the losses of a hydro-generator [1].

The yield is determined by summing up the separate losses in several functioning regimes of hydro- generators, namely: unstressed empty functioning, stressed empty functioning and symmetric try phased short circuited functioning.

Thus, there is presented a method of determining the losses in stator iron, in the coil age of the stator and rotor and in the venting, respectively the supplementary losses by measuring the evacuated heat via the cooling agent, which is the air used by the motors on the rotor, air that takes up the losses from the generator and transmits them to the cooling agent- the water from the stator air coolers.

The temperature of the cooling agent, temperature of the statoric coil ages of the hydro-generator [2], the temperature of the cooling water, the temperature of the generator hood, all are measured with thermoresisants and the air speed is measured with the anemometer.

By measuring the drops in temperature and the used air volume through the air coolers one can observe, sufficiently precise, the proofs of the generator losses.

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Overview of the wind energy and renewable energy sources in Romania

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The modern society becomes aware of the necessity to conserve and protect the environment, increasing the gained benefits from a rational use of the natural resources. The pollution and the limitation of the fossil fuels, associated with the political situation worldwide that affects direct the energy strategies, has made opportunities in the area of development and exploitation of alternative energy sources.

The development of the exploitation of renewable energy sources are directly linked to the energy politic, which, in terms of Romania, has the focus to integrate in the European Union energy market. The year 2014 brought in Romania many legislative changes to the support scheme through green certificates, that proves, once again, the legislative unpredictability and limitations introduced by the legislator "during the game" that overthrew all economic profitability calculation of the existent and planned investments in this sector. The actual stage of the wind energy across Europe and the particular situation in Romania are highlighted; also a 2020 forecast for Romania tries to evaluate the perspective for the wind, and general, renewable energy market. The actual Romanian renewable energy support scheme, mainly regulated by "Law 220" [1] ends in December 2016. The so called ready to build projects, especially wind or hydro plants projects, can hardly be finalized until this deadline, and are so not able to qualify to this support scheme. Another legislation that has to clarify how investments in the renewable energy sector will be supported is for the moment not in place, increasing the uncertainty of project development, implementation and economical benefit of the producer.

The paper presents an updated overview of the Romanian renewable energy sector, its perspective and how the technical developments of the different technologies [2] can offer a profitable exploitation in the context of reducing the support reducing.

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The study of the partial discharge level from the hydro-generator stator insulation of high power

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The paper presents a determining and evaluating method from an experimental point of view of the partial discharges level from the insulation of the stator of a synchronous hydro-generator of high power that appear at different temperatures [1].

The temperature is measured directly on the coil with placed thermoresisants between the superior and inferior bars. Also, the level of partial discharges with the coil age [2] in a cold state, at the temperature level of the surrounding environment from within the stator, but also in a warm state at different temperatures, is measured.

Through this method there is created the possibility of highlighting some eventual degradations of the coil insulation of a hydro- generator [3].

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Kinetic parameters of decomposition under thermal condition of PLA/PBAT blends by conventional TGA and Hi-Res MTGA

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The importance of research for finding renewable resources for our many petroleum-based products, particularly for food packaging materials, is nowadays emphasized by the economic impact of petroleum resources depletion, and by the concerns regarding the environmental protection. Headway is being made with a polymer called poly(lactic acid) (PLA), an affordable, recyclable, innovative packaging material made from renewable resources.

Despite these qualities, PLA has a weakness: it is very brittle, and this makes processing difficult. To reduce brittleness, in order to improve processability without affecting the main quality of PLA - biodegradability, PLA is compounded with other semicrystalline and thermoplastic copolyester, such as poly(butylene adipate-co-terephthalate) PBAT [1, 2]. Their blends give interesting materials for industrial packaging applications, due to their increased ductility as PBAT content increases. However, like many aliphatic polyesters, the PLA matrix degrades upon melt processing, thus affecting the thermo-mechanical features of the blended material.

In this work, we studied the thermal stability upon melt processing and thermal degradation at higher temperatures of PLA, PBAT and blends with different PLA/PBAT ratio using a thermogravimetric analyzer Q5000IR (TA Instruments) and four run methods:

- Conventional TGA at eight constant heating-rate between 1 and 30°C/min to 700 °C;
- Isothermal TGA was performed at eight temperatures: 160, 180, 200, 220, 240, 260, 280 and 300°C for 600 minutes;
- Modulated Standard (MTGA): ± 5°C for 180s, Ramp 5°C/min to 700 °C;
- Modulated TGA with Hi-Resolution (Hi-Res MTGA): ±5°C for 180s, Ramp 5°C/min, Resolution=5°C to 700°C, Sensitivity=1.

Modulated TGA is based on a method first proposed by Flynn in 1968 [3] and patented by TA Instruments. In MTGA, a sinusoidal temperature modulation is superimposed on the underlying linear heating-rate profile used in traditional TGA. These modulated temperature results in an oscillatory response in the rate of weight loss, deconvolution of which via real-time discrete Fourier transformation produces the desired kinetic parameters. The activation energy of degradation (Ea) and pre-exponential factor (A) can then be determined at any point in the decomposition reaction [4].

Results given by MTGA and Hi-Res MTGA were in good agreement with values calculated from conventional TGA using isoconversional methods (Kissinger, Flynn-Wall-Ozawa, Friedman, Kissinger-Akahira-Sunose) with recommendations developed by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) [5].

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Kinetic studies of the dehydroxylation and crystallization of kaolinite

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The dehydroxylation and crystallization processes of the kaolinite during the thermal treatment are extensively studied because of the practical interest for the production of ceramics and refractories. The metakaolinite resulted after the controlled annealing of some clays or kaolins shows interest for cement admixtures or additives for dry mortars, due to its pozzolanic activity [1, 2].

The aim of this work was to investigate the effects of some fluoro compounds (LiF, NaF, CaF_2) on the kinetic of dehydroxylation and crystallization of kaolinite. High purity kaolin was used, with the composition (wt. %): 46.98 SiO_2, 36.73 Al_2O_3, 0.42 CaO, 0.30 MgO, 0.04 Na_2O, 1.24 K_2O, 0.24 TiO_2, 0.72 Fe_2O_3 and 13.33 losses on ignition. Starting from the initial kaolin (K-0), 3 samples were prepared with 1% fluorine, introduced as LiF (K-Li), NaF (K-Na) and CaF_2 (K-Ca).

Thermal behaviour of the samples was studied using a Netzsch STA 449C TG/DSC instrument, in air atmosphere, at a flow rate of 20 mL min^{-1}. The non-isothermal TG/DSC curves were recorded in the temperature range of 25–1200°C at heating rates of 8, 10, 12, 14 and 16 K min^{-1} and Pt crucibles. The mass of the samples was 20 mg. The phase composition of the K-0 sample–before and after annealing at 700 and 1000°C was established by XRD, using a Rigaku Ultima IV diffractometer ($Cu_{K\alpha}$ radiation). Specific surface area of the powders, S_{BET}, was measured by BET (Brunauer, Emmett, Teller) nitrogen gas adsorption technique using a Micromeritics ASAP 2020 instrument.Kinetic studies of the dehydroxylation reaction were carried out using the TG curves. DSC curves were used to study the crystallization process. The activation energies of the dehydroxylation and crystallization processes were calculated using the isoconversional methods described by Kissinger-Akahira-Sunose (KAS) and Vyazovkin [3]. The enthalpies of the two processes were evaluated by the DSC peak area, using the Netzsch software, Proteus 4.8.5. The enthalpy of the dehydroxylation endothermic process increases in the presence of fluorides from 379±7 J g^{-1} for K-0 to 496±14 J g^{-1} for K-Li. The enthalpy of the crystallization exothermic process is relatively small and slightly decreases in the presence of fluorides from -60±5 J g^{-1} for K-0 to -45±5 J g^{-1} for K-Na. For the dehydroxylation process, the values of the activation energy calculated as a function of the conversion extent are not significantly influenced by the fluorides presence. For the crystallization process, all the samples with fluorides show values of the activation energy higher than those of the sample without fluorides in the entire range of the conversion extent.

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Researches concerning the rapid decomposition of ammonium nitrate and the interpretation of the thermal phenomena in order to increase the security level

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The work is aimed at studying the thermal decomposition of ammonium nitrate suffered through thermal methods, regarding the increasing of the security of products based on ammonium nitrate. Ammonium nitrate has become particularly important as chemical substance through its physical and chemical properties as a main component in preparation of various types of explosives, from the second half of the nineteenth century and much later, after I World War as chemical fertilizer of great value. [1]

Most natural substances suffers a series of changes after heating or cooling. These changes may underlie analytical information: qualitative, quantitative and structural. Subjecting the ammonium nitrate to programmed heating using MOM derivatograph type, has allowed by recording and interpreting the thermogravimetric curves the characterization and deeper knowledge of the phenomena of rapid decomposition, explosion type and phase transformations. [2]

A thorough knowledge of the properties and phenomena underlying the agglomeration and thermal decomposition suffered by ammonium nitrate, is particularly important in the study of type explosion accidents due to loss of control of processes, resulting casualties and important material damage.

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Classification and thermogravimetric characterization of early and late wood through the growth rings

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The aim of this study is to classify, characterize, and compare wood corresponding to different areas of annual rings in trees of temperate regions. Wood growth rings or annual rings are visible in the cross section of the trunk of a tree. Annual rings appear due to new diameter growth in the vascular cambium. In temperate regions, due the strong differences between seasons, the appearance of growth rings results from the different growth speed through the year. Inner parts of annuals rings are related to rapid wood growth. This less dense wood is named “early wood” or “spring wood”. Outer regions of growth rings are denser and correspond to the wood formed in summer or autumn, also named “late wood” [1].

Statistical learning methods of classification and analysis of variance models are applied to thermogravimetric curves (TG) corresponding to early wood and late wood of *Castanea sativa* in order to check differences with respect to wood thermal stability. Each TG curve is firstly smoothed using the local polynomial regression estimator. Then, using these estimated curves, the different wood classes are discriminated employing a nonparametric functional data analysis (NPFDA) technique, based on the Bayes rule and the Nadaraya-Watson regression estimator, and also novel functional generalized additive models (GAM) [2]. The latter allows to classify materials using simultaneously more than one type of thermal curves (namely TG and differential thermogravimetric curves, DTG). The results are compared with those obtained using classical and machine learning multivariate supervised classification methods, such as Linear Discriminant Analysis, Quadratic classification, Naïve Bayes, Logistic Regression, k Nearest Neighbors, Neural Networks and Support Vector Machines [2].

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Dielectric relaxation study of hyperbranched polymers of different molecular weight and their interaction with an epoxy resin

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The objective of this work is to determine the effect of the molecular weight of a hyperbranched polymer (HBP) on its glass transition and secondary relaxations, and to investigate its relaxation behaviour when incorporated into an epoxy resin matrix. For this study we have used three different commercial hyperbranched polyethyleneimines: Lupasol® FG, Lupasol® PR8545 and Lupasol® WF, with molecular weights (MW) of 800, 2000 and 25000 g/mol, and denoted as PEI800, PEI2000 and PEI25000, respectively. These HBP's have been studied separately and in stoichiometric mixtures with a DGEBA epoxy resin, DER331, denoted as follows with their corresponding Lupasol proportion by mass: ELP800 (15.3%); ELP2000 (16.6%); ELP25000 (17.5%). The glass transition temperatures determined by DSC for the neat HBP's are -61.9°C, -55.4°C and -52.9°C, respectively, and those for the pre-cured mixtures are -19.5°C, -18.8°C and -17.8°C, respectively. It is noted that only a single glass transition is seen by DSC in these mixtures, though optical microscopy shows that ELP800 and ELP2000 are phase separated whereas ELP25000 is not.

Dielectric relaxation spectroscopy (DRS) carried out at frequencies from 0.1 Hz to 100 kHzand at a heating rate of 0.5 K/min shows three dipolar relaxations: γ, β and α for all three HBP's. In all cases the relaxations appear at higher temperature the greater is the MW of the HBP. From the plot of the logarithm of frequency versus reciprocal peak temperature, the activation energies for the γ- and β-relaxations have been determined. For the γ-relaxation, the activation energy is very similar for all three HBP's, between 42.0 and 46.2 kJ/mol; this seems reasonable as this relaxation is associated with the motion of the terminal groups, which are the same in all cases. For the β-relaxation, the activation energies are much higher: 181 kJ/mol for PEI800, 162 kJ/mol for PEI2000 and 175 kJ/mol for PEI25000. There appears to be no significant effect of MW on the activation energy for the β-relaxation, implying that the same segment of the branches participates in this relaxation with no influence of the length of the branches.

For the mixtures with epoxy resin, the secondary γ- and β-relaxations follow closely the behaviour of the resin alone, implying that it is the epoxy resin which dominates the molecular mobility in all these mixtures. On the other hand, the α-relaxation, or glass transition, shows a significantly different behaviour for the high MW sample. For ELP800 and ELP2000, the α-relaxation splits into two peaks (ELP2000) or a peak and a shoulder (ELP800), which correspond to relaxations in the two phases identified by optical microscopy, and which appear particularly at low frequencies. For ELP25000, however, this splitting of the α-relaxation is not observed, which is consistent with its single phase appearance observed by optical microscopy.

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Rheological and thermal properties of Nanoclay/MDI/Bitumen Composites

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Bitumen, residue from crude oil distillation, is a complex mixture of different organic molecules, comprising predominantly hydrocarbons with a small amount of structurally analogous heterocyclic species and functional groups containing sulphur, nitrogen and oxygen atoms. Because of its good viscoelastic properties, it is widely used as a binder in road construction. However, vehicle loadings and environmental factors may affect its properties, leading to problems like rutting or cracking. The addition of different substances (polymers, acids, etc) has proved to enhance bitumen resistance and behavior. In that sense, the viscous flow behavior of MDI-modified bitumen and nanoclay/MDI/bitumen composites has been investigated in this work. Modified bitumens were prepared by melt blending of a base bitumen with nanoclay (Bentone® 34) and polymeric MDI

Results from viscous flow curves show that neat bitumen can be considered as a Newtonian fluid at 60ºC, as viscosity remains nearly constant in the entire shear rate interval studied. Systems containing 2 wt.% MDI present a Newtonian region at the lowest shear rate values, followed by a shear-thinning region. This behaviour may stem from the formation of new compounds, which yield more structured systems. Longer blending times in MDI-modified bitumens reveal a noticeable increase in viscosity. On the one hand, reaction proceeds to a larger extent, creating new urethane/urea bonds. On the other hand, the sample is also affected by oxidation provoked by the long-lasting processing.

Finally, the addition of nanoclay produces a noticeable modification in the rheological response, giving rise to a highly marked shear-thinning behaviour (no zero-shear-rate viscosity was found). The addition of MDI to the bitumen previously modified with the nanoclay leads to a further significant increase in the viscosity values. This result hints a synergistic effect between both modifiers may take place, probably as a result of local reactions between –NCO groups in MDI and -OH groups available on the nanoclay surface.

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Comparative Combustion Study of Raw and Clean Lignite Samples By TG-DTG-MS

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Lignite is one of the main energy sources in Turkey; used in power plants and also consumed for domestic heating. Therefore, reducing the ash and sulfur content by washing has become a compulsory process to obtain an environmentally friendly product. On the other hand, the main studies of lignite using thermal analysis techniques include characterization, high-pressure application to coal hydrogenation, catalytic effects due to inorganic substances, combustion, pyrolysis and kinetic analysis. Thermal analysis techniques such as, thermogravimetry (TG-DTG), differential thermal analysis (DTA) and differential scanning calorimeter (DSC) were employed at a growing rate in the evaluation and characterization of fossil fuels [1-2].

In this research, six different raw and clean lignite samples are prepared according to the ASTM Standards (D 2013-72). All TG-DTG-MS experiments were performed at different heating rates. Air flow rate through the sample pan was kept constant at 50 ml min-1, in the temperature range of 20-900 ^{o}C. A small amount of sample was used to avoid heat transfer limitations and to minimize mass transfer effects.

TG-DTG curves revealed three reaction regions. The first region is due to the evaporation of moisture in coal. Release of volatile matter and burning of carbon can be called the second region-the primary reaction region because weight loss mainly occurred in this region. The third region is related to the decomposition of mineral matter in the lignite. It is obvious that the second region is the most important region from the point of view of combustion of lignite. In TG-MS experiments, depending on the combustion environment, different compounds are observed at different temperature intervals (m/z 18 = H_2O, m/z 44 = CO_2 and m/z 64 = SO_2). In the experiments, in the temperature interval of 20-200 ^{o}C decomposition of water is observed in different intensities. With increasing temperature, in addition to decomposition of water, CO_2 is observed in high intensities.

[1] Different kinetic methods were used to determine the activation energy for raw and clean lignite samples. It was observed that activation energies of the samples were in the range of 45-56.6 kJmol^{-1} for raw and 44.1-54.4 kJmol^{-1} for clean lignite samples.

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Thermo-physical Characterization of Crude Oils By TG-DTA and TG-FTIR

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Thermal characterization and kinetics of crude oils is of great importance for the petroleum industry. Much of the work on thermal analysis of crude oil was directed toward the oxidation and/or cracking-combustion behavior of the samples and kinetic studies by thermal research using differential scanning calorimeter (DSC), thermogravimetry -differential thermal analysis (TGA-DTA) and simultaneous thermogravimetry - Fourier transform infrared (TG-FTIR) and others [1-2].

In this research, experiments with four different origin crude oils were performed with *Seteram* TGA-DTA (Thermogravimetry – Differential Thermal Analysis) and *Perkin Elmer* TG - FTIR (Thermogravimetry-Fourier-Transform Infrared) modules. The experiments are carried out with a sample size of ~10 mg. Air flow rate through the sample was kept constant at 50 ml/min. All the experiments were conducted in the temperature range of 20-900 ^{o}C at different heating rates 10 ^{o}C.

In non-isothermal combustion experiments by thermogravimetry and differential thermal analysis (TG-DTA), two main reaction regions were identified. In general a reaction between 130-450 ^{o}C was actually the first reaction region and called as low temperature oxidation (LTO). These reactions are characterized by the low levels of carbon oxides in the effluent gas stream and low peak temperatures. A second reaction which takes place between 450-670 ^{o}C contributes most of the exothermic heat of reaction and known as high temperature oxidation (HTO). It was observed that the main mass loss of the samples is occurred in LTO region. Around 70-90 % of mass loss in this region referring to the hydrocarbon of low molar mass and 10-30 % of mass loss in HTO referring to the degradation of hydrocarbon of medium molar mass. The TGA-FTIR instrument is composed of a thermogravimetric analyzer and a Fourier-Transform Infrared (TG-FTIR) spectrometer for the analysis of evolved gases. During the heating operation of sample, the evolving volatile products are carried out of the furnace directly into a gas cell where the gases are analyzed by FT-IR spectroscopy. The FT-IR spectrometer can obtain spectra every forty seconds to determine quantitatively the evolution rate and composition of several hydrocarbon compounds.

Throughout the study, it was observed that the activation energy values of the crude oil samples are varied between 17 - 21 kJ/mol in low temperature oxidation and 80 - 161 kJ/mol in high temperature oxidation region

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Thermal cycling as a novel method to experimentally derive the "equilibrium" Pu-Ga phase diagram

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There are currently two versions of the Pu-Ga phase diagram namely US phase diagram and Russian phase diagram. The major difference between them is that based on the US phase diagram, the phase structure at room temperature for a Pu-Ga alloy containing Ga in the range of 2 at% to 9 at.% is a single δ-plutonium phase, whilst the Russian phase diagram predicts that the room temperature structure should be a mixture of α-phase plutonium +Pu_3Ga. It is now widely accepted that the single δ phase shown in the US phase diagram is thermodynamically meta-stable and that it is the Russian phase diagram which is more likely to represent the true "equilibrium" phase diagram, with the mixed phase structure arising from the eutectoid decomposition of $\delta_{7.9at\%Ga}$ into α+Pu_3Ga at 97°C under ambient pressure. However, the kinetics of the eutectoid reaction under ambient temperature and pressure conditions is exceedingly slow, involving times on the order of 10,000 years.

The Russian "equilibrium" phase diagram was derived experimentally by applying long-term (thousands of hours) annealing at temperatures ranging from 130-200^{0}C after one of two types of high pressure pre-conditioning treatment on well-homogenized δ-stabilized Pu alloys. The role of pressure and plastic deformation was to "precondition" Pu alloys and thus enhance the kinetics of the δ- phase decomposition. So far as the author is aware, the Russian method is the only one that has been actually adopted to enhance the kinetics of the δ-phase decomposition under ambient pressure.

In this presentation, the feasibility of using thermal cycling to experimentally derive the "equilibrium" Pu-Ga phase diagram is discussed; in particular the effect of thermal cycling on the decomposition of δ-stabilized Pu alloys at ambient pressure. This is an alternative/novel to the Russian method and was originally proposed by the author and co-worker on the basis of a thorough analysis of data from a systematic thermal cycling experiment performed on annealed and aged δ-stabilized Pu-Ga alloys. The thermal cycling works were performed by differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The alloy specimen was thermally cycled from 25 °C to 180 °C within the DSC furnace enabling coincident collection of phase transformation information. It was found that the repeated thermal cycling in the temperature range 25 °C to 180 °C had the effect to drive and accelerate the Pu-Ga system toward its "equilibrium" state, as demonstrated by continuous α-phase in-growth with each thermal cycle. An experimental programme to confirm these initial observations is proposed and the "constrained" equilibrium Pu-Ga phase diagram that might be expected from this method is outlined.

Effect of doping on the crystallization kinetics of phase change memory materials on the basis of Ge-Sb-Te system

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Phase change memory devices are actively developed now. This type of memory can be one of the candidates to replace flash memory, due to the number of advantages, such as a high cycling endurance, high operation speed, and extended scalability. Promising materials for phase change memory are materials of Ge-Sb-Te system, and $Ge_2Sb_2Te_5$ is one of the most perspective. However, it is necessary to vary the properties of materials for technology optimization, which is usually performed by doping. Despite the fact that doping of chalcogenide semiconductors is a hard problem, we have shown that such dopants as Bi, In, Ti may affect on the thermal and electrical properties of $Ge_2Sb_2Te_5$. However, these impurities may affect the kinetics of crystallization, which determines the operation speed of the memory. Thus, the aim of the work was to study crystallization kinetics of the thin films of $Ge_2Sb_2Te_5$ doped with Bi, In, Ti.

Thin films of $Ge_2Sb_2Te_5$ with different amounts of Bi, Ti, and In (from 0 to 5 mass. %) were prepared by thermal evaporation of presynthesized materials. Structure of the thin films was investigated by XRD method. Compositions of films were checked by Rutherford backscattering. Differential scanning calorimetry (DSC-50, Shimadzu) was used for the investigation of thermal properties. Measurements were carried out at 8 different heating rates (from 1 to 90°C/min) in a nitrogen flow (20 ml/min). To determine the kinetic parameters of crystallization model-free Ozawa-Flynn-Wall and model-fitting Coats-Redfern methods were used simultaneously.

It was shown that crystallization proceeds in two stages nucleation and nucleus growth. The contribution of the first process decreases while for the second – increases. Such behavior observed almost for all compositions. In general it can be noted that In have pronounced affect on the nucleation. It was found that second- and third-order models are most probable models describing crystallization of the investigated thin films.

Estimated kinetic parameters were used to calculate the crystallization times. Possible recording and storage times in memory devices based on investigated materials were evaluated. It was shown that doped compositions allowed to achieve better results in comparison with undoped $Ge_2Sb_2Te_5$. Composition with 0.5 mass % Bi have most promising properties. It shows fast crystallization at operation temperatures, which may lead to fast operation rate, and demonstrate slow crystallization at room temperatures, which means good stability and long storage times.

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Crystallization or amorphization? Defining the dominant process using thermal analysis

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Co-crystallization and co-amorphization are considered key methods [1, 2] in overcoming challenges of the ever increasing proportion of APIs, in the pharmaceutical industry pipeline, with low solubility in aqueous media. Furthermore, it is desirable that the solid forms of the APIs are engineered by means of green chemistry. As such generation of co-crystals and co-amorphous systems using methods such as hot-melt extrusion (HME) are being increasingly investigated [1]. During melt extrusion, for example, the cooling of the molten APIs/formulation can result in four possibilities: (1) the compounds convert into their unique crystal form(s), (2) become kinetically trapped at different rates resulting in two distinct amorphous phases with different T_g values, (3) generation of a single crystalline form with a crystal lattice containing each compound (co-crystal) or (4) generation of a single amorphous phase with a single T_g (co-amorphous). Herein we investigate which process dominates upon cooling a molten mixture (1:2, 1.1 and 2:1 molar ratios) of two miscible compounds (Pindolol (PD) and Acebutolol (AC), respectively) - *one with strong crystallization tendency (PD) and the other with a strong glass forming tendency (AC)* - at different scan rates (1 to 40°C/min) by means of DSC.

Initial results show that mixtures of the two compounds generate eutectics (Fig.1a) and upon co-melting and subsequent cooling a single amorphous phase (co-amorphous) is detected at all the molar ratios studied (Fig. 1b), at all cooling rates. However, when the ratio of the PD is increased to 2:1 (Fig.1b), small amounts of crystals are generated which seeds the rubbery amorphous phase after the T_g resulting in crystallization at 88 ± 1°C (onset) followed by a melt at 143°C (onset). The results show that amorphization dominates over crystallization when two miscible compounds are co-melted and cooled and this is independent of the cooling rate. Furthermore this study demonstrates the use of DSC to screen co-formers for the generation of co-crystal or co-amorphous solids using HME.

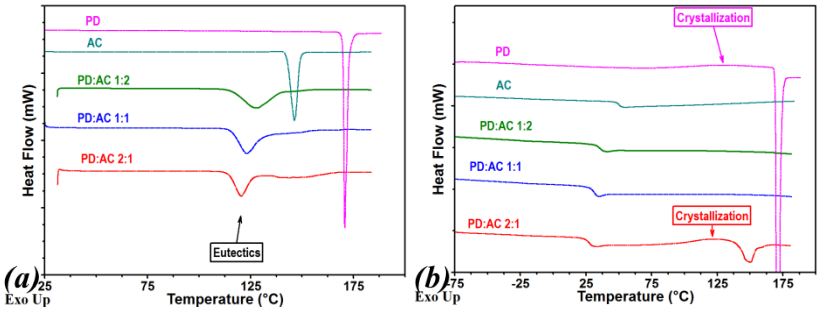

Fig.1 *DSC thermograms of Pindolol, Acebutolol and their physical mixtures heated at 10°C/min , (a) initial heating of samples from ambient temperatures and (b) heating after cooling the co-melts at 1°C/min to -90°C.*

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Solution calorimetry as the method for determining Proton acceptor scale of ionic liquids

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Ionic liquids are organic salts with melting point lower than 100ºC. Due to their unique properties, they can be used as universal catalysts, solvents and coolants. Ionic liquids have low vapor pressure, high chemical and thermal stability, the ability to dissolve many organic and inorganic substances. It allowed them to be widely adopted in catalysis, synthesis, electrochemistry, nanotechnology and etc. However, their thermodynamic properties haven't been extensively studied. Especially, there is lack information about energies of intermolecular interactions in solutions of ionic liquids with different solvents.

We studied the thermodynamics of dissolution of aprotic ionic liquids in chloroform and tetrahydrofuran at 298.15 K. The objects of our study were ionic liquids with the imidazolium cation, different anions and different length of alkyl groups. Tetrahydrofuran and chloroform were taken as solvents due to several reasons. First, they have equal parameters of van der Waals interactions. Second, tetrahydrofuran is proton acceptor and chloroform is proton donor. So, difference between enthalpies of solution of ionic liquids in these two solvents (enthalpy of transfer) can be a measure of hydrogen bonding strength. Also, depending the sign of this difference one can say that studied ionic liquids have higher proton donor or proton acceptor ability. In order to obtain thermodynamic data at infinite dilution concentration effect on the heat of dissolution was studied. It was shown based on calorimetric data that studied ionic liquids exhibit predominantly proton acceptor abilities. The strength of hydrogen bonding increase in the range Trif < $(CN)_2N$ < SCN < $BuSO_4$ < $EtSO_4$ < $MeSO_4$. Also we have observed that proton acceptor ability of studied ionic liquids slightly depend on the length of alkyl group. Obtained calorimetric data were confirmed by FTIR-spectroscopic results.

New praseodymium polyselenide $PrSe_{1.95}$: thermodynamic modelling, crystals growing and study of their structure

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Rare-earth polyselenides ($LnSe_{2-x}$, $x = 0 – 0.5$) are of interest due to their ability to formation of anionic clusters in solids. They are layered compounds and anionic layers consist of selenium atoms which can realize extended Se-Se bonds in solids and create the superstructures. The displacement of selenium atoms in new positions of superstructures is a favorable factor for the existence of structural and electronic transitions, whose probability increases for the polyselenides with small Se/*Ln* ratio. Synthesis of compounds, which are poor by selenium, is difficult task due to the lack of regulated thermodynamic parameters ($p_{Se}=f(T, x)$).

Earlier we had investigated the $PrSe_2$–$PrSe_{1.5}$ system by static method with quartz membrane-gauge manometers [1]. This research has shown that in the investigated range of compositions ($x = 0 – 0.5$) the phase regions composed of discrete compounds, whose compositions can be described by the general formula Pr_nSe_{2n-1} (n = 5, 7, 10, 20). Praseodymium polyselenides with n = 7 ($PrSe_{1.85}$) and n = 10 ($PrSe_{1.90}$) were described in literature, phase with n = 5 ($LnSe_{1.80}$) was known for samarium and gadolinium, but the existence of $PrSe_{1.95}$ (n = 20) was found in our work [1] for the first time.

The information obtained was used for thermodynamic modelling in Pr-Se-I system with the aim of obtaining the crystals of $PrSe_{1.95}$ composition. Thermodynamic functions ($\Delta_f H_{298}$, S°_{298}, $C^\circ_{p,298}$) found in [1] provided the basis for thermodynamic calculations of crystal growth process by I_2 vapour transport reactions. The calculations of the equilibria are based on minimization of the total Gibbs energy of the investigated system. As a result of these calculations the most optimal conditions (p_{Se}, T, ratio of atomic concentrations elements) were found for the synthesis of $PrSe_{1.95}$ crystals.

These conditions were reproduced in closed reactor and single crystals of $PrSe_{1.95}$ were grown. These crystals were identified by microprobe and X-ray analysis.

X-ray diffraction analysis showed that the crystals are not monophasic and consist of units of the tetragonal and monoclinic symmetry having a common structural prototype (PbFCl). The chemical compositions of these crystals are the same in the limits of the standard deviation value. The symmetry of the tetragonal crystal is a rare symmetry for polychalcogenides, and the investigated crystal is a splice of the tetragonal phase and some uncertain additive whose symmetry isn't still determined.

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Assessment of measurement accuracy for experimental construction of phase diagrams

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Thermodynamic methods of phase diagrams calculation with application of various modern software are highly developed. However, the experimental results obtained mainly with the use of thermal analysis methods are the initial data for receiving of desirable parameters and development of various thermodynamic models. Therefore it is necessary to receive the accurate data described parameters of phase transitions for experimental studying of various systems in the best way.

The purpose of the present work is estimation of received results total accuracy as an example of ternary Cu-Co-S system alloys [1]. Estimated accuracy can be standard value for studying of multicomponent systems on the basis of Fe, Ni, Cu, Co, and S. Total accuracy will include: the accuracy of determination compositions with the use of ICP-OES method (Inductively coupled plasma-optical emission spectrometry); precision of phase transitions temperature determination with application of thermal analysis methods (DTA or DSC) and accuracy of obtained results mathematical treatment. Defined accuracy values allow showing the reliability of measurement techniques, including samples synthesis and thermoanalytical experiments.

In the course of this work two sets of experimental samples of Cu-Co-S system are prepared (% wt): 10.9Cu, 61.6Co, 27.5S and 86Cu, 12Co, 2S (each composition is repeated ten times). All synthesized samples are investigated by ICP-OES and DTA methods. The results have shown a slight deviation between received and desirable compositions (in the limit of ±1 % wt.). Therefore, temperature parameters of phase transformations in the “liquid–solid” region are in the good agreement (the total error doesn’t exceed ±1,2°C).

Assessed measurement accuracy has shown the reliability of experimental results, that were used for multicomponent phase diagrams construction for a number of sulfide-metal systems Cu-Me-S (Me: Co, Ni, Fe) [1-4]. Thus, the discussed technique is suitable for research and construction of phase diagrams of quaternary Fe-Cu-Ni-S and Fe-Cu-Co-S systems.

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Thermal analysis and combustion calorimetry of wood lignin and it pyrolysis products

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Lignin, along with cellulose, is one of the most prevalent natural organic polymers. Lignin is built from phenylpropane structures and their methoxy and hydroxyl derivatives. Contained in the plant cells, lignin provides cell wall strength, where it forms different three-dimensional structures. Content of lignin in wood is about 20-30% of whole mass, what makes it a potential source of different organic compounds. Only wastes from pulp and paper mills contain about 50 million tons per year of lignin. 98% of this amount is just burnt without further processing.

In the near future, development in biotechnological methods of vegetable raw materials conversion into biofuel and biopolymers will increase the amount of lignin wastes. It will require effective technologies of lignin processing for different fields of industry. One of pre-treatment methods of lignin wastes processing into low molecular weight products is a thermochemical conversion, in particular, pyrolysis.

In this study, thermal decomposition of hydrolysis lignin was carried out and studied using thermal analysis techniques in temperature interval from 30°C to 700°C in inert atmosphere. Amounts of solid (coal like), liquid and gaseous products of decomposition were determined. Heating value (HV) of lignin and its products were measured by combustion calorimetry method. It was shown, that solid residue produced from lignin decomposition has larger HV than other species.

Simultaneous thermogravimetry and differential scanning calorimetry technique with mass-spectrometric gas detection was used for studies of heat effects of pyrolysis and its kinetics. It was shown that pyrolysis of lignin and its products is a complicated process which consists of several stages. Start temperatures of pyrolysis process for all three samples were similar, about 320°C. Mass loss of samples increases in the series: solid residue < lignin < liquid fraction. Heating rate impact on the pyrolysis process was examined. Activation energies of lignin pyrolysis were determined based on the measurements at four heating rates using different model-free methods.

Kinetic analysis of lignin decomposition was obscured by model-free methods of activation energy calculations. Analysis was carried out independently for every stage of decomposition. Data was obtained from DSC, measured on different heating rates. According to ICTAC recommendations, three different kinetic computational methods were used.

Study of Eutectoid Decomposition Kinetics of $Cu_{50}Zr_{50}$ Alloy

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According to the Cu–Zr phase diagram [1], the CuZr phase is stable above 986 K and it undergoes eutectoid decomposition to $Cu_{10}Zr_7$ and $CuZr_2$ below this temperature. The $Cu_{50}Zr_{50}$ alloy was prepared by arc melting from the mixture of pure Zr (99.95%) and Cu (99.99%) metals in ultra-high purity argon atmosphere. The alloy was melted several times to increase the compositional homogeneity. The kinetics of the eutectoid decomposition in the $Cu_{50}Zr_{50}$ alloy under isothermal and non-isothermal conditions has been studied by differential scanning calorimetry (DSC) using a NETZSCH STA 409 PC Luxx instrument.

The time-temperature-transformation (TTT) diagram for the decomposition of CuZr has been determined over a wide temperature range. The nose of the TTT curve was obtained at ~ 800 K. At that temperature, the eutectoid decomposition starts after 6 min annealing. The DSC curves obtained under isothermal conditions were analyzed by the Johnson–Mehl–Avrami model [2].

The continuous-cooling-transformation (CCT) diagram for the eutectoid decomposition was obtained in the cooling rate range of 1.5–22 K/min.We find that above the critical cooling rate of 25 K/min eutectoid reaction $CuZr \rightarrow Cu_{10}Zr_7 + CuZr_2$ is not observed. The rate of the eutectoid decomposition in CuZr is extremely high in comparison to those for many other copper-based systems which have critical cooling rates of the order of 1–10 K/s [3].

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Kinetic study of light crude oil combustion and pyrolysis using TG/DSC/MS techniques

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High-pressure air injection (HPAI) is one of the promising thermal methods of light oil recovery from low-permeability reservoirs. Air injection into the well induces the rise of the pressure and oxidation reactions after air contacts with oil. Preliminary tests have shown that the use of HPAI technology can achieve the great performance of recovery rates compared with other methods. Heat generated directly inside the oil reservoir and produced amount of gaseous products like carbon oxides, nitrogen and light hydrocarbons significantly reduces the heat loss, reduces power consumption and affect the oil displacement. There are some examples of field applications of HPAI nowadays. For more detailed analysis of using HPAI on a certain reservoir, a number of research methods have been developed in recent years. The most widely-spread of them are thermogravimetry and differential scanning calorimetry. These methods can be used for more deep analysis of oil oxidation mechanism, for fast screening of HPAI technology and for determination of kinetic parameters of oxidation process.

In this work we applied simultaneous TG/DSC technique for study of light crude oil from Vishanskoe oilfiled. Experiments were carried out in two gas atmospheres (air and argon) in order to study separately oxidation and pyrolysis processes. For kinetic analysis crude oil sample was measured at four heating rates. Also, crude oil was divided into SARA fractions and for each fraction the same experiments as for crude oil were carried out. A detailed kinetic study was conducted by different mathematical approaches. This research also intended to reveal the heating rate effect on combustion properties and kinetics of crude oils for a possible in-situ combustion process. DSC experiments show that crude oil and its SARA fractions undergoes two major transitions when subjected to an oxidizing and constant rate environment known as low (LTO) and high temperature oxidation (HTO) at each heating rate studied. In case of TG/DTG data third peak appeared for crude oil and saturates fraction which is induced by evaporation of low volatile compounds. According to the kinetic results, apparent activation energies in HTO region were considerably higher than those in LTO except resins fraction.

Kinetic Study of Thermal Decomposition of Rigid Polyurethane Foams by Artificial Multilayer Neural Network

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Rigid polyurethane foams (RPF) have a rigid highly cross-linked polymeric network. Inorganic fillers addition in their manufacture process, such as alumina industrial waste, increases the mechanical strength of the foams and besides is an economic and environmental choice [1]. Kinetic models describe the foams decomposition process. However, not always the adjustments made by the models are suitable. In order to overcome this problem, the use of Artificial Neural Multilayer Network is originally proposed in this work for kinetic investigations. The proposed Neural Network structure sets the weights in the input layer according to the rate constants determined by fitting the experimental data for each considered kinetic model. This linearization ensures the use of models as activation function of neurons in the hidden layer and the interconnection weights between this intermediate and the output layer determining the contribution of each model in the overall fit [2,3]. The proposed network is a powerful mathematical procedure, which considers the contribution of several models for the process. It presents a significant reduction in the residual error by fitting the experimental data. These fitting improvements allow detailed study of the physical process and therefore the accurate calculation of the kinetic parameters such as the activation energy, frequency factor and half-life. Two samples were used for RPF, load (Al_2O_3) and no inorganic filler, both synthesized from a polyol extracted from Ricinus communis seeds. The isotherms were obtained at a thermobalance Shimadzu TGA-50H in an alumina crucible, N_2 flow at 50mL/min and a heating rate of 20°C/min to temperatures of 220, 228, 230 and 232°C due the significant loss of mass in this temperature range in the TG curve. The adjusted results obtained by the neural network were higher than those obtained by individual model analysis. Therefore, reduced residual errors are on average 10^2 times lower for both materials. The decomposition process of RPF loaded by alumina was best described by the R3 model at all temperatures but at 220°C, the R2 model contributes 78.86% for the overall adjustment. The D4, R2 and R3 models best adjust the decomposition data for non-loaded samples, with contributions depending on the analyzed temperature.

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Influence of the water/cement mass ratio on the type II cement early stages hydration

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This work is part of the activities of a project aiming CO_2 and SO_2 capture by cementitious materials. Its objective is to study the influence of the water/cement (W/C) mass ratio on the hydration of a type II Portland cement, which was selected after a previous hydration kinetics comparison with other three cements, to prepare the cimenticious absorbent materials. The study was done by thermogravimetry (TG) and derivative thermogravimetry (DTG) on calcined mass basis [1,2, 3]. For CO_2 capture, cement pastes can be used mainly due to their calcium hydroxide (CH) content formed during hydration, which reacts with CO_2 forming calcium carbonate in the cement matrix. [4]. After a previous determination of the maximum W/C ratio for the miscibility of this type of cement with water, which was 0.66, pastes of type II cement and water were prepared with W/C mass ratios equal to 0.40, 0.50, 0.60 and 0.65. As was seen by a previous study that the best conditions for carbonation of another cement were at the early stages of hydration [5], the main hydrated phases formed and the CH content formed in the first 4 and 24hours were quantified from TG and DTG curves. These analyses were performed in a TA Instruments, model Q600 equipment, at a heating rate of $10^{o}C.min^{-1}$, which were preceded by a drying step at $35^{o}C$, to allow the determination of the unreacted water of each case. The results show that, although at 4h of hydration the higher calcium hydroxide content was obtained for the lowest W/C ratio, at 24 h the higher was the W/C ratio, the higher was the CH content of the pastes, as well as the of the other hydrated phases.

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Thermal decomposition of polyurethane rigid foams from castor oil polyol and isothermal kinetic parameters

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Rigid polyurethane foams are materials widely used in thermal insulation for refrigeration systems and construction. The reactants used in polyurethane synthesis are from petrochemical sources and after its useful life, disposal should be insightful, because they are polymeric materials and their degradation is not easy. Thus, the preparation of polyurethane materials from alternative reactants and a better understanding of their degradation processes are very important to proper application, as well as its final destination. In order to have a better understand of the polyurethane degradation process, it was performed a isothermal degradation kinetic study of a polyurethane rigid foam and a composite synthesized from modified castor oil. The composite was obtained by adding to the polyurethane formulation, as filler, an inorganic waste generated in the Bayer process (alumina production process) containing high concentrations of Al_2O_3 and $Al(OH)_3$ [1]. The waste provided excellent mechanical and flame retardant properties to the rigid polyurethane foams.

Thermogravimetric (TG) curves were obtained on Shimadzu TGA50H thermobalance using approximately 4 – 5 mg of samples in alumina crucibles, in dynamic N_2 atmosphere (50 mL min^{-1}). The polyurethanes and the composites showed thermal stability up to 200 ^oC and the total weight loss in two principal steps. The isothermal thermogravimetric experiments were performed at 220 – 232 ^oC with heating times of 150 minutes. For the pure polyurethane foam the parameters values found were: activation energy (E) = 41.0 kJ mol^{-1}; pre-exponential factor (A) = 4.5 s^{-1}. For the synthesized polyurethane-waste composite, the values were: E = 28.0 kJ mol^{-1} and A = 0.2 s^{-1}. The decrease in the activation energy of the composite, when compared to the pure foam, may be related with interactions between inorganic filler and polymer network, which modifies the relationship between the polymer layers and decrease the material stability. The characterizations by FTIR showed characteristic polyurethane bands shifts in the samples with waste, indicating interactions of alumina filler with the polymer [2]. The scientific literature shows quite different values for the evaluated parameters, evidencing the heterogeneity of different polyurethane systems [3].

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Humic acids extracted from Romanian lignite – thermal, spectral and agrochemical behavior

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Humic acids are macromolecular organic compounds resulted by polycondensation of aromatic nuclei on which are grafted carboxylic, carbonyl and hydroxyl radicals. They are used in medicine, also as chemical fertilizers, or in soil bioremediation processes. Humic substances can also be pollutants of the groundwater in mining regions [1].

Humic acids studied in this paper are obtained from Romanian lignite (Rovinari-Oltenia) by alkaline-oxidative extraction at 70-80 °C for 6-8 hours. Their characterization was performed by thermal analysis (TG, DTG, DTA and DSC) and FTIR spectroscopy. They were studied compared with other standard humic acids. Agrochemical testing was done by introducing the humic acids in a matrix containing nitrogen (N), phosphorous (P), potassium (K), meso (Ca, Mg, S) and micro elements (Cu, Zn, Fe, Mn).

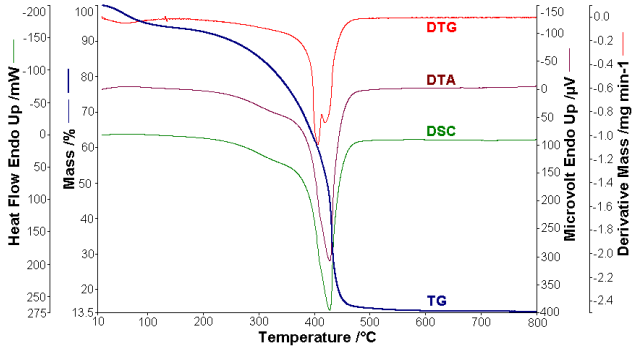

Fig. 1

Fig. 2

Thermal analysis of the humic acid with Romanian provenience (Fig. 1) shows that it has 8 % humidity and complete oxidative decomposition occurs between 150-600 °C. Decomposition occurs in two exothermic stages, of which the latter is stronger. A 13.5 % residue is obtained at temperatures above 700 °C, after the complete decomposition. Humic acid chelating ability is evidenced by FTIR spectrum (Fig. 2). It contains peaks generated by carboxyl, carbonyl and hydroxyl functional groups, and by single, double, and aromatic carbon bonds [2]. Due to the carboxyl and hydroxyl groups present in the macromolecule, humic acids function as chelating agents for inorganic cations, in particular for those involved in the metabolism of the plants, thus having stimulating properties. Confirmation of humic acids stimulating properties was done by agrochemical testing on the sunflower crop. Thus, were compared the effects of foliar application of a classic NPK fertilizer and of a fertilizer that associates NPK classical matrix with humic acids. The fertilizer containing humic acids has led to production increases by 27.2 %.

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Comparative analysis of agricultural materials influenced by anaerobic fermentation for biogas production in terms of ash melting behaviour

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Nowadays, the use of biomass represents one of the most accessible ways of valorification for renewable materials. In this context, using of residual agricultural residues has a major role relative to the fact that this type of materials can be found in large quantities.
There is a high potential of available biomass (wood, energy crops, agricultural products) [1].
The thermal processes, i.e., pyrolysis, combustion, gasification , appear as suitable to convert the biomass into an energy source [2].

Anaerobic fermentation is one of the ways in which the agricultural substrate can be converted in biogas, which, in its term can be used as fuel for firing processes with influence on obtaining clean energy.

The influence of anaerobic digestion can be observed from the modifications it brings to the general properties of the used materials.

The aim of this paper is to present a comparative study in terms of determining general properties of four different agricultural residual substrates before and after the anaerobic fermentation process inside a pilot installation dedicated to this type of applications.

The overall analysis will be conducted both in terms of chemical and physical characteristics, while the ash melting behavior will be monitored, ash melting points (shrinking starting temperature (SST), deformation temperature (DT), hemisphere temperature (HT) and flowing temperature (FT)) will be determined for the studied materials [3] and conclusions will be traced relative to influence factors (temperature, residence time, pH correction) which can modify the general material properties.

This work underlines the necessity to have informations upon material properties with direct impact on further usage for firing or co firing processes at small and large scale for possible development of proper technologies which can use this kind of materials.

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Thermogravimetric studies performed on memantine hydrochloride to determine its thermal behaviour and the kinetic parameters of the degradation process

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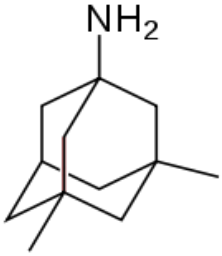
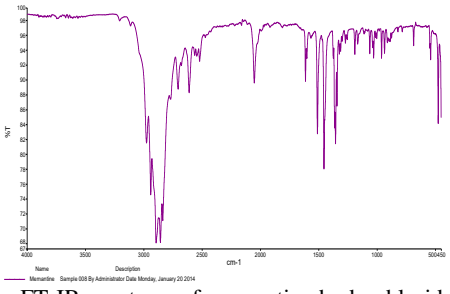
Glutamate is a neurotransmitter or a brain chemical that is involved in the memory and learning process. Higher amounts of glutamate make it toxic to the brain, having the possibility to kill brain cells. Too much glutamate might be one of the reasons why people with Alzheimer's disease have problems with learning and remembering new things. Memantine is a good candidate drug to stop glutamate from harming the brain because it is an uncompetitive antagonist of N-methyl-D-aspartate glutamate receptors [1], hence it can help reduce memory loss and thinking problems.

In this study we used memantine hydrochloride, which chemically is an adamantane derivative. The TG/DTG curves showed a complete degradation of the pharmaceutical agent, excluding the possibility of a sublimation process since the vapour pressure of the compound is negligible. All thermoanalytical data were recorded in air flow at 5 different heating rates: 5, 7, 10, 12 and 15°C·min^{-1}, according to the ICTAC 2000. Similar to other studies performed in our research center [2,3], all methods used to determine the kinetic parameters were isoconversional: Friedman, FWO, KAS and modified NPK.

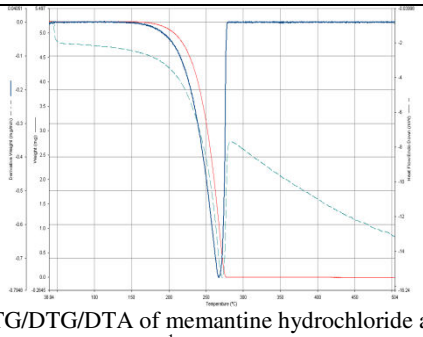
The modified NPK method of kinetic analysis showed that the thermal degradation is characterized only by a chemical process that can be separated into two reaction steps, the first one having an apparent reaction order of n=2 and the second one of n=1, respectively.



Chemical structure of memantine



FT-IR spectrum of memantine hydrochloride



TG/DTG/DTA of memantine hydrochloride at 5°C·min^{-1} in air atmosphere

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Studies of surface properties of chemical modified biochar

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Biochar (biocarbon) is a material similar to charcoal but has far wider properties and uses. It is used in a few areas of our lives, e.g.: in agriculture, environmental protection, the garment industry, construction, energetic. Biochar properties owe its raw materials from which it is derived: plant material, agricultural residues. Knowing the structure and chemical composition of the material, researchers introduce modifications of biochar in order to achieve the most desirable physicochemical parameters, tailored to a particular use. It is produced by pyrolysis, which is a slow combustion of organic matter at low (or completely limited) oxygen supply. Applied as an additive to the soil to improve fertility and carbon sequestration, in order to mitigate climate change. Already in pre-Columbian times the indigenous peoples of of the Amazon have used addition of biochar to the soil, creating fertile soil today called "terra preta do Indio".

The aim of this study was to investigate the effects of different extractants on the properties of biochar. The selected solutions were used for extraction, eg. HCl, NaOH - each at a different concentrations. Adsorption of water vapor were used to investigate the effect of the solutions on the sorption properties and specific surface area.

The thermal analysis technique was used for study the physicochemical properties of biochar sample surfaces.

The adsorption isotherms of water vapor were measured by gravimetric method and the specific surface area was obtained in agreement with the Polish standard method (PN-Z-19019-1, 1997). The monolayer capacity (N_m) and surface area (S) of biochar samples was evaluated from adsorption isotherms using the Brunauer-Emmett-Teller (BET) method, from the BET plot in the range of relative pressures $0<p\cdot p_0^{-1}>0.35$. The surface area was calculate the dependence $S=N_m\cdot M^{-1}\cdot L\cdot\omega$, where L is the Avogadro number ($6.02\cdot10^{23}$ molecules per mole), M is the molecular weight of gas or vapour (gram per mole) and ω is the molecule cross-sectional area for gas or vapour (m^2 for molecule). The BET surface area was calculated assuming the area occupied by a single water molecule equal to $10.8\cdot10^{-20}$ m^2. The specific surface area of biochar treated with solutions of the higher concentration was visible bigger in comparison to the control sample of biochar.

Life Origination Hydrate Theory (LOH-Theory): on the thermodynamic possibility of formation of amino acids from natural gas and niter

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The Life Origination Hydrate Theory (LOH-Theory) is the instrument for understanding the physical and chemical mechanisms applied by Nature for the living matter origination and propagation [1, 2]. We affirm that living matter originated as a result of thermodynamically caused chemical transformations, which are inevitable under definite ambient conditions and are governed by physical and chemical laws universal for any celestial body. According to the LOH-Theory, living matter originated from the unique set of mineral substances: CH_4, niter, phosphate, and H_2S. The syntheses of living matter simplest elements (LMSEs), i.e., nitrogen bases, riboses, and nucleosides, and of simplest forms of the precellular living matter (DNAs) proceeded at 273±20 K within the cavities of the CH_4-hydrate honeycomb structure, localizations of which represented natural thermostated "incubators". DNAs were synthesized on the basis of the intra-structural CH_4 and of NO_3- and PO_4-ions that diffused into the CH_4-hydrate structure from the outside. The reaction process was initiated by Konovalov's reaction between CH_4 and NO_3-ions. The formation of cells and first symbiotic reactions between DNAs proceeded within the semi-liquid media produced after liquation of the hydrate structure as a result of excessive H_2O formation through polycondensation reactions.

The thermodynamic calculations [3, 4] showed that formation of LMSEs, DNAs, and proto-cells from CH_4, niter, and phosphate is thermodynamically possible on the basis of the internal energy of the source substances with no ambient energy; moreover significant energy amounts liberated.

Here, we consider the chemical and thermodynamic possibilities of formation (on the basis of natural gas and niter) of the amino acids (AAs) that enter into living matter. Living matter contains 20 AAs, including two S-containing ones. Meanwhile, the gas-hydrate deposits contain, along with CH_4, admixtures of H_2S, CH_4S, and other S-containing substances. The thermodynamic calculations are made on the basis of available data on the standard thermodynamic functions of the source substances and AAs. It is shown that the thermodynamics allows formation of the entire set of AAs from natural gas and niter. The S-containing AAs can be formed on the basis of CH_4, KNO_3, and H_2S and other S-containing components of the natural gas; however, just the reaction of CH_4 and KNO_3 with H_2S that is the most abundant S-containing component of the natural gas goes with the highest decrease in the Gibbs free energy. The results of calculations are discussed in the LOH-Theory context.

The work was supported by the Russian Science Foundation (project 12-05-01082-a).

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Thermal behavior and kinetic study of a bioactive hydroxyapatite/gelatin hybrid organic/inorganic composite

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In the last two decades an important part of the research on bone substitute materials was focused on ceramic materials, like calcium phosphates because of their biocompatible, bioactive, biodegradable and osteoconductive properties[1]. Great interest has been focused on inorganic nanoparticles which are embedded in a polymeric matrix. This is also the main path by which hard tissue forms naturally, suggesting that the temple-based synthesis is an optimum way for preparing biomimetic materials. Among most used biodegradable polymers as organic matrix are collagen, gelatine, chitosan and starch, respectively. Despite their small size, bone nanoparticles are stable and resist to dissolution because of the interactions that occur between the acidic peptide sequence in the extracellular matrix and the Ca^{2+} ions present in the mineral nanocrystals [2].

A biomimetic bioactive composite based on hydroxyapatite (HA) was prepared by using inorganic precursors for the mineral structure of the composite and a gelatin aqueous solution to provide the organic matrix as template for the HA crystal growth. Samples of the organic/inorganic hybrid material were characterized before and after the sinterization process by FTIR, XRD, SEM and EDAX analysis. The results indicate that the crystallization process ends only after sinterization at high temperature. This sinterization process also has an effect on the size and shape of the HA crystals[1].

TG/DTG/DTA analysis was performed on the biomimetic hydroxyapatite composite in order to determine the thermal behaviour of the hybrid material. The thermoanalytical data obtained at five heating rates, β = 7, 10, 12, 15 and 20 °C·min^{-1}, in air atmosphere, were used to determine the kinetic parameters of the main degradation process. All the kinetic methods used in this study, as well as in our other ones [3,4] were isoconversional according to ICTAC2000 Protocol, using Kissinger-Akahira-Sunose, Flynn-Wall-Ozawa and the modified NPK methods to estimate the activation energy of the studied process.

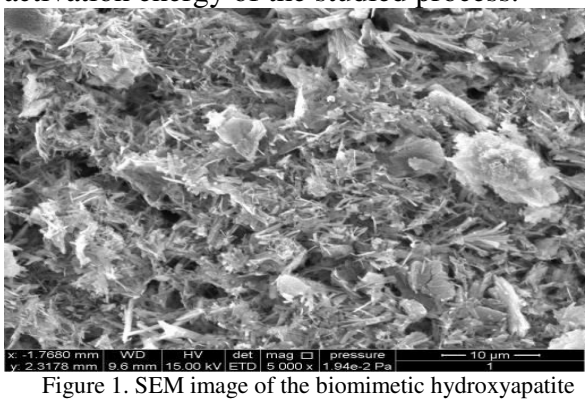

Figure 1. SEM image of the biomimetic hydroxyapatite composite - before sinterization

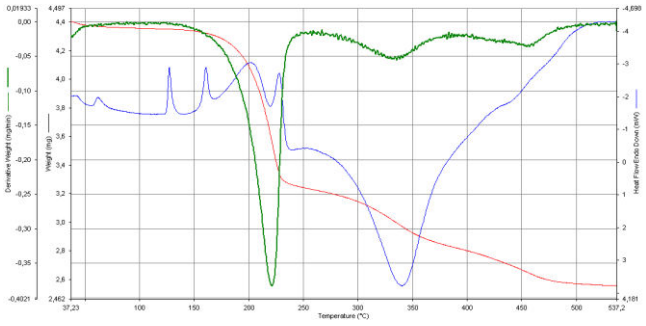

Figure 2. Thermogravimetic curves of biomimetic hydroxyapatite composite

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Thermodynamic and kinetic studies of Cu(II) sorption onto an iminodiacetic acid chelating resin

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The efficient and cost effective removal and recovery of copper from industrial wastewater is a problem of the modern society in the context of sustainable industrial production [1]. Different treatment techniques for copper and other heavy metal removal from wastewater have been developed in last years in order to improve the quality of the treated effluent. Of these, one of the most used and efficient technique is based on ion exchange process.

In this study, the Purolite S930 Plus resin with iminodiacetic acid functional groups was tested for the Cu(II) removal from diluted aqueous solutions in batch mode. The sorption capacity of the chelating ion exchange resin was investigated varying different parameters (pH, stirring rate, initial concentration of copper, resin amount, temperature and contact time) which have been optimized for maximum copper removal.

The equilibrium data were analyzed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich sorption isotherm models. It has been found that copper sorption was best described by the Langmuir isotherm model. The thermodynamic parameters such as ΔG, ΔH and ΔS were calculated and were used to explain the adsorption mechanism, proving that, in this case, the sorption is an endothermic and spontaneous process. The results were also analysed using pseudo-first-, pseudo-second-order, intra-particle and film diffusion kinetic models, revealing that; the pseudo-second order reaction was the best model for the copper sorption onto the chelating resin.

Furthermore, the Purolite S930 Plus resin presented a good regeneration capacity without significantly losing of its sorption capacity and can be successfully used to remove Cu(II) ions from wastewater at levels that are accepted by the environmental legislation.

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Acknowledgements

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The utilisation of fossil fuels in direct carbon solid oxide fuel cells

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Direct carbon solid oxide fuel cells are electrochemical devices which convert the chemical energy of carbonaceous fuel directly into electricity without combustion involving flame. The electrical efficiency of DC-SOFCs is indeed very high (practically in excess of 80%) and the products of conversion consist of almost pure CO_2, thus eliminating the most expensive step of sequestration: the separation of CO_2 from flue gases. A direct carbon fuel cell with a solid electrolyte (DC-SOFC) is characterised by uncomplicated maintenance and construction. It can be designed using planar or tubular SOFC construction, with a fixed or fluidised solid carbon bed.

In DC-SOFCs, carbon can be directly electrochemically oxidised to CO_2 according to the equation $C+O^{2-}\rightarrow CO_2 + 4e^-$ (1) as well as formed in a sequence of the following electrochemical reactions: $C+O^{2-}\rightarrow CO + 2e^-$ (2) and $CO +O^{2-}\rightarrow CO_2 + 2e^-$ (3). The Boudouard reaction (4), involving CO_2 and C as reactants, is an additional source of CO consumed in reaction (3): $C+CO_2\rightarrow CO$ (4)

This complex course of reactions (1–3) may constitute a potential asset for the fuel cell, because it enables a choice of different design options leading to the optimisation of the cell's performance.

[2] This research is focussed on investigating the effect of certain raw and de-ashed coal varieties on the efficiency of a DC-SOFC. Prior to being tested in the fuel cell, the phase composition and structure of the coal samples were characterised by X-ray, Raman, and infrared spectroscopy.

[3] The relationship between the structure and morphology of solid particles, mineral matter and their performance in DC-SOFCs is presented and discussed. The power density obtained for a DC-SOFC at 850°C was above 90 mW/cm^2. The stable performance of a DC-SOFC under load was observed for more than 100 h.

Water thermoporosimetry as a tool of characterization of the textural parameters and the secondary mesopore system in hierarchical zeolites

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Distinctive properties e.g. high surface area and thermal stability, as well as the presence of the Brønsted and Lewis acid sites of high strength, are the most important features of zeolites responsible for their frequently application as catalysts in various chemical processes [1]. However, two main advantages of the micropores of molecular dimensions such as the extremely desired high surface area and the shape selectivity are overwhelmed by the diffusional limitation which induce a poor catalytic performance or even deactivation of zeolitic catalysts [2]. To improve the catalyst effectiveness in chemical reactions the secondary system of mesopores is introduced to reduce the diffusional limitations.

One of the most important features responsible for enhanced catalytic performance in hierarchical zeolites is the character of the generated mesoporosity. Deep characterization of the textural properties of the resulting samples, the tasks of this work, is attempted to answer the question if desilication induced the formation of the intercrystalline mesoporosity or intracrystalline secondary system of mesopores. The method that is being considered as standard one for the characterization of the texture of porous materials is adsorption isotherms of nitrogen or argon. However, its limitations are usually not taken into account. Thermoporosimetry is an alternative but still not well recognized and underestimated method, allowing a better characterization of mesoporous materials [3]. It has been known since works of Thomson [4], that a fluid confined in the pores of a solid material experiences an important shift of its liquid to solid transition temperature and that this shift is related to the size of the pore, in which the liquid is trapped [5]. This idea is the basis of the thermoporosimetry. Application of this technique is very simple, fast, inexpensive, and nondestructive. Soaking the porous material in the liquid and measuring the melting or crystallization temperature by differential scanning calorimetry (DSC) is enough to perform the pore characterization. It is also important to emphasize that the TPM measurements are relatively fast, highly reproducible and usually no previous sample preparation is needed. In this study the textural parameters of hierarchical zeolites were established with water thermoporosimetry and supported with IR and low nitrogen sorption methods.

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Thermal analysis and modelling study of carbon activation processes

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Thermal analysis instruments and their applications are useful for characterizing activated carbon precursors, intermediates and final products. Proximate analysis is performed in the TGA to determine the amounts of moisture, volatile matter, fixed carbon and ash content in activated carbons. Activation studies are carried out in the TGA to determine appropriate conditions for activation of carbon samples in larger scale test facilities.

Partial gasification of the precursor leads to the formation of an activated carbon with a developed network of pores and increase of the specific surface. Modification of the activated carbon parameters can be controlled by varying the heating rate and the degree of gasification. Thermogravimetry (TG) provides a method for direct monitoring, both the rate and extent of activation, in the course of reaction.

This study was aimed at establishing the optimal conditions for obtaining the activated carbon from walnut shells by activation with phosphoric acid and potassium hydroxide.

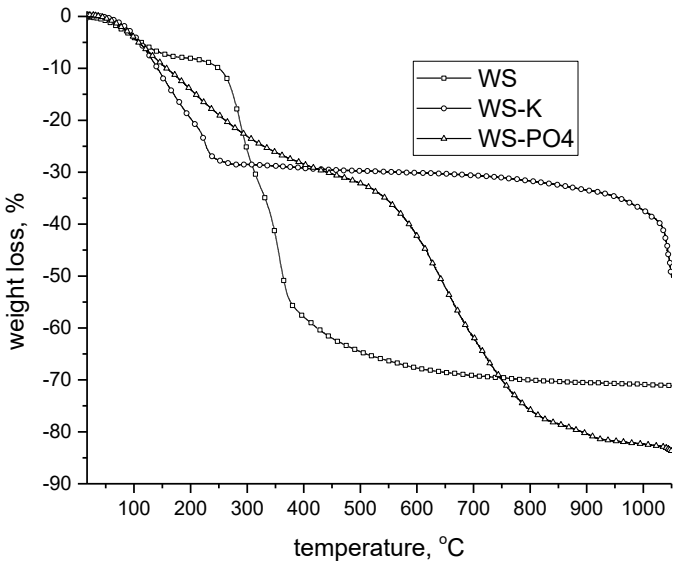

Fig.1 TG curves of walnut shells (WS), KOH- impregnated walnut shells (WS-K) and phosphoric acid-impregnated walnut shells (WS-PO4). Heating rate 10 C/min, nitrogen atmosphere.

Taking into consideration the data of thermal analysis, it was determined that optimal temperature for obtaining activated carbons constitutes 650 ^{o}C in the case of phosphoric acid activation and 850-900 ^{o}C- for activation with potassium hydroxide. Adsorption parameters of the activated carbon were determined by nitrogen adsorption method.

Crystallization Kinetics and Sintering of β-Spodumene/Cordierite-based Glass-Ceramics

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Glass-ceramics based on β-spodumene ($Li_2O \cdot Al_2O_3 \cdot 4\text{-}10SiO_2$) and cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) have been studied because of their beneficial properties, e.g., good mechanical properties, low dielectric constant and low thermal expansion coefficient. The properties of glass-ceramics are dependent on the chemical composition and the thermal history. Therefore, in order to obtain high performance materials from these glass-ceramics, a better understanding about the crystallization process and sintering plays an important role. The crystallization phenomena of these glass-ceramics has extensively been investigated as single phase but there is a lack of studies based on the glass-ceramic comprising both crystalline phases (β-spodumene and cordierite) [1-4]. The purpose of the present work is to investigate the crystallization kinetic and sintering of ß-spodumene/cordierite glass-ceramics. Thus, three glasses were prepared with compositions based predominantly on cordierite phase (C) β-spodumene phase (L) and a molar ratio 1:1 of both phases. The kinetics parameters were determined by means of non-isothermal methods using differential scan calorimetry (DSC). A multi-peaks fit method based on the Fraser-Suzuki equation [5] was used to determine kinetics parameter such as the peak crystallization temperature and the full width at half maximum (FWHM). The samples were crystalized according to DSC analyses and characterized by using X-ray diffraction (XRD). Additionally, the glass compositions were milled and pressed to investigate the sintering by means of optical dilatometry. The results showed that the activation energy for crystallization ranged from 150 to 370 kJ/mol and Avrami exponent ranged from 0.8 to 13. The main crystalline phases were β-spodumene in the composition L, cordierite in the composition C and β-quartz, mullite and spinel in the composition CL. The temperatures of maximum shrinkage rate of the glasses were found to range between 700 and 900 ^{o}C. Considering the thermal and electrical properties of the crystallized phases and the sintering temperature of the glasses, this glass-ceramic system has potential of using as LTCC (Low Thermal Co-fired Ceramics) application.

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Kinetic Parameters Determination of the Oxidation and Decomposition Reactions of Pyrite for Magnetic Materials Obtaining

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Nevertheless being a mineral with a great occurrence in nature and one of the main SO_2 emition source in industrial processes [1], there are little definitive information about the oxidation and decomposition reaction kinetics of pyrite, as well as the mechanisms by wich they occur.

This work had as objective to determine the application viability of the Friedman method for kinetic parameters determination of oxidation and decomposition reactions of pyrite from coal mining industry. This method is based in experimental data of weight loss using thermogravimetry analysis (TG) for the determination of activation energy of the reactions. Thus, the activation energy (E_a), and the pre exponential factor (A) and the reaction order (n) were obtained using TG curves with different heating rates (2.5; 5.0; 7.5 and 10.0 $K.min^{-1}$).

For inert atmosphere, the calculated activation energies agree with them found at literatures [2], being approximately 280 $kJ.mol^{-1}$.

The reaction in oxidant atmosphere showed two predominant regions of weight loss, suggesting the existence of two different reactions. The value obtained for activation energy of the second weight loss (482 $kJ.mol^{-1}$), that occurred around 770 K, showed similar results presented by other authors [3].

As regards the observed weight loss at around 650 k, were not found similar values in the literature comparing with Friedman method. For this reason, the theoretical activation energy was determined with empirical equations. Was obtained as theoretical value for the decomposition of pyrrhotite approximately 1000 $kJ.mol^{-1}$. Values found for the others kinetics parameters showed inconsistent.

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Thermal evaluation of ceramic matrix for storage of latent heat

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Taking into account the global demands for energy savings, and even thermal comfort inside the ambiences, phase change materials (PCMs) have been investigated over the years [1]. In this context, the thermal evaluation of the matrix containing the phase change material takes an important role [2]. Thus, this work aims to evaluate the thermal properties of rice husk ash and coal ash from an electricity generation unit as ceramic matrix for obtaining PCMs. Ashes were characterized by X-ray fluorescence, X-ray diffractometry and scanning electron microscopy (SEM). A vacuum impregnating apparatus was assembled to incorporate the phase change material (Calcium Chloride Hexahydrate, $CaCl_2.6H_2O$) into the matrix (open porosity). The effectiveness of the impregnating process was evaluated by thermal analysis (DTA) and structural analysis (FTIR and SEM). PCM-based mortars (PCM's varying from 0 to 10 wt%) were prepared. Thermal cycle tests were carried out in order to evaluate the thermal behavior of the compositions. Results showed that a reduction of 5 °C inside the specimens containing 10 wt% PCM was obtained, showing potential use for storage of latent heat.

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Luminescence Properties of $Ba_2Ca(BO_3)_2:Gd^{3+}$ Phosphor

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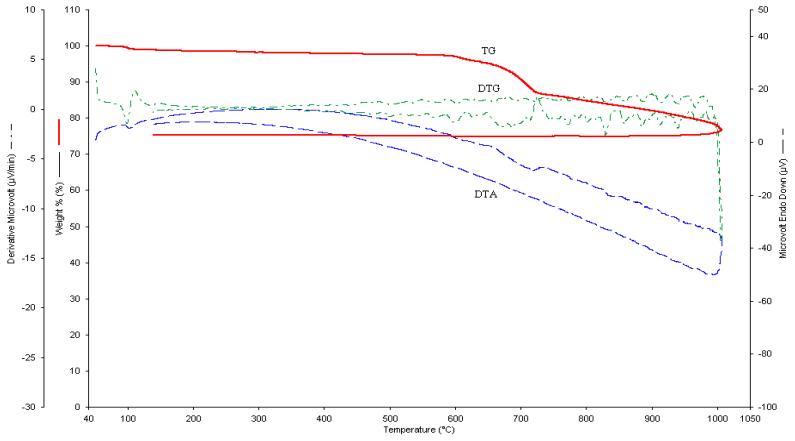
Research of luminescent materials has several aspects. There is, for example, the influence of sample preparation on the luminescence properties. Some materials are required in the form of large crystals of high quality, others in the form of powders with specific requirements on particle size distribution and morphology. Additionally, insight into the physics of the luminescence properties is required to obtain optimum properties in a controllable way. A special aspect is the way in which the luminescence properties depend on the chemical composition of the material [1, 3].

In this study new phosphor $Ba_2Ca(BO_3)_2:Gd^{3+}$ was synthesized using solid state reaction method. The mixture to achieve a solid-state reaction was heated in porcelain crucibles at 780 ^oC for 48 hours. The reaction products obtained in an open atmosphere were characterized by XRD. Optimization of reaction condition were carried out by, differential thermal analysis methods (DTA/TG/DTG). Surface investigations and elemental analysis were determined by using SEM-EDX instrument. Photoluminescence spectrophotometer (PL) was used for the observation of the excitation and emission spectra.



Thermograms of $Ba_2Ca(BO_3)_2$: Gd^{3+} phosphor

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Relaxation processes in tetragonal tungsten bronzes by dielectric spectroscopy and resonant ultrasound spectroscopy

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The tetragonal tungsten bronze (TTB) structure ($(A1)_2(A2)_4(C)_4(B1)_2(B2)_8O_{30}$), where the inclusion of particular metals into the five different TTB sites gives the prospect of finding many interesting and useful novel materials by tuning the electric and magnetic properties through compositional variation; these structures which have even greater compositional flexibility than the perovskite one and may offer better properties and over larger operating ranges.

Of particular interest are the niobium-based TTBs due to their enhanced ferroelectric and relaxor properties over other analogues such as tantalum or tungsten [1]; the family of tetragonal tungsten bronzes of composition: $Ba_6M^{3+}Nb_9O_{30}$ (M^{3+} = Ga^{3+}, Sc^{3+} and In^{3+}) [1,2-4] are such candidates. Material characteristics, structural transitions and electrical properties of the tetragonal tungsten bronzes were investigated by microstructural analyses (XRD, TD-PND, SEM), and impedance & dielectric spectroscopy.

Here, we have complemented the above mentioned investigations by more powerful methods like acousto-mechanic (resonant ultrasound spectroscopy – RUS) and calorimetric (differential scanning calorimetry – DSC) ones, in order to observe all elastic and anelastic properties and transitions [5]. The resonant ultrasound spectroscopy (RUS) is a technique used to investigate the fundamental properties involving elasticity: solid objects resonate at specific frequencies corresponding to various vibration modes, when mechanical vibrations are applied, and they depend on the elasticity, the size and the shape of the object; the temperature when these resonant frequencies start shifting represents the characteristic temperature of phase transition. Small pieces of parallelepipedic TTB ceramics (~ 1-5 mm) were cut and placed between two transducers where frequencies between 50 HZ and 1.2 MHz were applied in the temperature range 10 K – 1200 K (both at cooling and heating), and fine resonant frequencies were recorded. The quality factors were calculated for each temperature as $Q=f_0/\Delta f$, where f_0 is the frequency of the peak maximum and Δf is the frequency width at the half maximum of the peak; for a better correlation, more peaks were selected to calculate Q at room temperature. The elastic constants were possible to be determined by RUS for the polycrystalline TTB materials ($Ba_6M^{3+}Nb_9O_{30}$) at room temperature, while the elastic properties such as bulk & shear moduli were calculated and compared to those of single crystal TTBs with similar formulae (SBNN) [6]. Dielectric spectroscopy studies carried out at extreme frequencies (low: 10 mHz-10 Hz and high: 1 MHz-44.6 GHz) were able to provide better insides for the Vogel-Fulcher representation of the dielectric relaxation processes [7-9].

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Poster Session 2

Materials: ceramics, metals & alloys, cements, glasses, nanomaterials, thin films and polymer composites

The effect of graphene nanoparticles on the thermal and thermo-oxidative degradation of high density polyethylene

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Graphene, a monolayer of sp^2-hybridized carbon atoms arranged in a two-dimensional lattice, has been intensively studied as the next generation reinforcing material for polymers due to its large aspect ratio, high strength and stiffness, and sublime mechanical and thermal properties [1]. In this work, we studied the thermal and thermo-oxidative degradation behaviors of HDPE/graphene nanocomposites. For this purpose HDPE/graphene nanocomposites with different weight percents of graphene were prepared using melt rheo-mixing. The dispersion of graphene in polymer nanocomposites as well the crystallinity of nanocomposites was characterized using X-Ray Diffraction (XRD) and Differential scanning calorimetry (DSC). Thermogravimetric analysis (TGA) was used to analyze the effect of the introduction of nanofillers into a polymer matrix on the thermal stability of the polymer matrix. Finally, Gas chromatography-Mass spectrometric (GC-MS analysis) analysis was used to separate and identify the products of decomposition.

Thermogravimetric analysis demonstrates that in nitrogen atmosphere (N_2) the addition of graphene nanoparticles increases the onset decomposition temperature and the HDPE/graphene nanocomposites show better resistance to thermal degradation than pure HDPE. The thermal stability of HDPE in air atmosphere is prominently reduced by oxidative dehydrogenation accompanied by hydrogen abstraction [2]. Meanwhile, it is obvious that graphene has beneficial effects on stabilizing the thermal oxidative degradation of HDPE under air. GC-MS analysis shows a pattern for the distribution of hydrocarbons compounds and a series of triplets from C4 to C32 which were identified in pure HDPE and HDPE/graphene nanocomposites. The intensity of pyrolyzates of HDPE/graphene nanocomposites in heavy compounds is stronger than that of pure HDPE, indicating that more heavy compounds are found in pyrolysis of them. The ability of radical trapping of graphene nanoparticles should respond to the improvement of thermal behaviors of HDPE.

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Synthesis and structural morphological and thermal characterization of Mg-Ni-RE alloy produced in an induction furnace for hydrogen storage

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On the surface of the metal hydrides, the diatomic molecule of H_2 giving splits hydrogen atoms which then diffuse into the solid structure. Pd and other metals such as Ni show a similar behaviour, as well as some rare earth (RE) or some binary alloys consisting of two different metals or a metal and elements belonging to the group of the rare earths. In metal hydrides, generally, the bond H-Me is relatively weak and this involves an easy hydrogen absorption and desorption under conditions not too far from the room temperature and pressure [1]. The problem, in this case, is the excessive weight of the metal, compared to the amount of hydrogen stored. When, instead, in the hydride, the metal is an alkali metal or an alkaline earth metal, the hydride weight is quite lower than the previous one, and thus its features are most attractive for hydrogen storage. Typical examples is magnesium hydride [1,2], but in this case it is necessary a higher temperature to break the chemical bond H-Me and to release hydrogen. In this study both the synthesis and characterization of a Mg-Ni alloy doped with La and Ce, which are usually present in a commercial alloy named "Firesteel", have been performed. The alloy, obtained in an induction furnace by a two-step melting process, has the general formula $Mg_{68}Ni_{26}M_5X$, where X represents Si and Fe (acting as impurities), while M represents the mixture of RE elements. This alloy has been characterized by several techniques, like SEM, XRD, DSC, TG and BET analysis and tested by a Sievert type apparatus. The TG/DSC experiments revealed that the hydride activation is achieved only at temperatures higher than 300 °C and a strong dehydrogenation requires working at temperatures close to 375°C, resulting in 5 wt% of desorbed hydrogen. Activation energy of hydrogen desorption, determined by an integral isoconversional method through processing of TG data recorded at several heating rates, has been found (as average) to be close to 160 kJ mol^{-1}, being the highest desorption rate determined at 345 °C. X-ray diffraction spectra has been performed on both raw and cycled materials, showing that Mg_2Ni present in the raw material is transformed into Mg_2NiH_4 and MgH_2 after hydrogenation. The alloy has been tested by the Sievert apparatus at 345-350°C, corresponding to the temperature referred to the highest desorption rate. It has been shown that hydrogenation occurs in three stages at three different pressures: 3, 4 and 7 atm involving 0.15, 0.4 and 2.2 wt% of hydrogen, respectively. In particular, the second and third stages are related to the formation of different hydride phases like MgH_2 and Mg_2NiH_4.

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Thermal stability of the V-doped TiO_2 oxide nanopowders obtained by microwave assisted sol-gel method

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Oxide nanopowders have been intensively studied due to their specific properties. Among them, TiO_2 has applications in various fields such as photocatalysis,[1] gas sensors, dye sensitized solar cells, optical coatings[2,3], antimicrobial materials,[4] pigments.

In the present paper, V-doped TiO_2 (TVO) powders with TiO_2:V_2O_5 molar ratios 98:2 and 99.95:0.05 were prepared by sol-gel and microwave (MW) assisted sol-gel synthesis. The reagents used were tetraethyl orthotitanate, vanadyl acetylacetonate and ethanol as solvent The starting solutions were homogenized by stirring for 2 h or were exposed to microwave (MW) for 5 min at 300 W into an oven operating at a frequency of 2.45 GHz with a maximum powder of 2000 W.

The solutions were gelled and a comparative thermal (DTA/TG/EGA) and DSC study was realized in order to establish the influence of the preparation method on their thermal properties.

A significant increase of the thermal stability of the gels obtained by microwave assisted sol-gel method was observed. According to the results obtained, the resulted gels were thermally treated at 300 and 450 °C for 1 hour in air, using a heating rate of 1 °C/min.

The powders were characterized from the point of view of their structure, morphology and adsorption properties. The catalytic properties of the samples were also investigated in order to establish the influence of increased thermal stability of the powders on their properties.

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Experimental investigation and thermodynamic calculation in quaternary Al-Zn-Sn-Ga system

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The results of the experimental investigation and thermodynamic calculation in quaternary Al-Zn-Sn-Ga system are presented in this paper. Selected alloys from two vertical sections, from Al-corner (section I) with molar ratio Zn:Sn:Ga=70:27:3 (in at%) with different aluminum molar contents, and from Zn-corner (section II) with molar ratio Al:Sn:Ga=70:27:3 (in at%) with different zinc molar contents were experimentally examined using differential scanning calorimetry and scanning electron microscopy with EDS in order to define their thermal and structural properties. Thermodynamic calculation was applied using different predicting models - general solution model, RKM, Muggianu, and Toop model and adequate partial and integral molar thermodynamic properties in quaternary Al-Zn-Sn-Ga system were obtained in temperature range 1000-1300K. Also, a computed phase diagram version of two investigated vertical sections has been calculated using CALPHAD method and compared with obtained experimental data.

Keywords: Al-Zn-Sn-Ga system, quaternary alloys, thermodynamics, phase diagram

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Solid state rheology of polymer films and layers: Influence of the thickness on mechanical properties of a PU-adhesive between metallic substrate

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Dynamic mechanical measurements on polymer layers between metallic substrate show a dependence of the mechanical properties on the thickness of the polymer layer. This is discussed on the example of a polyurethane adhesive between gold interfaces. Measurements of the shear modulus show a decrease of the glass transition temperature with increasing the thickness of the polymer layer. This behavior can be described by an empirical equation.

For the behavior of coatings and adhesive layers, the interface to the substrate is important. Therefore the analysis of such layers should be performed in contact to the actual substrate. A preferred method for the dynamic analysis of mechanical properties of such laminating systems is the measurement in the shear mode. In the glass transition region such measurements require an advanced instrument with a high stiffness, an excellent displacement and good opportunities for preparation of small samples.

The analysis of a polyurethane adhesive between gold interfaces shows that the glass transition temperature increases with the decrease of the layer thickness. We can show that the empirical equation corresponds to the behavior of a simple ideal mixture of the polymer bulk with a polymer interface layer with different characteristics. This result is unexpected.

Structural, thermal and chemical stability of $LiMn_2O_{4-y}S_y$ cathode materials

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Lithium manganese oxide spinel is still of a great interest as a cathode material for lithium-ion batteries. Its practical capacity is about 140 mAh/g and is comparable to capacity of commercially used layered cobalt oxide and related compounds [1]. In addition, LiMn2O4 remains attractive in terms of safety, high abundance, nontoxicity and low cost [2,3]. An important problem standing in the way of the wider application of the stoichiometric spinel is a considerable loss of capacity during subsequent charge and discharge cycles. The poor cycling performance can be ascribed to a reversible phase transition derived from the Jahn-Teller distortion of Mn3+ ions as well as Mn dissolution from the spinel [4]. Oxygen substitution with sulphur has been reported to improve the structural and electrochemical properties of LiMn2O4 spinel [5,6].

This study focuses on the effect of sulphur on structural, thermal and chemical stability of Li-Mn-O-S spinel materials investigated by thermal analysis methods.

Synthesis of nanostructured LiMn2O4-ySy (y = 0, 0.01 or 0.05) powders was carried out by a modified sol-gel method [5,7]. Optimal conditions for the preparation process as well as thermal stability of Li-Mn-O-S systems were determined by thermal analysis methods (TGA/DTG/SDTA/EGA-QMS). All samples were characterized by X-ray powder diffraction (XRD) to identify the crystal structure. Information about phase transitions occurring in the obtained samples as well as their chemical stability toward the liquid electrolyte was achieved using a differential scanning calorimetry (DSC). Atomic absorption/emission spectroscopy analysis (AAS/AES) was employed to determine the manganese dissolution from the spinel materials. To evaluate the electrochemical properties of Li/Li+/LiMn2O4-ySy cells, galvanostatic charge/discharge tests (CELL TEST) were performed on R2032 coin-type assembly.

From the results obtained using thermal analysis methods, it can be concluded that sulphur substitution is an effective way in increasing the structural stability of the lithium manganese spinel (the unfavorable phase transition near room temperature has been suppressed), as well as enhancing the chemical stability and therefore, in the improvement of the cycling characteristics and capacity retention.

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Crystallization from mechanically induced defects

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Formation of crystals is known to proceed either from surface or volume-located nuclei. This concept, however, seems to be more complicated in practice. We have recently found (e.g. [1 - 5]) that in the case of powdered glassy materials, the grinding/milling procedures create large amounts of "mechanically induced defects", which can adopt the features of heterogeneous surface nucleation and lead to the formation of another type of crystallization center. Currently, the corresponding micro-mechanism is not known and probably differs for different materials. The defects appear to either markedly accelerate the nucleation or crystal growth, or create internal surfaces where the heterogeneous nucleation proceeds. In other words, the process kinetically akin to surface crystallization appears to originate within and proceed throughout the whole grain volume in the case of certain fine powders. In this regard, it was indeed found that the macroscopic crystallization mechanism is similar (indistinguishable) for the surface crystallization and the crystallization from mechanically- or stress-induced defects.

Despite the apparent general validity (at least for chalcogenide glasses) of the discussed concept, there are still some unanswered questions associated with the particular micro-mechanism being employed in the crystal growth process. One of the most important issues is the so-far unachieved direct confirmation of the true existence of new crystallization centers associated solely with the mechanically-induced defects and micro-fractures. Until now, the existence of these centers was only indirectly derived from the DSC kinetic data, where many of the observed kinetic aspects could also be explained by certain alternative theories (e.g. the formation of internal surfaces during heating of the damaged/stressed glassy grain, or anisotropic acceleration of the surface growth along the micro-fractures).

Apart from the detailed kinetic description of the features associated with the crystallization from mechanically induced defects, the main aim of the present contribution is to provide (for the first time) direct confirmation of the existence of crystallization centers originating from the mechanically-induced defects. Combined data from differential scanning calorimetry (DSC) and infrared microscopy will be used in this regard.

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Structural transitions of Ln_3MO_7 (*Ln* = rare earths, *M* = transition metals) by specific heat and DSC measurements

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We report structural transitions and magnetic properties of ternary metal oxides with general formula Ln_3MO_7 (*Ln* is a rare earth element; *M* is a pentavalent transition element such as Mo, Ru, Re, Os, or Ir) by the high temperature X-ray diffraction, magnetic susceptibility, specific heat, and DSC measurements. These compounds have an ordered, defect-fluorite structure. The relationship to the fluorite structure is as follows. The fluorite unit cell for oxides has the composition $M^{4+}{}_4O_8$. If the four tetravalent metal ions are replaced by three trivalent ions (*Ln*) and one pentavalent ion (*M*), one oxide vacancy is formed per fluorite cell. Due to significant differences in radii between the Ln^{3+} and M^{5+} ions, cation ordering occurs on the metal sites and the oxide-vacancy orders on the anion sites. These compounds crystallize in an orthorhombic superstructure of cubic fluorite with space group *Cmcm*, in which Ln^{3+} ions occupy two different crystallographic sites (8-coordinated and 7-coordinated sites) [1].

A variety of space groups such as *Pnma*, *Cmcm*, $P2_12_12_1$, $C222_1$, $P2/n$ and $P2_1nb$ have been proposed for the Ln_3MO_7. We confirmed that these compounds undergo a structural phase transition. For a series of Ln_3MO_7 compounds (*M* = Mo, Ru, Re, Os, Ir), the structural phase transition temperatures decrease greatly with increasing the ionic radius of Ln^{3+}. Since the transition temperature increases with decreasing the ionic radius of Ln^{3+}, this transition is stress-induced and it occurs with lattice contraction on cooling [2]. Each transition temperature within a series is separated by approximately the same temperature interval except for the case of Ln_3MoO_7. The reason for this may be related to the difference in their high-temperature structures, that is, Ln_3MO_7 (*M* = Ru, Re, Os, Ir) compounds exist in the *Cmcm* structure, whereas Ln_3MoO_7 exists in the *Pnma* structure [3].

In Ln_3MO_7 structure, the M^{5+} ion is coordinated with six oxygen ions, forming a MO_6 octahedron. These octahedra share corners forming one-dimensional chains which are oriented along the *c*-axis. Due to this unique crystal structure, many peculiar magnetic properties have been observed at low temperatures [4].

Recent results on the structural transitions of Ln_3MO_7 (*M* = Nb, Sb, Ta) by the specific heat and DSC measurements will be reported.

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Structures and magnetic properties of quadruple perovskites $Ba_4LnM_3O_{12}$ (*Ln* = rare earths; *M* = Ru, Ir)

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Perovskite-family oxides have attracted much interest due to their exotic electronic, magnetic, and structural properties. It is well known that a perovskite ABO_3 with a tolerance factor less than 1.0 forms a three-dimensional frame network of corner-sharing BO_6 octahedra, which can be described as a stacking sequence *abc*… Perovskites with a tolerance factor (*t*) greater than unity form face-sharing BO_6 octahedra, and the stacking sequence varies with the value of *t*.

If two kinds of cations are present in the B site, the ordering ratio of B and B' cations increases with an increasing difference in charge and size between B and B' cations. Most perovskites $BaLn_{1-x}M_xO_3$ containing both transition metal (*M*) and rare earth (*Ln*) ions exhibit a perfectly ordered B sublattice due to the difference in their ionic radii. The stacking sequence is controlled by changing the ratio of the *Ln* and *M* ions; double perovskites Ba_2LnMO_6 have a 1:1 type B-site cation ordering with the sequence *abc*.., and triple perovskites $Ba_3LnM_2O_9$ crystallize in a 6H-perovskite structure with a 1:2 type B-site cation ordering (the *abacbc*… sequence).

In this study, we report preparation, crystal structures and magnetic properties of quadruple perovskites $Ba_4LnM_3O_{12}$ through magnetic susceptibility, specific heat measurements.

From the powder x-ray and neutron diffraction measurements, it was found that *M* ions are octahedrally coordinated by six oxide ions, and three MO_6 octahedra share faces forming a M_3O_{12} trimer, and that the M_3O_{12} trimers and LnO_6 octahedra are alternately linked by corner-sharing and form the perovskite-type structure with 12 layers (Fig. 1).

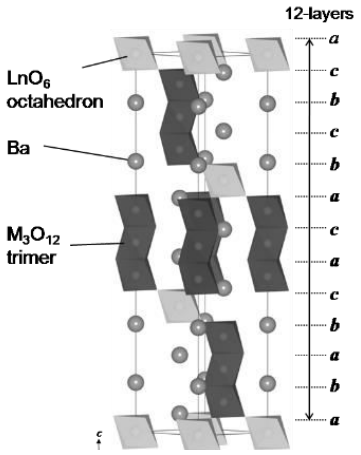

Figure 1: Crystal structure of $Ba_4LnM_3O_{12}$ (*M* = Ru, Ir)

The change of lattice parameters and volume for $Ba_4LnM_3O_{12}$ against the ionic radius of Ln^{3+} show that except for the compounds having *Ln* = Ce, Pr, and Tb, they increase monotonously with the Ln^{3+} ionic radius. However, the values for *Ln* = Ce, Pr, and Tb compounds are considerably smaller than this trend. For both *M* = Ru and Ir cases, the *Ln* –O bond lengths are close to the Ln^{4+}-O^{2-} lengths calculated from Shannon's ionic radii. These results show that the Ce, Pr, and Tb ions are in the tetravalent state. Therefore, the oxidation states of Ru and Ir are also tetravalent ($Ba_4Ln^{4+}Ru^{4+}{}_3O_{12}$, $Ba_4Ln^{4+}Ir^{4+}{}_3O_{12}$). For other *Ln* ions, the mean oxidation state of Ru and Ir ions is +4.33 ($Ba_4Ln^{3+}Ru^{4.33+}{}_3O_{12}$, $Ba_4Ln^{3+}Ir^{4.33+}{}_3O_{12}$) [1].

At the conference, the results of the specific heat and magnetic susceptibility measurements will be presented.

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Thermal hazard assessment on three C-rates for Li-polymer battery

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There are numerous approaches to Li-polymer battery development, such as long charge time, short cycle life, and how the battery can receive energy with more efficiency and superior thermal safety. Different sample C-rates (1 C, 3 C, and 5 C) were prepared under various conditions for 100 cycles, followed by recording the temperature variation with the time track.

The measures, in turn, applying the vent sizing package (VSP2) with a customized stainless steel test can evaluate thermal hazard characteristics, such as apparent exothermic onset temperature (T_0), self-heating rate (dT/dt), pressure rise rate (dP/dt), pressure-temperature profiles, maximum temperature (T_{max}), and maximum pressure (P_{max}) to realize thermal runaway mechanisms. We investigated the relationship of charge/discharge rate and thermal stability. Running with the higher C-rate, showed enormous temperature rise in the discharge process [1].

The results led to the prepared batteries in fastest C-rate 5 C having the most unstable parameters. Here, the lowest T_0, T_{max}, and P_{max} during the runaway reaction reached 133 °C, 530 °C, and 132 psig, respectively. Compared with the batteries' exterior, the 5 C Li-polymer batteries demonstrated ruptured and burned phenomena [2–3].

Keywords C-rates. Cycles. Li-polymer batteries. Thermal runaway mechanisms. Vent sizing package (VSP2)

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The usability of thermal techniques for studying intumescent coatings deposited on wood

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Efforts to reduce the flammability of wood began in ancient times. The use of fire-retarded coatings is one of the easiest, oldest and most efficient ways to protect substrate against fire. Intumescent coatings are mineral based or organic-resin based products, which upon the heat of flame expand up to several times of their original thickness and form a protective carbonaceous char that acts as an insulative barrier between fire and the substrate. However, the use of the described coatings has the temperature limit upon which coatings brake down due to combustion of char itself. In this manner they are regarded as materials which mainly prolong an early stage of fire development.

Thermal methods of analysis (thermogravimetry – TG and differential scanning calorimetry – DSC) were used to determine some properties of three different commercial intumescent coatings, deposited on spruce, beech and oak wood samples. Dynamic measurements of bare wood pieces and those with deposited coatings were performed under air atmosphere. From the mass-loss curves and DSC curves the upper temperature limit of the intumescent coatings was determined, and enthalpy of the combustion process of bare wood pieces and those with deposited coatings as well. Coupled TG-MS (thermogravimetry – mass spectrometry) was used to determine gases evolved during thermal decomposition of fire protection layers.

Curing behaviour and thermomechanical properties of benzoxazine-epoxy based copolymers reinforced with cellulose

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Polybenzoxazines, formed by thermal initiated ring-opening polymerization of benzoxazine precursors, are promising material due to their excellent thermal and mechanical properties [1-2]. However polymer brittleness, which is result of relatively low crosslink density, is their main drawback. A way to increase crosslink density and consequently further improve its thermal properties is the addition of epoxy groups into its network [2]. The introduction of natural fibers and fillers is another way to reinforce benzoxazine and/or epoxy polymers [3]. Compared with conventional reinforcing materials natural reinforcing materials have a number of benefits, including low density, high specific strength and modulus, biodegradability and low cost. However slightly reduced thermal stability was observed for the majority of bio-based composites [3]. By far the most used natural fibers are cellulose fibers. Therefore the effects of cellulose addition, on thermal and viscoelastic properties of the polybenzoxazines and polybenzoxazine/epoxy composites were investigated.

Firstly thermal curing process of benzoxazine-cellulose and benzoxazine/epoxy-cellulose systems was examined. Bisphenol A-aniline-based benzoxazine (Ba-A-BOX), diglycidyl ether bisphenol A type epoxy resin (DGEBA) and natural raw cellulose fibers (CF) were used as benzoxazine, epoxy and natural component, respectively. From DSC thermograms single exothermic peak, indicating the curing reactions was observed for all formulations. The heat released during curing decreased with increasing CF content as expected, since the amount of reactive oxazine rings in composites was reduced. Interestingly the onset temperature and temperature of exothermic peak of curing decreased with increasing CF concentration. The *–OH* groups, present in cellulose, may act as accelerator for benzoxazine and epoxy polymerization and therefore may become part of the cross-linked structure. Curing process also occurred at higher temperatures, when the ratio of DGEBA/BOX in the mixture was increased.

The DMA analysis was used to determine thermomechanical properties of cured composites. The value of storage modulus (*M'*) at room temperature was increased for around *10 %*, if the amount of CF in the composite mixture increased from *0 wt%* to *5 wt%*. On the other way, higher DGEBA/BOX ratios reduced the value of storage modulus in the glassy state and consequently lower the composite stiffness.

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The influence of thermal treatment on the rate of fire spread on the wood surfaces

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Thermal treatment is one of the environmental friendly wood modification processes to improve wood's natural durability. Thermal modification is used only for lining elements due to deterioration of mechanical properties of thermally treated wood. Properties of the bulk and especially surfaces depend upon wood species and in thermally modified wood also on the temperature and duration of heat-treatment.

Thermal modification improves wood performance in fire. The reason is that during previous thermal treatment a set of chemical reaction took place. Heat-treatment of wood in the temperature range between 200 and 260 °C causes strong hemicellulose degradation with an important release of acetic acid, water and carbon oxides. Depolymerisation and condensation reactions result in a lower gas permeability of wood. When exposed to elevated temperature, the mass flow of different flammable (and also inflammable) gaseous species (of unit area) is lower from thermally treated wood then from untreated one, leading to improved thermal stability.

Medium or large scale testing of material's performance after exposing to pilot flame are cost demanding and cannot predict the result in the case of various fire scenarios. On the contrary, computation methods allow a lot of different possibilities. Fire dynamics simulator (FDS), is a computational fluid dynamics (CFD) model of fire-driven fluid flow. With the help of this tool, the difference between the rate of vertical fire spread on thermal treated vs. non-thermally treated spruce wood will be shown. Initial data for this model were obtained from dynamic thermogravimetric measurements of these two samples. The surface changes due to thermal treatment at 230 ^{o}C in thermally wood were observed with scanning electron microscopy.

Oxidation of Carbon Deposited on Anode Material Ni-YSZ in Solid Oxide Fuel Cells

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Solid oxide fuel cells (SOFCs) are electrochemical devices that convert chemical energy of fuels directly into electricity with high conversion efficiency. A major advantage of SOFC systems compared to low temperature fuel cells is that SOFCs can use humidified hydro-carbons as fuel. However, the use of hydrocarbons may lead to an undesirable carbon deposition as hydrocarbons are oxidized at the anode side in SOFC. Such carbon deposits on the anode material nickel- yttrium stabilised zirconia (Ni-YSZ) are the most probable mode of deactivation of SOFC.

Therefore, commercially available anode material NiO-YSZ for high-temperature fuel cells was activated by a temperature-programmed reduction in a hydrogen atmosphere. In the next step carbon was deliberately deposited on the reduced samples by isothermal deposition in a methane-argon atmosphere. The carbon deposits were then burned out with a temperature-programmed oxidation (TPO) in an oxygen-argon atmosphere at different heating rates using thermo-analytical equipment. The TPO was followed by TG, DTG, DTA and QMS measurements. The easiest way to distinguish among various types of deposited carbon was to follow the QMS curves. The obtained QMS curves were processed with Netzsch Peak separation software in order to extract several peaks corresponding to various forms of carbon deposits. It was found that high amorphous and low amorphous carbon are burned out at relatively low temperatures (up to 650 °C), fibrous carbon is oxidized up to 750 °C, graphite is burned out up to 850 °C and finally, carbon diluted in nickel leaves the system in the range 900-1000 °C.

The isoconversional method was used to calculate activation energies of various carbon oxidation processes. The absolute values of the activation energies increase from amorphous carbon via fibrous carbon to graphite. Finally, the lowest activation energy value was calculated for burning process of carbon diluted in nickel.

Thermoelastic Martensitic Transformation in Cu-Al-Mn alloy

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Cu-Al-Mn shape memory alloys are commercially attractive for application of superelasticity, shape memory effect and high damping properties [1,2]. Cu-Al-Mn alloys with Al content less than 18 at. % show an excellent ductility because of low degree of order of β-phase [3, 4]. Thermoelastic martensite transformation is first order solid-solid transformation and it is explained by collective atom motion [5]. Cu-Al-Mn alloys were prepared and heat-treated at different temperatures. Temperatures of martensite transformations were followed by simultaneous thermal analyzer STA. Martensite phase and type of martensite was determined by SEM and XRD measurements. Dynamic-mechanical analysis was used to determine damping properties of alloy. Results show completely formed martensite in material, low transition temperature and high damping properties of material.

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Thermal and structural studies of sol–gel derived yttria-doped ZrO_2 nanoparticles: effect of annealing condition

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Sol-gel derived zirconia, ZrO_2 (stabilized by yttria in 5 mol %) nanocrystals (5YSZ) were annealed at different temperatures in different atmosphere conditions (air and vacuum) and investigated. Prepared samples were characterized by X-ray diffraction (XRD), differential thermal analysis (DTA), Fourier-transform infrared spectroscopy (FT-IR) and micro-Raman spectroscopy.

The results of DTA and XRD analysis show the zirconia crystallization onset at temperature no lower than 400 ºC. Average crystallite size of the 5YSZ annealed in air at 400, 600, 700 and 800 °C were calculated to be 10, 15, 22 and 33 nm, respectively. On the other hand, crystallite size remains in the range 4–13 nm when the heat treatment was conducted in vacuum. Annealing atmosphere affects crystallization, resulting in lower thermal treatment requirements and enabling controlled crystallite growth.

XRD and micro-Raman spectroscopy showed nanocrystalline 5YSZ samples were successfully stabilized in the tetragonal phase and preserved phase stability over the investigated thermal treatment range.

Thermal behaviour of concretes with micro silica addition

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A comparative study of several concrete composites with different quantities of micro silica was conducted. The effect that micro silica addition has on the behavior of concrete was discussed. The experimental program implied production of "referent" concrete composite based on Portland cement and river sand, and concretes with 5, 10, and 15 wt.% addition of micro silica. Micro silica was used as micro filler in the concrete mass. The influence of this additive on the concrete mechanical properties and on its thermal behavior was investigated. This research highlighted the role that fine micro silica particles have in improvement of composite microstructure packing, the decrease of the porosities values and enhancement in the compressive strength due to the decrease in pore size. The thermal behavior of the concretes was studied at temperatures ranging from ambient to 1100°C as adopted maximum. Mechanisms of thermally induced processes were observed by differential thermal analysis, at $10^{\circ}C \cdot min^{-1}$ heating rates, and by thermo gravimetric analysis. The variations in concretes performances were discussed with support of scanning electron microscope imagining and ***X-ray diffraction*** results. The composites with addition of micro silica exhibited properties that met the requirements for the concretes suitable for use in severe conditions and environments.

Thermal characterization of glasses from Fe-Sb-S-I system

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Thermal characterization of glasses from the $Fe_x[(Sb_2S_3)_{0.75}(SbSI)_{0.25})]_{100-x}$ system, for x = 0, 0.01, 0.1, 0.5, 0.8, 2, 3 and 5 at. %, in the temperature range from 300 K to 770 K, was done. The DSC recordings, obtained at different heating rates, revealed three processes: softening, crystallization of the corresponding structural units and melting of formed crystal units.

The process of softening was characterized by onset softening temperature T_g and by activation energy of softening E_g. Also, the impact of increasing the content of iron in the glass composition on the T_g value was determined.

The complex crystallization process corresponds to the crystallization of at least two structural units: SbSI and Sb_2S_3. Due to the considerable overlapping of the exothermic peaks, crystallization kinetics was done for Sb_2S_3 structural unit from the composition with 0.01 and 0.5 at. % of iron. Analysis was carried out by using the Johnson-Mehl-Avrami (JMA) theoretical model [1, 2, 3], under non-isothermal conditions. The activation energy of crystallization E_c and the value of the Avrami index n were determined. The value of Avrami index n was calculated by using the Matusita-Sakka theory [4]. It has been shown that volumetric nucleation and three-dimensional growth occur.

The shape of endothermic peaks, which appear behind the crystallization processes on thermograms, indicates the parallel progress of a multiple processes. It has been found that in addition to the melting of the crystalline SbSI structural units, at given temperatures, the process of thermal decomposition of the glass begins.

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Thermal decomposition and reaction mechanism of sulphide copper concentrate oxidation process

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Oxidation of sulfide minerals present in copper concentrate is a process, where in a specific temperature interval various reactions of decomposition and oxidation mostly occur simultaneously or successively, which implies to the complexity of physical and chemical changes in material during heating at elevated temperatures.

Due to better understanding the reaction mechanism and the oxidation process of sulfide copper concentrate from domestic ore deposit (ore body "H", Bor, Serbia), firstly the chemical analysis was done using ICP-AES, AAS and electrogravimetry. Characterization of the mineral forms present in the initial sample and oxidation products at 25, 450, 650 and 900 °C was done by XRD analysis. SEM/EDS analysis was done for the initial concentrate sample. Thermal analysis (DTA/TG) was done under heating rate of 10 °C min^{-1} in the temperature range 25 - 1000 °C and in the air atmosphere. Based on phase stability diagrams for Me-S-O (Me = Cu, Fe, As) at 450, 650 and 900 °C, the oxidation mechanism of the process was determined. Kinetic analysis of the concentrate oxidation was done using Ozawa's method of non-isothermal kinetics under heating rates 5, 10, 15 and 20 °C min^{-1}.

The obtained results showed that concentrate is chalcopyrite – enargite type. The reaction mechanism showed that in the investigated temperature range, sulfides are unstable in the oxidative conditions. At lower temperatures, present ternary sulfides (chalcopyrite and enargite) decomposed into binary copper and iron sulfides and volatile arsenic oxides. Further heating led to sulfides oxidation into iron oxides and copper sulfates and oxysulfates. At higher oxidation temperatures sulfates and oxysulfates decomposed into oxides. Kinetic analysis of the concentrate oxidation showed that all stages of the process in the investigated temperature range (25-1000 °C) occurred in the kinetic field.

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Influence of E-glass fibre content on thermal properties of glass-fibre reinforced composites

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Versatile applications of glass-fiber reinforced composites are still growing despite the fact that they have been is use for several decades. They exhibit a good mechanical performance along with a low density and these are some of the advantages due to which they have replaced metals in the past years, especially in transportation and electro industry.

The properties of composites are dependent on individual phases, i.e. the polymer-matrix, type of reinforcement and mineral filler, and can be tailored by properly selecting individual constituents and their ratio.

The polymer resin based on unsaturated polyester, glass fibers and $CaCO_3$ mineral filler are most commonly employed in Bulk Molding Compounds (BMC), i.e. in a pre-prepared mixture of aforementioned constituents. The most common processing methods for BMCs are compression or injection molding, especially used for the mass production of small, complex-shaped components. Since such materials are exposed to thermal stresses during processing as well as during service conditions, it is of great importance to study their thermal stability, thermal behaviour and properties.

The aim of this study was to investigate the effect of E-glass fiber weight content on physical properties and thermal behaviour of composites by means of thermal analysis techniques. The BMC formulations with varying E-grade glass fibers and $CaCO_3$ mineral filler weight fractions, while keeping the content of polymer resin constant (polymer matrix: 21 wt%, glass fibers from 0-20 wt% and $CaCO_3$ mineral filler from 58-73 wt%), were commercially prepared. The test specimens were prepared by compression molding. Scanning Electron Microscope images revealed that at low fiber fractions the microstructure was homogeneous (up to between 10 and 12.5 wt% of fibers), while with increasing the fiber concentration, the fibers clustered together, resulting in heterogeneous microstructures. The influence of the glass fiber content and their distribution on the enthalpy changes in the materials followed by differential scanning calorimetry and their mechanical properties, i.e., the storage and loss modulus, followed by dynamic mechanical analysis are reported and discussed in the contribution.

Thermal and mechanical properties of epoxy nanocomposites prepared by silane-modified montmorillonite

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In the last decade extensive research has been devoted to organically modified layered silicates, especially montmorillonite (Mt), as reinforcement for polymers. However, a pristine Mt is not suitable for the direct preparation of polymer nanocomposites due to its hydrophilic nature leading to phase separated structures. To enhance compatibility with organophilic polymers yielding intercalated or exfoliated structures, chemical modification of Mt plays a crucial role in Mt polymer nanocomposite formation and morphology. Incorporation of hydrophobic organic groups onto layered Mt surfaces increases the interlayer distance, which facilitates the intercalation of the polymer chains inside the Mt interlayer spaces. The most commonly used procedure to prepare organophilic Mt or other clay minerals is the cation exchange reaction with a quaternary ammonium salt [1]. However, this kind of surface modification does not provide an efficient linkage between the clay mineral and polymer matrix. Moreover, most of alkyl ammonium surfactants are not stable at the processing temperature of plastics. For these reasons, the silylation reaction between the silane coupling agents and reactive silanol groups of the clay mineral layers has attracted a great interest [2,3].

In this work, the silylation of sodium montmorillonite (Na^+-Mt, Nanofil 757®) was performed using (3-aminopropyl)triethoxy silane (APTES). Different reaction conditions were used, varying the reaction time (4-24 h) and the APTES : Mt ratio (0.33 to 1.5). Epoxy-based nanocomposites were prepared with 1, 3, and 5 wt.% of silylated Mt or commercial organically modified Mt intercalated with stearylbenzyldimethylammonium chloride (Nanofil 2®) or distearyldimethylammonium chloride (Nanofil 8®), respectively. The grafting/intercalation of the aminosilane inside the Mt interlayer spaces was studied by means of Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), nuclear magnetic resonance (NMR) and thermogravimetric analysis (TGA).

After isothermal cure at 90 °C the Mt epoxy nanocomposites were analyzed by XRD and dynamic mechanical analysis (DMA). The glass transition temperature (T_g) of the nanocomposites containing silylated Mt is slightly higher than that of the neat epoxy (2 to 5 °C). The storage modulus (*E'*) of Mt epoxy nanocomposites containing up to 5 wt.% silylated Mt increases for 5 to 15% at 25 °C, as compared to *E'* of neat epoxy matrix, while *E'* for nanocomposites with commercial Mt Nanofil 2® and Nanofil 8® increases for only 0–4 %.

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Determination of the pozzolanic activity of selected ashes by means of three different methods: the strength activity index test, the Frattini test, and DTA/TG analysis

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According to the definition given in ASTM C125 [1] pozzolan is a "siliceous and aluminous material which, in itself, possesses little or no cementitious value but which, when in finely divided form in the presence of moisture, reacts chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties". Pozzolans can be naturally occurring minerals (volcanic ashes, pumice), or industrial by-products such as fly ashes [2]. Pozzolans are used in different building materials, e.g. as supplementary cementitious materials, as additives in concrete, or as precursors for geopolymers.

In this study the pozzolanic activity of three fly ashes and two biomass ashes, which differed significantly according to their chemical compositions, mineralogical compositions, and particle size, was investigated in order to verify the possible utilization of these by-products. Many different methods can be used for the assessment of pozzolan properties [3], but, within the scope of this study, three different methods were applied: the strength activity index (SAI) test according to EN 450-1 [4], the Frattini test according to EN 196-5 [5], and differential thermal analysis and thermogravimetry (DTA/TG) [6]. The SAI test method is an indirect one, in which the measured compressive strength of CEM-I is compared to the compressive strength of a mixture where 25% of the CEM I is replaced by pozzolan. The Frattini and DTA/TG methods are, on the other hand, direct test methods, since they involve direct measurements of the decrease of the $Ca(OH)_2$ which is spent in the reaction. The Frattini test method is based on chemical titration, and is used to determine the amount of dissolved Ca^{2+} and the OH^- concentrations in a solution containing the tested pozzolan. DTA/TG is one of the preferred methods for the characterization of pozzolanic activity, since it measures the $Ca(OH)_2$ reduction, which reflects very well the pozzolanic action of the admixture as a function of the percentage used and time from the beginning of the hydration process [6].

The results obtained when using the above-mentioned test methods are compared in order to determine whether there was any correlation between them with regard to assessed pozzolanic activity.

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Novel advanced biomedical applications of Ni_xCu_{1-x} nanoparticles

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The aim of this study was to incorporate three model drugs with different pharmacological activity into superparamagnetic Ni_xCu_{1-x} nanoparticles. First, the Ni_xCu_{1-x} nanoparticles with narrow size distribution were prepared using a sol-gel method with suitable Curie temperature in the therapeutic range of 42 °C – 46 °C. The nanoparticles were prepared in a silica matrix that prevented their agglomeration during thermal treatment and retains pore sizes in the nano-range, suitable for stable entrapment of drug molecules.

Assessment of the as-prepared nanoparticles' applicability in drug delivery, the release of the incorporated drugs was studied using an *in vitro* release system (based on Franz diffusion cells), whereas UV-Visible Spectrophotometry (UV/Vis) was used for quantification of the released amount of drug. Samples were released at the same time intervals for each sample and parallel. All release studies were performed in at least two parallels. The Ni_xCu_{1-x} nanoparticles were characterized using X-ray diffraction (XRD) analysis, thermogravimetric analysis (TGA/SDTA), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), magnetic measurements (SQUID). Surface area and pore size were determined by using BET analysis. The suitable Curie temperature, determined using modified thermogravimetric analysis on a TGA/SDTA (Mettler Toledo), and different release profile of superparamagnetic Ni_xCu_{1-x} nanoparticles makes them suitable for magnetic hyperthermia and drug-delivery applications.

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Thermochemical Phase Transformations of $CaCO_3$ Polymorphs in New Consolidant Based on the Soluble Calcium Compounds

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Conservation of cultural heritage materials represents an irreplaceable value for humanity, meaning that each damaged or destroyed object is lost and therefore also the resources and evidence of human history and culture. When restoring important historic monuments, calcium carbonate ($CaCO_3$) based consolidants are preferable due to their physical-chemical compatibility with original material. Currently the most commonly used consolidants for restoring carbonate based materials are nanolime $Ca(OH)_2$ nanoparticles in different solvents (mainly in iso-propanol and ethanol). Due to its limitations (small penetration depth, whitening of the surfaces, limited solubility, ect.) new $CaCO_3$ forming consolidants have been developed based on the soluble calcium compounds [1]. Newly developed consolidant decomposes to $CaCO_3$ which furthermore transform through three different structures – from amorphous phase (ACC) to vaterite (V) and finally calcite (C) crystal structure. The rate of decomposition of the consolidant into $CaCO_3$ and its transformation into different phases is dependent on many factors, such as temperature (T) and relative humidity (RH).

In this study the transformation of metastable amorphous calcium carbonate and vaterite into the stable calcite was investigated by means of thermal analysis (differential scanning calorimetry - DSC and thermogravimetric analysis - TGA), together with X-ray diffraction (XRD) and FT-IR spectroscopy.

Research activities have been carried out in the scope of the European project "Protection of cultural heritage objects with multifunctional advanced materials ".

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Investigations on thermo-physical properties of composite sorption materials for solar energy storage

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Sorption materials attract broad interest because of their potential applicability in the field of thermal energy storage, e.g. low temperature sorption heat storage, which is based on a reversible physico-chemical process: adsorption/desorption of water on porous solid sorbents. Solid/vapor adsorptive systems are very promising for heat transformation applications as they can utilize efficiently solar energy or waste heat as driving force and they can render the burning of fossil fuels for heating much more effective compared to modern condensing boiler heating systems. Therefore, a reasonable amount of the resulted environmental pollution can be avoided. The most promising adsorbent material among microporous aluminophosphates in terms of equilibrium data was found to be APO-Tric [1]. Under relatively mild conditions, e.g. adsorption at 35 ºC (1,23kPa) and desorption at 95ºC (5,67 kPa), it shows maximal water loadings of up to 32wt%. The advantages of this material are also the energy density in the working temperature range from 40 to 140^{o}C of 240 kWh/m^{3}, its hydrothermal and thermal stability (up to 900^{o}C) and water desorption at 95 ^{o}C. The main disadvantage of this material is its low thermal conductivity (~ 0.1 W/m/K) that reduces heat exchanges rates during sorption process.

One of the strategies for the improvement of thermal conductivity is a combining aluminophosphate sorption material with material with high thermal conductivity, like porous carbon, in the form of coatings.

We have prepared composite sorption materials by mixing of APO-Tric aluminophosphate and different carbon precursors, such as sucrose and citric acid. Thermo-physical properties of the composites were determined. Composite samples were structurally characterized by XRD to determine structures of the composites. The results showed that the preservation of structure of APO-Tric after carbonization at 650C in inert gas was dependent on the method of composite preparation. Thermo-gravimetrical analysis results showed that the amount of carbon in the samples depends on the type of used carbon precursors and on method of preparation. Water sorption capacity was determined by gravimetric method and showed that composites had similar water uptakes.

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An effect of dopant ions on a thermal stability of α-MnO_2 nanorods

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α-MnO_2 nanoparticles in one-dimensional morphology doped with Fe^{3+}, Cr^{3+} and Co^{2+} ions were prepared by hydrothermal decomposition of $KMnO_4$ in acidic media at temperatures between 90 and 170 °C [1]. The morphologies of the as-synthesized products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) in combination with energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM). It was found out that reaction temperature and as well dopant ions have a crucial role on the morphology of synthesized nanoparticles and on secondary structure. In the case when the dopant ion was Fe^{3+} nanoparticles grow in the nanotube morphology [2] while when the dopant ions were Cr^{3+} and Co^{2+} products were grown in the nanowire morphology. At lower reaction temperatures (90 and 130 ºC) the nanotubes and nanowires were self-assembled into 3D microstructures with diameters between 2–3 μm. Thermogravimetric studies revealed that dopant ions have influence on thermal stability of the as-synthesized products.

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Synthesis of nanocrystalline Co_3O_4 nanopowders via self-propagation combustion reaction

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Over the past two decades, a considerable effort has been devoted to research of the p-type semiconducting materials, which found diverse applications in industry. As the p-type material with a spinel AB_2O_4 structure and direct optical band gap of 2.19 eV, cobalt oxide, Co_3O_4 has drawn special interests in gas-sensing and solar energy absorption research community. At the same time, it has found the usage as an electrode material in lithium ion batteries, catalyst, ceramic pigment, field-emission and magnetic material. A powerful strategy to improve the Co_3O_4 performances in some of the mentioned applications is the utilization of a nanocrystalline powder with a high surface to volume ratio, which can be successfully produced by self-propagation combustion reaction.

In this work, cobalt nitrate (oxidizer) and glycine (fuel) of required amounts were dissolved in the minimum amount of deionized water to obtain a clear solution. According to the rules of propellant chemistry, the glycine/metal ion ratio was adjusted to provide stoichiometric or fuel-lean conditions of the redox reaction. The sols were dried at 80 ^oC to obtain the gels, and then subjected to the rapid heating, where the gels auto-ignited at approximately 250 ^oC (depending on the amount of the fuel) and spontaneously underwent a smouldering combustion with evolution of large amounts of gases, subsequently forming a voluminous nanosized Co-oxide powder.

It is worth to mention that the dual role of the glycine (chelating agent and fuel) in this synthesis was of great importance in preventing the precipitation of the solution during rapid heating, and in liberation of the required energy for the synthesis of the Co_3O_4 powder with desired Co^{+2}/Co^{+3} oxidation state, necessary for its further use in production of gas sensors and catalysts. The processes involved in formation of the pure Co_3O_4 powder and especially the exothermicity of the reaction, were followed by simultaneous thermal analysis (thermogravimetric and differential thermal analysis coupled with evolved gas analysis). According to the X-ray diffraction analysis the phase-pure Co_3O_4 was obtained only when the precursor powder was prepared from the fuel-lean redox reaction. The field emission scanning electron micrographs revealed the spongy aspect of the calcined powder, where small primary particles formed the agglomerates. The transmission electron microscopy was used to get deeper insight in the particle size and purity of the as prepared nanosized powders. The formation of the single Co_3O_4 powder from the solution to the combusted powder was also analysed by Fourier transformed infra-red spectroscopy.

Behaviour of high energy milling activated egg-shells during thermal treatment

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The main object of investigations in this work is the chicken eggshell. The effective high energy milling (HEM) treatment and utilization of chicken eggshells (ES) as a bio-waste have been investigated for the environmental and economic concerns. The chemical composition of the ES is mainly inorganic (94% calcium carbonate as calcite, 1% calcium phosphate, 1% magnesium carbonate), but also organic matter is present (4%) [1, 2].

The high-energy milling (HEM) is well-known method used for modification of structure and properties of materials [2]. During HEM activation so-called mechanical activation process takes place. The HEM activation of wide variety of materials leads to the improvement of their properties [2-4].

The waste eggshell samples after HEM activation were characterized by thermal analysis, X-ray diffraction, Fourier transform infrared spectroscopy and Scanning electron microscopy, respectively.

The decarbonization process were carried out using a thermal investigation in air flow gas conditions, where with increasing HEM activation time decrease the temperature of decarbonization.

Keywords: chicken eggshell, solid waste, high energy milling, utilization

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A new method for investigating the Alzheimer's disease and methods for its prevention based on differential scanning calorimetry (DSC)

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In this work we develop a new approach based on differential scanning calorimetry (DSC) for diagnostics and characterization of the changes in the brain at molecular and supramolecular level associated with the Alzheimer disease (AD). In order to test the DSC potential in studies of AD, we used an experimental animal (mice) model of scopolamine-induced AD. The DSC measurements performed on supernatants of brain tissue homogenates isolated from healthy animals and animals with scopolamine-induced AD showed that thermograms for animals with scopolamine-induced AD strongly differ from the respective thermograms for healthy animals. The effects of preventive treatment with various substances and their combinations expected to have protective effect hindering the development of AD (myrtenal, ellagic acid, lipoic acid, ascorbic acid) are also clearly displayed in the thermograms. These measurements show that DSC is an appropriate method for detection and characterization of the compositional changes taking place in the affected by AD brain tissues.

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Peculiarities of thermal decomposition of synthetic simonkolleite

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Simonkolleite, $Zn_5(OH)_8Cl_2.H_2O$, is a layered double hydroxide with the structure built of stacked two-dimensional units. Morphologically, crystalline simonkolleite particles can be characterised as honeycomb-shaped plates of nanoscale thickness. Commercial uses of such compounds include ion exchange and molecular sieves, flame retardants, additive to high grade PVC materials and cosmetic, high basic heterogeneous and superior shape selective catalysts, antacid, drug fillers, clay-modified electrodes and anticorrosion agent, while potential areas of application can be extended to utilization in waste recycling, waste water cleaning and in medical field as drug supports or matrices [1, 2]. Thus, simonkolleite represents an extremely versatile technological material and full understanding of its properties and formation conditions is the key point for the future industrial implementation and extension of its technical applications.

In our previous study, the optimal conditions providing formation of pure simonkolleite with the highest experimental yield have been already found out [3]. In that investigation we have employed simple precipitation method using NaOH and $ZnCl_2$ which are cheap and the most common reagents for preparation of $Zn_5(OH)_8Cl_2 \cdot H_2O$. As continuation of our study, in present contribution, our attention is focused on the effect of the synthesis conditions (in particular Zn/OH ratio in the matrix solution) on microstructural properties and stoichiometry of the obtained products. To this purpose, we have used thermoanalytical tools (TGA and DTA) which in combination with XRD analysis can provide detailed description of thermal transformations of the investigated material leading to valuable conclusions over its initial stoichiometry and microstructural peculiarities.

According to the literature, simonkolleite undergoes the following transformations during heating:

1. $Zn_5(OH)_8Cl_2 \cdot H_2O \rightarrow 3ZnO + 2\beta\text{-}Zn(OH)Cl + 4H_2O$ (~170°C);
2. $2\beta\text{-}Zn(OH)Cl \rightarrow ZnO + ZnCl_2.0{,}25H_2O + 0{,}75H_2O$ (between 220-230°C);
3. $ZnCl_2 \cdot 0{,}25H_2O \rightarrow 0{,}25\ ZnO + 0{,}5HCl + 0{,}75\ ZnCl_2$ (above 230°C);
4. $ZnCl_2$ sublimation (~450°C).

Each of these stages is characterised by particular weight loss and thermal effect, which were monitored for our samples under different heating conditions. In addition, intermediate products which were obtained using independent heating cycles have been analysed by XRD analysis. The results have been interpreted with main focus on effect of the synthesis conditions on thermal behaviour and related properties of the investigated materials.

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Viscosity of Ag and Au doped arsenic trisulfide

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Viscosity is one of the most important physical parameters of every material. Knowledge of viscous behavior is also necessary for technology and production of glassy materials. Moreover viscosity relates with crystal growth in undercooled melts and with structural relaxation of glass. Crystallization is significantly influenced by diffusion and this process is connected with viscous flow. Because glass is thermodynamically unstable material, we can observe structural relaxation to equilibria state and relaxation time is influenced by viscous flow.

Glassy arsenic trisulfide belongs to the most important chalcogenide semiconductors. This glass is used in optoelectronics and for construction of optical elements for the near and middle infrared region [1]. Doped As_2S_3 by metals changes many of its physical properties [2]. However viscosity of doped As_2S_3 has never been investigated.

We prepared pure glassy As_2S_3, ternary $(As_2S_3)_{100-x}(Au)_x$ where (x = 1, 5) and $(As_2S_3)_{100-x}(Ag)_x$ where (x = 1, 2.5, 5, 7.5, 10, 12.5). All compositions were used for viscosity measurements except for $(As_2S_3)_{95}(Au)_5$ due to phase separation of elementary Au. Viscosity was measured using thermomechanical analyzer by two methods – parallel-plate method [3] and penetration method [4]. Whole measurable region of undercooled melt and part of glass region were measured by use of these two methods. Measured samples show Newtonian behavior and the viscosity dependence on temperature can be described by Arrhenius equation. Above that the kinetic fragilities and temperature of glass transition (equal to viscosity 10^{12} Pa·s) were calculated from this simple equation.

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Important issues connected with differential thermal analysis of Fe-C based alloys

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The paper deals with issues connected with the investigation of Fe-C based metallic systems by DTA method. There are many experimental factors that can influence resulting experimental data. Influence of heating (cooling) rate [1] must be considered, sample mass also [2], sensors and crucibles used by experiment alone, etc. [3]. There are general suggestions how to perform experiments with metallic materials to obtain the desired data. But, in many cases it is necessary to modify the experimental conditions with respect to the obtaining of needed data – corresponding data.

The problems that can be encountered by investigation of metals with carbon content are also decarburisation and oxidation. The paper presents results of experimental measurements performed using DTA method and experimental laboratory system Setaram SETSYS 18_{TM} with respect to the possible decarburisation [4] of studied alloys in low and high temperature region. The degree of decarburisation and its influence on DTA response is discussed. OM and SEM study and change of carbon content of studied samples was performed to determine the possible ratio of decarburisation. The degree of decarburisation can be in some cases considerable [4]. The way how to prevent or minimise the decarburisation degree of Fe-C based samples is suggested.

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Comparison of DTA and DSC method related to the heat effects of phase transitions of Fe-alloys in low and high temperature region

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The paper deals with issues connected with the investigation of heat effects ("Latent Heats") of phase transitions of Fe based metallic alloys. Results obtained using Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) are the methods that are subject of presented work. Both two methods are suitable for obtaining of thermo-physical and thermo-dynamical data. This paper deals with the influence of settings of the experimental conditions [1] of the used DTA and DSC methods in relation to the obtained data (heat effects of phase transitions).

The paper is focused mainly on the study of heating/cooling [2] rate and mass influence of the sample [3] on size of the thermal effects of alpha-gamma (gamma-alpha), gamma-delta (delta-gamma) phase transformations and on melting (solidifying) of "pure Fe". Measurements with Setaram SETSYS 18_{TM} equipped with "2D" tricouple DTA sensor and Setaram MHTC (Multi High Temperature Calorimeter) equipped with 3D heat flux DSC sensor were performed under the same and precisely defined experimental conditions. Typical peculiarities of DTA (2D) and DSC (3D DSC) sensors are compared and discussed. Statistical evaluation is discussed also. Natural relations are derived with respect to the utilisation of DTA and DSC to the metallic systems in high temperature region: up to 1600 °C.

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Calorimetric measurements of real steel grades with use of DSC method

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DSC method (Differential Scanning Calorimetry) is one of the calorimetric methods which is suitable for studying the thermodynamic properties of steels. Heat capacities of steels are one of the crucial thermophysical parameters used for process behaviour prediction in many applications. Heat capacity is an input variable for many thermodynamical (e.g. ThermoCalc) and kinetic programs. The dependences of heat capacity on common variables (temperature, pressure,...) are also commonly used as the input data in software packages (e.g. ProCast, Magmasoft, ANSYS Fluent, …) that are applicable in the field of applied research for simulations of technological processes. Experimental data of heat capacities can be found in literature, but it is difficult to find data for given steel (with exact chemical composition) [1, 2].

The paper deals with the investigation of real steel grades in the solid phase under strictly defined conditions for controlled heating. Heat capacities of steels were obtained using high-temperature calorimeter Setaram MHTC 96 (Multi High Temperature Calorimeter) with 3D DSC sensor. The experiments were supported by theoretical calculations using software ThermoCalc (CALPHAD method) and also using Neumann-Kopp rule. Factors which may influence the experimental results obtained by DSC method were studied. These factors include the heating rate and the size of the analyzed sample. Experimentally acquired heat capacity ("Apparent Heat Capacities") of real steel grades were confronted with the calculated theoretical data and with data reported in the available literature.

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Application of DTA (2D sensor) and DSC (3D sensor) methods to metals: influence of experimental conditions

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DTA (Differential Thermal Analysis) and DSC (Differential Scanning Calorimetry) are two of the methods that are suitable for obtaining thermo-physical and thermo-dynamical data. This paper deals with the influence of the experimental conditions settings of the used DTA (2D measuring sensor) and DSC (3D measuring sensor) methods in relation to the obtained experimental data.

The paper deals with the study of heating/cooling rate and mass influence of the sample on shifting of the phase transformations temperatures (alpha-gamma, gamma-delta phase transformations and melting) of “pure Fe”. Sample mass and heating/cooling rate belong to the frequently and easily changing parameters and their influence on the obtained data is substantial [1]. The study was aimed both at low temperature and high temperature regions. DTA measurements were realised using the Setaram SETSYS 18TM laboratory system with 2D sensor, and DSC measurements using the Setaram MHTC 96 (Multi High Temperature Calorimeter) with 3D DSC sensor. The samples of “pure Fe” (with different mass) were analysed at several controlled heating/cooling rates. On the basis of adjusted experimental conditions, the experimental data set was obtained and corresponding dependences were derived. Using the corresponding dependences the corrections can be applied to minimise the influence of experimental conditions on studied data for investigated alloys (samples).

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Thermal behaviour of carboxylate precursor mixtures for $YBa_2Cu_3O_7$ superconducting thin films

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Coating solutions based on metal carboxylate salts are attractive alternatives to the standard trifluoroacetate route for the manufacture of long $REBa_2Cu_3O_7$ superconducting tapes. However, depending on the length of the ligand used in such solutions, widely different film microstructures and superconducting performance are obtained [1].

Based on a detailed study of the thermal behaviour of the precursor solutions containing all cations and comparison with the decomposition of the individual salts, it was possible to link the superconducting film quality to specific features of the pyrolysis steps.

The occurrence of melting, followed by gas release in the liquid state in some precursors is believed to induce a rougher surface and thus degrade the connectivity and preferential orientation degree of the superconducting crystallites.

Further optimisation of the process based on propionate precursors allowed reaching a critical current density of 3.7 MA/cm^2 at 77K. Comparisons are made with superconducting films produced by means of a “low-fluorine” process.

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Heating rate effect on the thermal behaviour of some clays and their mixtures with oil shale ash additives

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The heating rate effect on the thermal behaviour of green clays from Arumetsa and Kunda deposits (Estonia), and, for comparison, on illitic clay from Füzérradvány (Hungary) as well as on their blends with oil shale ash additives was studied. Two different ashes were used: the cyclon ash (CA) formed at pulverized firing and the eletrostatic precipitator ash (ESPA) formed at circulating fluidized bed combustion of Estonian oil shale (OS).

Experiments were carried out under non-isothermal condition up to 1050°C using a Setaram Setsys 1750 thermoanalyzer coupled with Pfeiffer Omnistar Spectrometer at the heating rates of 1.25, 2.5, 5 and 10°C min^{-1} in an oxidizing atmosphere containing 79% of Ar and 21% of O_2. Standard 100 µL Pt crucibles were used, the mass of samples was 50 ± 0.5 mg. The differential isoconversional method of Friedman was applied to calculate the kinetic parameters.

Depending on the heating rate the emission of hygroscopic water, and from samples based on Kunda clay also the emission of crystal water from dehydration of gypsum prolonged up to 200-300°C. In temperature range from 200-300°C up to 550-600°C the emission of H_2O is caused by dehydroxylation of illite, illite-smectite, mica, and kaolin. The emission of carbon dioxide is resulted from the burning of organic matter contained in clays, and the emission of SO_2 at thermal treatment of Kunda clay from the thermooxidation of pyrite. At temperatures from 550-600°C up to 700-900°C the mass loss is caused by lasting the dehydroxylation processes, and, for Kunda clay there was fixed also the emission of SO_2 resulted from the second step of thermooxidation of pyrite. The total mass loss up to 1050°C for Arumetsa and Kunda clay was 6.3% and 4.8%, respectively, and for illitic clay 7.1%.

At thermal treatment of blends containing 60% of clay, 20% of fired clay and 20% of ash there was fixed well-seen endotherm in DTA curves with the corresponding maximum in the H_2O emission profiles between 405°C and 465°C indicating the decomposition of portlandite. The missing of SO_2 in evolved gases at thermal treatment of blends based on Kunda clay indicated the binding of it into the solid by CaO contained in ashes. At higher temperatures the mass loss for blends with OS ash additives is caused mostly by decomposition of dolomite and calcite.

The value of activation energy E along the reaction progress α varied between 85.1 - 193.8 and 135.4 - 179.1 kJ mol^{-1}, respectively, for Arumetsa and Kunda clay, and for illitic clay between 126.1 - 233.7 kJ mol^{-1}. For blends with OS ash additives the decomposition of samples can be devided into two steps: at first the dehydroxylation of clay minerals, and, secondly, mostly the decomposition of carbonates. For the first step the value of activation enery for blends based on Arumetsa clay varied between 117.0 and 193.9 kJ mol^{-1}, for these based on Kunda clay between 32.0 and 322.0 kJ mol^{-1}, and based on illitic clay between 113.0 and 240.1 kJ mol^{-1} indicating the complex character of decomposition of clays and their blends with Estonian OS ashes. For the second step the variation of the value of activation energy for all samples studied were more modest differentiating along the reaction progress α between 0.1 and 0.9 on the level of 20-30 kJ mol^{-1}only.

Thermal and mechanical characterization of a series of PLA/lignin blends

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Lignin, that is the second most abundant biopolymer on earth, is an amorphous polyphenolic macromolecule with a large number of polar groups which provides multiple functionalities. Although it was successfully used as flame retardant [1] and/or stabilizer [2] in platics the most effective use of lignin was in blends with various synthetic polymers [3]. As much more attention has been paid to environmental issues in recent years, bio-based polymers are poised to play an important role as a viable and biodegradable substitute for petroleum-based polymers. Nature biodegradable plastics are usually founded on polyesters derived from renewable resources such as corn starch and, due to its environmentally friendly cycle production and its comparable properties to conventional polymers, Poly(lactic acid) (PLA) was, in the last decade, the most considered for this purpose.

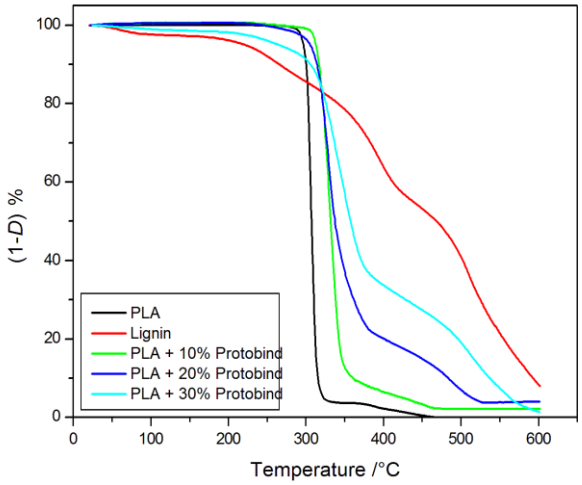

Fig. 1 TG degradation curve of PLA/lignin blends.

In this research, blends of PLA (NatureWorks LLC product) with different percentages of two kinds of lignin (Protobind2400 from GreenValue and LV1000 from Tecnaro) were prepared in a static mixer chamber measuring the torque of the melt at processing temperature (190°C). Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA) on the obtained compounds were carried out in order to evaluate the effect of lignin addition in PLA thermal and mechanical properties.

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Mono Alkyl substituted Polyhedral Oligomeric Silsesquioxanes (POSS): the influence of the nature of cage's periphery on the resistance to thermal degradation

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Polyhedral oligomeric silsesquioxanes (POSSs) are hybrid inorganic/organic compounds of general formula $(RSiO_{1.5})_n$, (R = H or organic substituents and n = 6, 8, 10 or 12). POSSs can be well used as drug materials and imaging agents, since these materials have potential advantages such as their biodegradation, thermodynamic stability and biocompatibility [1]. The increasing importance of POSSs is also due to their employment as fillers or end-linking agents in the production of polymer and shape memory polymers nanocomposites that can be used in a variety of technological fields ranging from medical to aeronautics [2]. Our group has in progress a wide research on the synthesis and characterization of new thermally stable POSSs [3-4] to be used as fillers for Polystyrene (PS) based nanocomposites. We report in this work the synthesis and thermal characterization of three series of mono alkyl POSS with different seven pendants groups (isobutyl, cyclopentyl and phenyl) and an aliphatic chain at different lengths (6, 8 and 10).

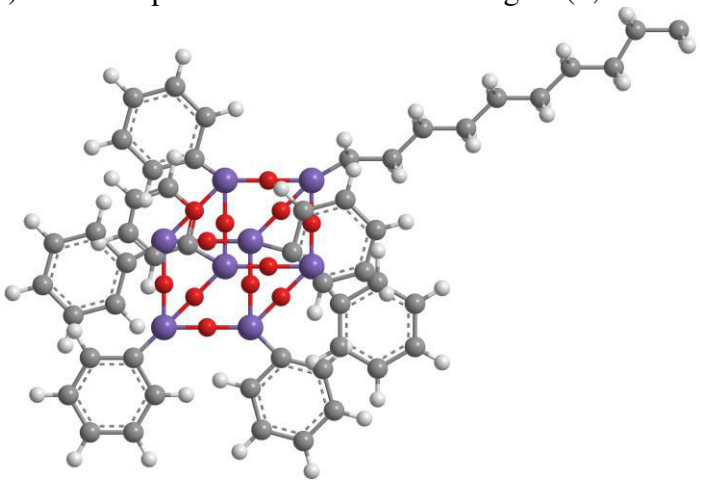

Fig. 1 Molecular structure of *n*-decyl hepta phenyl POSS.

POSSs were prepared by corner capping reaction and were characterized by elemental analysis and ^1H NMR. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were carried out to draw information about their resistance to thermal and thermooxidative degradation.

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The effect of microwave and hydrothermal treatments on the properties of hydrotalcite: a comparative study

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Layered Double Hydroxides (LDHs), also known as hydrotalcite-like compounds, have received much attention in potential applications such as catalysis, adsorption and etc. It is well-known that the most common preparation method of LDHs - the co-precipitation - has many drawbacks: the difficulty in obtaining high crystallinity compounds, a strong agglomeration of primary particles and others [1-2]. Thus, the application of more advanced techniques including microwave and hydrothermal heating in the synthesis of this group of compounds is a fast growing area and is an alternative in materials processing to save time and energy consumption. However, the most of the research is focused on the use of these treatments as a secondary synthesis step (after co-precipitation) and the literature concerning direct synthesis of hydrotalcite by microwave and hydrothermal treatments is limited [3-4].

For this reason, in this work, a comparative study of the application of two thermal methods (microwave and hydrothermal heating) for obtaining HT has been carried out to fully understand the effect of these treatments on the properties of hydrotalcite.

Mg-Al hydrotalcites having Mg/Al molar ratios of 1 and 2 were prepared by a simple synthesis techniques: hydrothermal and microwave treatments (200 °C; 1 and 3 h). It was determined that, in both cases, the interaction between raw materials proceed faster when the Mg/Al molar ratio is equal to 2:1. However, the duration of these syntheses has a significant effect on the crystal properties and texture of hydrotalcite: the highest crystallinity and fineness of this compound is obtained after 1 h of microwave treatment, while by using hydrothermal synthesis – after 3 h. In addition, the synthesis products show the same thermal behaviour.

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A study on the thermal stability of kilchoanite synthesized under hydrothermal conditions

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Natural $Ca_3Si_2O_7$ occurs in two modifications: rankinite and kilchoanite. Both minerals are typically formed during the pyrometamorphism of siliceous limestones [1]. Kilchoanite was first synthesized as a new phase by Roy, who called it Phase-Z and considered it to have the composition, $9CaO{\cdot}6SiO_2{\cdot}H_2O$ [2]. Mitsuda et al. [3] showed that by using the rapid heating method kilchoanite was obtained from lime and quartz at 280 - 600°C and 500 - 1000 bars. With further results, Mitsuda and Taylor [4-5] reported that if the heating rate was sufficiently rapid with finely divided quartz, the main products were kilchoanite at Ca/Si = 1.5 and kilchoanite and calciochondrodite at 2.0 above 250°C and 400 - 500 bars. The synthesis, structure and chemistry of kilchoanite were also studied by other scientists, however, their opinions differ.

The thermal stability and formation mechanism of both kilchoanite and intermediary compounds under hydrothermal conditions, when primary mixtures consisted of CaO and amorphous $SiO_2{\cdot}nH_2O$, were examined in detail. The synthesis was carried out in unstirred suspensions, when molar ratio of the primary mixture was CaO/SiO_2 = 1.5 and the duration of isothermal curing in a 175 – 220 °C temperature range was 4, 8, 16, 24, 48 and 72 h. In situ X-ray diffraction study on the thermal stability of synthesized compounds was performed in a modular temperature chamber from RT to 1200 °C temperature.

It was examined, that at 175 °C temperature kilchoanite does not form within 72 h in the mixtures of CaO and amorphous SiO_2. However, the increase of temperature positively affects the synthesis of this compound – kilchoanite was obtained at 200 °C after 24 hours, while at 210; 220 °C – after 8 hours. It should be noted that during hydrothermal treatment firstly the intermediary compounds – C-S-H (I), C-S-H (II) and α-C_2S hydrate – are formed and then they recrystallize to kilchoanite. It was determined that the latter compound is stable till 1100 °C and at higher temperatures, kilchoanite recrystallization to rankinite proceeds. The previous results were confirmed by XRD, STA, FT-IR, SEM, SBET analysis.

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The stability of synthesized CaF_2 and its influence on the thermal behaviour of C-S-H

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Fluoride is one of the well-known anionic pollutants worldwide that shows strong affinity with bone tissue cause skeletal fluorosis [1-2]. Because of the strict environmental regulations governing fluoride concentrations in water within many countries and safe disposal of fluoride containing wastes is still one of the critical environmental challenges [3]. In previous work [4], it was determined that silica gel waste contaminated with F^- ions is suitable for the hydrothermal synthesis of C-S-H and can be used/utillized as unconventional Si-containing raw material, because F^- ions were bound by CaO and formed a stable compound – calcium fluoride. However, the literature concerning the effect of CaF_2 on the stability of C-S-H is limited.

For this reason, in this work, the stability of synthesized calcium fluoride and its influence on the thermal behaviour of C-S-H were examined in detail. The hydrothermal synthesis of the different basicity calcium silicate hydrates was carried out at 200 °C for 16 and 48 h in unstirred suspensions, when the primary mixtures consisted of CaO and silica gel waste (CaO/SiO_2 = 0.55, 0.66, 0.83, and 1.0).

It was determined that under all experimental conditions together with the different basicity C-S-H, CaF_2 is always formed. However, the mineralogical composition of synthesized C-S-H did not correspond to the primary mixture C/S molar ratio. In the mixtures with the C/S molar ratio of 0.55, after 16 h of hydrothermal treatment, Z-phase and gyrolite gel were obtained. Meanwhile, with the highest C/S molar ratio (C/S=1.0), after 48 h of isothermal curing, the main synthesis products were 1.13 nm tobermorite and gyrolite gel. In addition, the intensities of diffraction maximums characteristic to calcium fluoride decreased with increasing C/S molar ratio.

Therefore, the mineralogical composition of products in a 600-1000 °C temperature range was highlighted. For characterization the XRD, STA, FT-IR, SEM, S_{BET} instrumental analyses were used.

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The effect of synthetic CASH additive on the hydration properties of OPC

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Geopolymers which are based on calcium aluminosilicate hydrates (CASH) ores presents a viable alternative for replacing OPC and are a novel eco-friendly construction material. This group of compounds, of general formula $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$, can be located in the $CaO–A_{l2}O_3–SiO_2–H_2O$ system, where the existing series with the end members known as grossular for x = 0 and hydrogarnet for x = 3 [1] have been synthesized by various preparative methods including aging of precipitated gels and sol-gels processes, hydrolysis of complex oxides, and hydrothermal method [2]. However, each of these methods has its own limitation: the high temperature-pressure hydrothermal method is complicated and has strict pressure conditions, while for the other preparative methods, firing is an essential crystallization step, which usually results in particle agglomeration [3]. For this reason, the mild hydrothermal synthesis below 240 °C and under homogeneous pressure has been a promising route for preparing these novel inorganic compounds [2-3]. It is well-known that CASH are a major products of the hydration of calcium aluminate cements, and occur in high-aluminum cement and to a lower extent in Portland cement [1, 4]. Thus, the aim of this work was to investigate the effect of synthetic CASH additive on the hydration of Portland cement.

CASH was synthesized under hydrothermal conditions for 8 hours at 130 ^oC temperature. The molar ratios of primary mixtures were $CaO/(SiO_2+Al_2O_3)$ = 0.55 and $Al_2O_3/(SiO_2+Al_2O_3)$= 0.1 or 0.15. CASH was added as a partial replacement of the OPC at levels of 0%, 5% and 10% by weight of the total cementitious material. Therefore the water and cement ratio of all OPC samples was equal to 0.5.

It was determined that calcium aluminium silicate hydrates affect the early hydration of OPC. These compounds effectively shorten the induction period and accelerate the dissolution of C_3S, C_3A and the formation of ettringite. Moreover, the mentioned effects grows as the C-A-S-H level increases in the OPC samples. Meanwhile, only the OPC samples with 10 % of calcium aluminium silicate hydrates shows similar effects to those of the usual pozzolanic additives, because the amount of cumulative heat grows with the increasing duration of hydration. The previous results were confirmed by XRD, STA, FT-IR, SEM analysis.

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Thermal behaviour of pozzolanic material synthesis from silica gel and clay

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Pozzolans are being widely used as a cement replacement in concrete which results in better chemical resistance, higher strength or better durability [1, 2] and reduce a significant resources of energy, CO_2 emission and the cost of building materials production [3, 4]. One of the earliest known pozzolanic materials is a burned clay. Unfortunately, clays of Lithuanian industrial quarries are rich in hydromica and have poor pozzolanic properties [5]. On the other hand, Lithuania is rich in technogenic waste silica gel, which forms during the production of AlF_3. Due to the fluoride impurities in the waste, silica gel is stored in the landfills and its usage is still a major problem from the ecological perspective. The synthesis and application of the active pozzolanic materials of clay with silica gel have not been studied at all.

For this reason, in this work, the thermal behaviour of pozzolanic material synthesis was investigated. The thermal treatment was carried out at 600-860 ˚C temperature range in the Dukstyna clay with 10-80 wt.% silica gel and silica gel–Dukstyna clay with limestone admixture (optional composition mixture) systems.

Results of research showed that silica gel significantly increases the Dukstyna clay pozzolanic activity, while growing temperature of thermal treatment (600-860˚C) had a negative effect for ability to bind CaO. Pozzolanic material with high pozzolanic activity was synthesized at 700˚C for 1h from the optional composition mixture. In addition, F^- ions fully were bound into thermal stable compounds and environmental pollution by volatile fluorides was avoided when a sufficient content of carbonates was in the system.

The synthesis products were characterized by pozzolanic activity, XRD, STA, FT-IR analysis and measurements by F^- ions selective electrode. Therefore, the influence of synthesized pozzolana on initial hydration process of cement samples with 5, 15 and 25 wt.% pozzolana additive was assessed by calorimetric analysis method.

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Heat evolution during hydration of $2CaO \cdot SiO_2$ polymorphs

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Low-energy belite β-$2CaO \cdot SiO_2$ (or β-C_2S) cements could contribute to cement industry's efforts to reduce CO_2 emissions and save energy. The main way of producing belite is solid state sintering at 1300 – 1450 °C [1]. More advanced method consists of two–stage process: hydrothermal synthesis of di-calcium silicate hydrate α-$Ca_2[HSiO_4](OH)$ (or α-C_2SH) and its thermal treatment at 500 – 900 °C [2]. However, obtaining of pure α-C_2SH is complicated [3]. In addition, this precursor might transform in few C_2S polymorphs during its thermal treatment at 500 – 1000 °C, including α, α'$_H$, α'$_L$, χ, β and γ. These calcium silicates exhibit different hydraulic activity which greatly affects their binding properties [4].

α-C_2SH and its mixture with killalaite $Ca_3([HSi_2O_7](OH)$ were synthesized under hydrothermal conditions (molar ratio of mixture CaO/SiO_2 = 2.0, duration of the isothermal curing at 200 °C – 4 to 12 h) from industrial lime (free CaO = 87.4 %), quartz sand (SiO_2 = 98.5 %) and NaOH solution. The formation of β-C_2S and other C_2S polymorphs during thermal treatment of synthetic calcium silicate hydrates in the temperature range of 450 – 1000 °C was examined and explained in detail. In addition, the dependence of the burned products mineral composition on their hydraulic activity was determined. The synthesis and calcination products were examined by XRD, STA, FT-IR and SEM analysis. Calorimetric investigations were conducted within 72 h by using TAM Air III calorimeter.

α-C_2SH transforms to dellaite $Ca_6(SiO_4)(Si_2O_7(OH)_2$ and x-C_2S already at 450 °C. Dellaite decomposes, the amount of x-C_2S increases and β-C_2S starts forming at 600 °C. Further increase of the temperature results in a gradual decrease of x-C_2S amount and increase in the amount of both β-C_2S and α'$_L$-C_2S (latter starts forming at 800 °C). It was determined that heat release during the hydration varies for the compounds obtained at different temperatures. Heat flow values of the main hydration reaction and total heat release exceed 3.1 mW g^{-1} and 140 J g^{-1} in the case of the samples treated thermally at 450 and 500 °C. Products obtained at higher temperature display lower hydraulic activity: total heat release decreases to 110 and 10 J g^{-1} for the products burned at 600 and 900 °C accordingly.

In the mixtures of α-C_2SH and killalaite, latter compound remains stable until 700 °C. In this case dellaite decomposes slower during the thermal treatment. As a result, no heat flow increase indicating the main hydration reaction was observed in the curves and the total heat release was determined to be 30 % lower. Therefore, killalaite formed during the hydrothermal synthesis has a negative influence on the hydraulic activity of the thermally treated mixtures.

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Thermal, structural and mechanical analysis of polymer/clay nanocomposites with controlled degradation

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The use of fillers in the form of nanoscale particles for the enhancement of polymer properties has been shown to be particularly efficient, especially for reinforcement purposes in polymer matrix nanocomposites (PCNs) [1]. In cases of applications where adequate degradability is an additional consideration, the limited release of water into the bulk of the polymer matrix must be controlled; this promotes the hydrolysis process [2]. This promotion can be decelerated through the presence of certain nanoparticles such as clays, silica, or carbon nanotubes, which are successfully used as reinforcements of the polymer matrix to enhance its mechanical properties. On the other hand, the use of e.g. the same nanoscale clay fillers in small amounts with low %wt values may also accelerate the degradation time of PCNs [3], though an improvement in mechanical properties is still obtained. The latter feature is desirable from the point of view of the food packaging industry as well as the waste management of plastic materials and can be ensured by the use of e.g. smectite clays, such as standard and surface-modified montmorillonite. These clay nanofillers are valuable minerals, widely used in many industrial applications because of their high aspect ratio, plate morphology, natural abundance and low cost [4].

The aim of this study was to investigate the influence of the addition of clay on crystallisation, glass transition and melting temperature during the degradation process of polylactide nanocomposites filled with a small amount of smectite clay (3 to 10 wt%), modified with organic quaternary ammonium salt (QAS) for better compatibility with the polymer matrix. The resulting thermal, structural and mechanical properties of the obtained nanocomposites were compared to those of neat polylactide.

The degradation process of the materials was examined during immersion in distilled water at 80°C for 60 days using Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). Macro- and microscopic changes were also monitored and mechanical properties tested prior to degradation to evaluate the capability of the modified clay filler to reinforce the polymer and enhance elastic modulus, mechanical strength and Brinell hardness.

The influence of the modified smectite filler on the thermal, mechanical and structural properties of the nanocomposites during degradation and its dependence on filler content were discussed and confirmed in the study.

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Influence of thermal treatment conditions on efficiency of PFA/MCM-48 composite and CMK-1 carbon replica in adsorption of volatile organic compounds

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High surface area, ordered pore system and surface properties make MCM-48 mesoporous sieves to be ideal adsorbents in removal of volatile organic compounds (VOCs). Furthermore, the adsorption capacities of these materials can be easily improved by an appropriate surface modification. Mesoporous CMK-1 carbon, which is an inverse replica of MCM-48 silica template, also exhibits excellent adsorption properties with respect to the elimination of various types of inorganic and organic contaminants [1,2]. The aim of the presented study was to investigate properties of PFA/MCM-48 and CMK-1 materials, which were prepared by carbonization of poly(furfuryl alcohol) at various temperatures. The obtained materials were tested as adsorbents of volatile organic compounds (VOCs).

The MCM-48 silica was synthesized using the soft-templating method in the presence of alcohol (used as a co-solvent). Hexadecyltrimethylammonium chloride was used as a structure-directing agent. The organic template was removed by calcination at 823 K in air. The PFA/MCM-48 composite and CMK-1 carbon replica was synthesized using the hard-templating method with poly(furfuryl alcohol) as a carbon source, which was deposited in the pore system of MCM-48 sieve by polycondensation of furfuryl alcohol performed in an aqueous suspension of silica template. The intended mass ratios of poly(furfuryl alcohol)/mesoporous silica were 0.10 and 1.25 for the composite and the replica, respectively. The resulting PFA/MCM-48 composites were subjected to a thermal treatment at temperature from the range of 523-1323 K under inert atmosphere. In the case of replica, the silica template was then etched using a sodium hydroxide solution. To characterize the synthesized samples X-ray powder diffraction (XRD), low-temperature nitrogen adsorption, X-ray photoelectron spectroscopy (XPS), thermogravimetry (TG) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) were used. Adsorption capacity of all materials was tested in the elimination of methyl ethyl ketone, isopropanol, heptane and toluene vapors.

The XRD results revealed that the materials characterized by the regular pore ordering were formed. Textural parameters (surface area, pore volume and pore size distribution), calculated based on the results of low-temperature adsorption of nitrogen measurements, proved the highly developed surface area, narrow pore size distribution and high pore volume. The determined adsorption capacities confirmed the high efficiency of the synthesized samples in the removal of VOCs. Carbonization at low temperatures enhanced the adsorption capacity of composite, while the carbon replicas showed a better performance after carbonizaton at higher temperatures. The role of the thermal treatment in the activation of surface was discussed.

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Thermoanalysis of composite coatings intended for direct laser-assisted electroless metallization

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The main aim of this work was to assess the ability of thermoanalitical methods to determine the surface activation properties of the coatings intended for laser-assisted electroless metallization. In this type of metallization technique the surface of polymer material have to be activated before immersing in electroless metallization bath. The activation may consist in compositional modification of polymer material and in laser irradiation. In this work coatings containing polyurethane resin, copper(I) oxide, copper(II) oxide, copper hydroxide and copper(II) acetylacetonate were laser irradiated and then electrolessly metallized. Usually, the surface activation properties are evaluated by means of scanning electron microscopy, energy-dispersive X-ray spectroscopy, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS) and optical imaging. In this work an attempt to evaluate these properties based on thermogravimetric measurements was proposed.

Keywords: polymer coating, laser modification, electroless metallization, thermoanalysis

Structure and properties of aluminium-magnesium casting alloys after heat treatment

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Due to the fact that the forming of the microstructure depends on the specific of the casting method, which directly affects further mechanical and physical properties of the material, it is important to understand how to control the microstructure of the cast in order to understand changes that taking place during the crystallization process. For evaluating the metallurgical quality of the liquid metal before casting the thermal-derivative analysis technique has been used for a long time, in both ferrous and nonferrous industries casting. The Universal Metallurgical Simulator and Analyzer platform is a rapid, sensitive, and affordable method of determining a wide range of solidification features. The work focuses on the thermal analysis and heat treatment of aluminum alloys. The liquidus and solidus temperatures, dendrite coherency point DCP and linear expansion coefficient are then characterized. The research show that the UMSA platform allows efficient determination and calculation of thermal parameters. The influence of the heat treatment on structure and properties of aluminium castings has been determined as well. Heat treatment was carried out to improve the mechanical properties of aluminium alloys. Based on findings above the influence of microstructure on properties of the alloys are discussed.

Thermal properties of flexible polyurethane foams with carbon nanotubes addition

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Flexible polyurethane foams (FPFs) are polymer materials with a large number of applications in daily life. They are used mainly in upholstered chairs, mattresses, automotive and packing, due to their low density and wide range of physical and mechanical properties, which can be controlled during production process [1-3]. FPFs are highly flammable materials. The factors which further increases flammability of FPFs are their porous and open-cell structure. It provides a serious fire hazard and it is extremely dangerous in case of fire because of toxic fumes evolved during combustion. For this reason foams used especially in furniture industry are required to fulfill many safety standards in order to provide health security for people [4]. Therefore, there is a large need for studies in this area. FPFs can be modified by the addition of flame retardants and other fillers, which can improve thermal stability of FPFs. Recently, some research has been carried out regarding the use of carbon nanotubes (CNTs) as a method of modification of some properties of FPFs [5,6], so it was decided to assess thermal properties of FPFs modified by the addition of this filler.

In the present work FPFs with the addition of 0.05 wt %, 0.15 wt% and 0.25 wt% of CNTs (Nanocyl) were examined. The mixture of polyol and carbon nanotubes were prepared by using a three-roll mill in order to obtain the best dispersion of CNTs in FPFs. Foams tested in this study were produced in Ciech Pianki S.A. The characterization of thermal properties of the foams were carried out using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Moreover linear flammability test were done to assess flammability of these foams. Results obtained in these studies show that the addition of carbon nanotubes to FPF leads to improve their thermal stability and fire resistance to a small extent, but it could be a base to form a multicomponent system with improved thermal stability and fire resistance.

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Thermal analysis on $C_6H_{10}Ge_2O_7$ – doped MgB_2 superconductor

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MgB_2 is a promising practical superconductor [1], due to its lightness, low price, wide availability and interesting physics. Most of the metalloid elements or their compounds have been added to MgB_2. The most intensively studied additions are Si and, especially, SiC [2]. The $C_6H_{10}Ge_2O_7$ addition to MgB_2, obtained by *ex-situ* spark plasma sintering, significantly enhances the critical current density J_c in high magnetic fields [3].

Thermal analysis (at 10 °C/min heating rate) was chosen to observe the thermodynamic transitions between 20 and 960 °C using pure argon, and was done by two methods (DSC between 20-600 °C, and TG-DTA between 20-960 °C). Samples were powder mixtures of 97% mol. MgB_2 and 3% mol. propagermaniu.

Differential scanning calorimetry (DSC) during heating up to 600 °C has shown the propagermaniu transformation to an amorphous state accompanied by weight loss. The MgB_2 component keeps its integrity. At higher temperatures, partial decomposition of MgB_2 phase was noticed. In these samples crystalline Ge, Mg and MgO and MgB_4 formed. Mg reacts with Ge and forms Mg_2Ge.

Detailed thermal analysis is supported by measurements of XRD and FTIR analysis.

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Green parts thermal debinding for lightweight metallic foams

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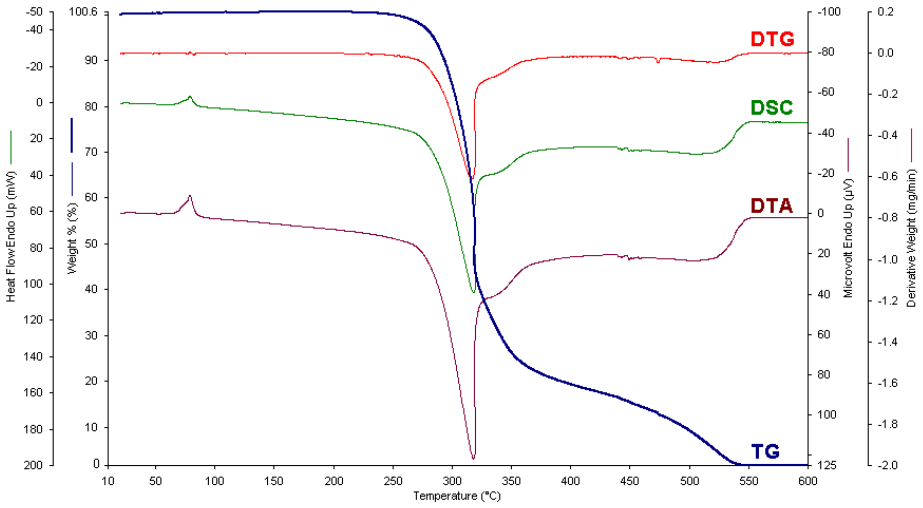
The light weighting continues to represent the advanced car concept design, able to meet new standard by metallic foams incorporation into the car structures, for relevant mass and cost savings [1]. The complexity of the automotive strength components requires advanced molding technologies and the medium-pressure injection molding (MEDPIMOLD) provides technical and economical advantages (max. pressure 5 MPa, max. injection temperature 120 °C) in comparison with the classic injection molding (at 60-100 MPa respectively 220-250 °C).

The raw material to be injected is represented by the mixture (feedstock) between the wax-based binder system (40-60 % mass.) and the aluminium alloy (ALUMIX 123) powder particles (balance). The binder system is made of paraffin, palm and bees waxes, ethylene vinyl acetate and stearic acid. The foaming effect is generated by the addition of calcium carbonate and ammonium bicarbonate as foaming agents.

The green parts obtained after the feedstock injection were submitted to the thermal debinding in order to remove the binders and the brown parts obtained will pass to the sintering treatment. The aim of our research was to study the influence of the thermal debinding parameters (temperature and dwell time) on the thermophysical and micro/macro-structural properties of the brown parts, monitored by thermal analysis (TA), Fourier transform infrared spectroscopy (FTIR), optical microscopy and mechanical tests.



In this abstract we present only thermoanalytical curves of thermal decomposition of one of binders: palm wax.

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Thermal studies on iron-carbon based nanoparticles synthesized by laser pyrolysis using iron-pentacarbonyl and acrylic acid vapours as reactive mixture

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Iron/carbon/polymer nanoparticles have been synthesized with laser pyrolysis technique. Iron pentacarbonyl vapours, acrylic acid (AAC) vapours, ethylene combined with an inert and or reducing (Ar+ H_2) atmosphere was employed. Ethylene was used as laser sensitizer and as carrier flow for iron pentacarbonyl vapours and an Ar or H_2 flow was used as carrier gas for AAC vapours. The operating variables were: the ethylene flow, the AAC carrier gas flow, the pressure in the reactive chamber and the laser power. In determined conditions composite core- shell nanoparticles has been synthesized: iron based core with a mixture of amorphous carbon and polymeric (PAAC) shell. In these conditions, nanoparticles with narrow size distributions and particles with about 8 to 13 nm mean diameters and the shell around 2-3 nm thickness were obtained. Some as prepared samples were also thermally treated at: 200, 350, 450 ^{0}C for 2 hours in high vacuum. The crystalline structures and elemental compositions of both as synthesized and treated samples have been investigated by XRD and EDS analysis. Also the polymeric/ amorphous carbon nature of the shell was established using TGA, FTIR and TEM investigations. The thermal treated sample revealed enhanced crystallinity and a phases mixture of iron carbide metallic iron (α phase) and iron oxide (Fe_3O_4/ γ Fe_2O_3).

Thermal investigation of organo-modified Mg- Al and Zn-Al layered double hydroxides

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Organic-inorganic hybrid assemblies, due to their versatile physicochemical properties, received much attention in view of their potential applications in different field such as catalysis, biomedicine, water purification, anticorrosive coating etc. Layered double hydroxides (LDHs) consists of layers, containing the hydroxides of different kinds of metal cations and possessing an overall positive charge, which is balanced by intercalation of anions in the hydrated interlayer space. The anionic exchange capability of LDHs can be utilized to incorporate organic anions into the interlayer space for preparing organo-modified LDHs converting a hydrophilic surface to hydrophobic one. We performed a comparative study of the intercalation of dodecyl sulfate anion (DS) in MgAl and ZnAl based LDHs. The pristine MgAl and ZnAl-LDH powders were prepared via co precipitation under low superasaturation conditions (Mg/Al and Zn/Al molar ratios = 2.5). The organo- modified -LDHs were prepared using two methods: direct coprecipitation and, reconstruction via the „memory effect". The as prepared samples were fully characterized through X-ray diffraction, chemical analysis, total carbon content (TOC and TIC), infrared spectroscopy (FTIR and DRIFTS). The thermal investigation (TGA, DTG) results were corroborated with the structural and spectral measurements. The results reveal a high thermal stability for the MgAl based LDHs and the partial DS intercalation for DS-ZnAl LDH prepared via reconstruction method.

Zinc electrodeposition from diluted aqueous solution. Effect of temperature and current density

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The pollution caused by zinc discharges from hot-dip galvanizing process gives rise to an environmental problem. Therefore zinc can be selectively separated by an anion exchange resin [1]. The solution obtained after the resin regeneration can be used for zinc recovery by electrodeposition.

The objective of this work was to determine the best conditions for minimizing energy consumption in the case of zinc electrodeposition. The effect of temperature (25 - 65ºC) and current density (40 - 80 mA/cm^2) was investigated. The cathode current efficiency was evaluated by weight measurement method. The current efficiencies obtained on a brass rotating cylinder electrode were between 85 % and 95% at different temperatures and current densities. The experimental results reveal that the increase of current density and temperature decreases the current efficiency. Considerably high current efficiencies (91 - 95%) were obtained at 25ºC and different current densities, with energy consumptions of 1.58 - 1.94 kWh/kg Zn. ***Scanning electron microscopy*** and optical microscopy were employed to study the morphologies of the obtained deposits. For low current densities, the zinc deposit presents a hexagonal-like crystalline shape with a strict layer-by-layer flat platelet structure on the brass surface [2].

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Nanostructured AgCu system at repeated melting - structure and thermal behaviour

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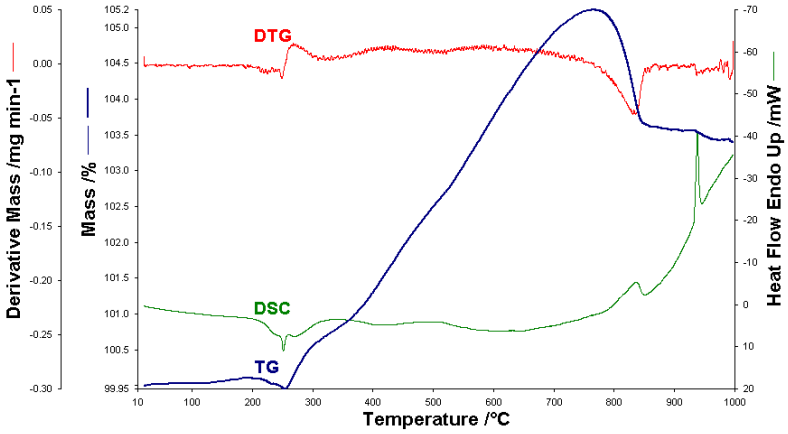
For few decades, the Ag-Cu materials system gained a special interest for advanced applications in various sectors. Extensive research has been done on AgCu based nanomaterials that are considered as part of new materials class with promising performance in the field of nanotechnology [1, 2].



The thermal behavior (Figure) of the eutectic powder particles mixture Ag-28% Cu (wt.) represents the aim of this research. This comportment is studied from the point of view the structural changes induced to the powder mixture processing by the wet mechanical alloying (WMA) technique. After 80 hours of WMA in ethylene glycol aqueous solution and argon atmosphere, the initial powder mixture becomes nanostructured composite particles, with bimetallic AgCu matrix reinforced by in-situ processed Cu_2O. The particle size distribution, depicted by laser diffraction technique, reveals the nanometric range of the composite particles between 60 – 80 nm. The phase identification, quantitative analysis as well as crystallite size measurements by XRD confirm the nanostructured feature of the bimetallic matrix, acknowledged by SEM with EDX and FIB, as well as the reinforcing components synthesis during the WMA process. Two successive melting have been developed to point out the increased melting point in range of 928.00-946.10 °C. The thermal analysis, developed in argon atmosphere, highlights the thermal effects of AgCu/Cu_2O nanoparticles generated by argon adsorbtion / desorbtion from the powders surface.

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Thermal aging effects on wood-plastic composite expansivity

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Wood reinforced thermoplastics were being developed initially accounting a practical issue arose from large residues during wood processing. Nowadays, these types of materials find niches in many practical applications, including structural and non-structural designs. Acknowledging the large amount of published work worldwide, one might size the area of subjects on ageing conditioning and consequently, property changes of composite architectures [1-2]. In addition, noteworthy are the authors' preference to debate mostly on the mechanical performance of their manufactured specimens, either environmentally conditioned or not, proven practical reasons [3].

The objective of the work was to evaluate the expansivity of wood-plastic composites subjected prior to a modified thermal aging process (ASTM D 3045:2010). Specimens having 10% and 40% wt. % of various species of wood fillers, individually (e.g. beech, pine, oak, sapele, etc.) or agglomerated, were mixed with poly-polyethylene (PP) in the absence of any additive. A modified thermal aging process was being further employed to size specimens' changes regarding their thermal expansion property and their sensitivity to degradation by heat exposure.

In general, test results showed that both filler content and wood species, as well as supplementary environmental conditioning influence the expansivity and derived linear coefficient of thermal expansion of thermoplastic reinforced composites. Close monitoring on the approached issue is of practical importance for real life applications.

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About Thermostability of Biocompatible Ti-Zr-Ta-Si Amorphous Alloys

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The present paper is focus on analysis of structural changes during heating of an amorphous alloy belonging to Ti-Zr-Ta-Si. Special attention was given to thermodynamics and mechanism of crystallization, to determine some aspects related to formation of crystalline phases. Amorphous ribbons with atomic composition $Ti_{42}Zr_{40}Ta_3Si_{15}$ were fabricated by mean ultra-rapid melt solidification. Resulting amorphous biomaterial is absolutely free of any toxic additions and is used as precursor for milled powder that could be hot pressed in porous bulk components with compression strength of approximately Rm = 350 MPa and calculated Young's modulus close to cortical bone.

Since preservation of amorphous structure during consolidation of amorphous powder is of utmost importance for resulting mechanical properties and biomechanical compatibility to human bone, differential scanning calorimetry and X-rays diffraction (XRD) were used to determine crystallization temperature of this alloy. Curves of differential thermal analysis for heating rates ranging between 1ºC/minute and 20 ºC/minute were used to determine activation energy of crystallization. Optimization of hot pressing parameters at temperature level of T = 525°C, pressure of p = 20 kN and pressing time of 3 minutes, allowed fabrication Ti-based amorphous alloy with high compression strength of approximately Rm = 350 MPa and calculated Young's modulus close to cortical bone of about E=55 GPa, which recommends it for orthopedic and dentistry applications.

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Thermal stability of the solvothermal synthesized $MnFe_2O_4$ nanopowder

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$MnFe_2O_4$ is a magnetic ferrite with cubic spinel structure extensively used in various technological applications. Several techniques have been reported for the synthesis of $MnFe_2O_4$ nanoparticles, such as solid-phase reactions, mechanical ball-milling, thermal decomposition, hydrothermal method, coprecipitation, combustion and microemulsion method [1,2]. Solvothermal method represents a suitable synthesis method for manganese ferrite, due to the possibility to obtain ferrite particles with tailored properties. The current study introduces an original, simple solvothermal method to synthesize magnetic $MnFe_2O_4$ nanopowder, using Mn(II) and Fe(III) chlorides as precursors, 1, 2-propanediol as solvent and potassium hydroxide as precipitant. This method was successfully used previously for the synthesis of Fe_3O_4/γ-Fe_2O_3 nanopowders [3]. The synthesis of $MnFe_2O_4$ nanopowders was performed at 200 °C for 12 hours.

Thermal behaviour of the as-synthesized powder (200 ^oC) and of the powders annealed at 400 °C and 500°C was studied using a Netzsch STA 449C instrument, in air and nitrogen atmosphere at a flow rate of 20 mL min^{-1}. The TG/DSC curves were recorded in the range of 25-1000°C with a heating rate of 10K min^{-1}, using alumina crucibles. Thermal analysis in air evidenced the exothermic process assigned to the transition of $MnFe_2O_4$ to $MnFeO_3$, with mass gain at around 600°C. This process was significantly reduced when the thermal curves have been registered in nitrogen atmosphere. The transition was evidenced also in case of the manganese ferrite powder annealed at 400°C, but was completely absent in case of the powder annealed at 500°C, evidencing that the oxidation of manganese had already occurred.

The phase composition of the samples was determined by XRD, using a Rigaku Ultima IV diffractometer ($Cu_{K\alpha}$ radiation). The spinelic ferrite was evidenced in the XRD pattern of the powders annealed at 200 °C and 400 °C, while in the powders annealed at 500 °C the spinelic phase was completely absent; the only crystalline phase was in this case $Mn_{0.176}Fe_{1.824}O_3$ containing Mn(III).

The annealing of the powder at 1000^oC led to $(Fe_{0.42}Mn_{0.58})_2O_3$ as single crystalline phase. FTIR spectra were carried out using a Shimadzu Prestige-21 spectrometer in the range 400-4000 cm^{-1}, using KBr pellets and resolution of 4 cm^{-1}. The morphology of the nanopowders was investigating by scanning electron microscopy (SEM), using a FEI Quanta FEG 250 microscope. SEM images evidenced the formation of very fine spherical particles (d < 15 nm) of manganese ferrite.

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Repair welding of the martensitic steels and the influence of the thermal field on the endurance to cavitation erosion

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The aim of this work is to investigate the influence of the thermal field in repairing by welding the components of martensitic steel for hydraulic turbines, because the non-uniform distribution of temperatures is influenced by the energy of the thermal source, by the thermo-physical properties of the raw material [1] and by the heat loss in the environment.

Four situations have been identified while manufacturing the components of the hydraulic turbines of martensitic steel or while repairing them for their use in the hydraulic stations. These situations have resulted in the design of different welding technologies which are meant to satisfy the actual conditions of each situation [2].

Also, this paper presents the results that describe the influence of the thermal field on welding components, by modelling and simulation, as well as by analytic determination.

The experimental determination of the temperature distribution in welded joints confirms the results obtained from finite element analysis, which means that the finite element numeric modelling and simulation of heat continuous transfer [3] and the welding process are useful tools in determining temperature values, their variation in different areas of the welded joint or the estimation of the size for the weld bath and for the thermal influence zone.

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Synthesis and characterization potassium niobate ($KNbO_3$) nanopowder obtained by sol-gel method

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Recently, there is an increasing demand for piezoelectrics ceramics in order to achieve alternative lead free solutions and in this context the perovskite ferroelectric $KNbO_3$ represent a suitable candidate.

In this work, we report the synthesis and the study of morfo- structural properties of potasium niobate $KNbO_3$.

Nanopowders of $KNbO_3$ have been successfully obtained by sol-gel method starting from $C_4H_4NNbO_9$. H_2O (ammonium niobate (V) oxalate hydrate), KOH (potasium hydroxide) solution and citric acid (used as a chelating agent). The samples were characterised by X-Ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR).

The thermal behaviour of the $KNbO_3$ compound was studied by thermogravimetric analysis at different temperatures and atmospheres. Moreover, in parallel different thermal treatments at 300, 600 and 800°C were made in order to study the thermal stability of the obtained samples.

Acknowledge:
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Synthesis and morpho-structural characterization of $NaTaO_3$ nanomaterials obtained by a fast synthesis method

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In recent years the preparation of nanomaterials has been of major interest due to their potential applications in the industry, in photocatalyst for the elimination of pollutants, in catalysis for CO_2 reduction and in environmental sciences for the production of hydrogen from water splitting [1-3].

A fast method for the preparation of $NaTaO_3$ nanomaterials is ultrasonic method with immersed sonotrode in the reaction medium. In order to remove organic material and increase the crystallinity of products, this powder was annealed at different temperatures.

The as-prepared samples were characterized by X-ray diffraction (XRD), thermal gravimetric analysis (TGA), surface area analysis (BET) and scanning electron microscopy (SEM/EDX). The structural characterization by X-ray powder diffraction revealed that heat treated materials at 600 ºC are well crystallized, the average size of the crystallites being approximately 60 nm, as confirmed by scanning electron microscopy (SEM). It was found that the BET surface area decreases with temperature increasing and the thermal analysis (TG/DTG/HF) has revealed five transformations process of $NaTaO_3$.

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Iron oxalate coordination compound – precursor of α-Fe_2O_3 nanorods

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Synthesis of architectural one dimensional iron oxides is challenging research topic because of their shape-dependent properties. Such structures have good electron transport abilities, which minimalize the electron-hole recombination, making possible the use of the materials as efficient photocatalyst.

As precursor for 1-D α-Fe_2O_3 nanorods was used a novel iron oxalate coordination compound, namely $[Fe_2(C_2O_4)_3(OH_2)_4]$. The precursor was characterized in terms of composition, morphology and thermoreactivity. It is noteworthy that the thermal conversion of the coordination compound takes place through an iron (II) intermediate and γ-Fe_2O_3.

The final oxide, was tested in the photocatalytical degradation of a dye, and as antimicrobian agent against a broad spectrum of bacterial strains, both in planktonic and biofilm form.

Aknowledgments

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Thermal decomposition of polynuclear coordination compounds: a versatile viable route toward mixed oxides

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The synthesis of materials *via* thermal decomposition of single source precursors such as coordination compounds represents a synthetic methodology, which is unfortunately too little investigated.

It is well known that the precursor through its composition and architecture, and implicit its subsequently thermal processing plays a decisive role in end products properties, costs and applications. Oxalates represents one of the most resourceful ligands due to their flexible coordination ability and low decomposition temperature. The first allows the precursors to adopt a multitude of structures that control the oxides morphology, while the second lets to oxides with high surface areas and low sizes.

Herein we present the thermoreactivity of a series of polynuclear coordination compounds precursors of spinelic ferrites, obtained by a new synthetic approach that contain oxalate as ligand. The thermal behaviour of the compounds depends strongly on the bivalent cation. The final oxides were MFe_2O_4 ferrites (M = Zn, Mg, Cu) with of surface areas (50 m^2/g) and interesting magnetic properties.

Aknowledgments:
„This work was partially supported by the strategic grant POSDRU/159/1.5/S/137070 (2014) of the Ministry of National Education, Romania, co-financed by the European Social Fund – Investing in People, within the Sectoral Operational Programme Human Resources Development 2007-2013”.

Crystallization of Ce^{3+} doped glass in the system Y_2O_3-Al_2O_3 and the effect of thermal treatment on the luminescence properties

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Yttrium aluminium garnet ($Y_3Al_5O_{12}$, YAG) has been recognized as one of the best phosphor host materials for rare earth ions because of its optical transparency in the wavelength range from ultraviolet to infrared [1]. The Y^{3+} and Al^{3+} ions can be, to a certain extent, substituted by many kinds of cations with different sizes and valence [2]. When substituted with a few percent of the activator ion Ce^{3+}, $Y_3Al_5O_{12}$ is a luminescent material that has nearly ideal photoluminescence properties for excitation by a blue solid-state light source; YAG:Ce is therefore a phosphor with high quantum efficiency, excellent chemical and thermal stability, high mechanical strength and excellent optical properties [3]. Hence, developing a simple and reliable synthetic method for phosphor particles with controlled morphology and structure is still a task of particular importance. One of the possible methods involves preparation of the polycrystalline material from glass by controlled crystallization.

In the present work we report the study on the preparation and characterization of the Ce^{3+} doped glass, Y40A60Ce0.5, with the composition of 76.67 mol.% (~60 wt.%) Al_2O_3, 23.08 mol.% (~40 wt.%) Y_2O_3 and 0.25 mol.% Ce_2O_3. The glass was prepared in the form of glass microbeads by flame-spraying technique and characterized by optical microscopy, SEM and XRD. The thermal properties of the prepared glass were studied by DSC; the glass transition temperature (T_g), onset of crystallization temperature (T_x), and the temperature at maxima of the exothermic crystallization peaks (T_{p1}, T_{p2}) were estimated from the DSC curve. The DSC record revealed two exothermic effects observed at the peak maxima temperatures 936 and 1000 °C, respectively, corresponding to crystallization of YAG phase as confirmed by XRD and high temperature XRD experiment. The crystallization kinetics was evaluated on the basis of the JMA model. Based on the phase diagram data, crystallization of the second phase, α-Al_2O_3, was also expected in the studied system: however, the crystallization of α-Al_2O_3 was observed only in the samples heat-treated at temperatures exceeding 1300 °C. Based on the results of thermal properties studies by DSC, the glass was heat-treated at several temperatures (corresponding to characteristic temperatures estimated from the DSC curve) for 3h and the effect of the thermal treatment on luminescence (PL) intensity was studied in detail. The emission PL intensity was found to increase with the heat-treatment temperature, reaching the maximum for the sample annealed at 1200 °C.

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The parametrization of thermal expansion of illite based ceramic body in dehydroxylation region during heating

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Illite is a clay mineral very often occurring in the input materials for producing the traditional ceramics [1]. To know how the dehydroxylation of illite influences the dimensional changes during heating, it is helpful to design an optimal firing regime. Furthermore, the underlying mechanisms of the process can be determined when a convenient kinetic method is used.

The basic material for this study is an illitic clay with over 70 % of mineral illite. This material originates from Füzérradvány in northern Hungary. It was milled to obtain particles of size below 100 μm and mixed with distilled water to create a plastic mass suitable for extrusion. Extruded cylindrical samples were dried freely in laboratory. Afterwards, the diameter of the samples was reduced to ~7 mm, and 20 mm pieces were cut for thermodilatometric measurements. We used a contact push-rod dilatometer Netzsch DIL 402 C with 40 ml/min N_2 flow. The heating rates were 2, 3, 5, 7, 10, and 15 °C/min in the temperature region from 25 to 900 °C.

We used a non-linear model fitting technique to find the kinetic parameters and the most convenient kinetic model. The dehydroxylation of illite occurs in two consecutive steps, and this fact has been taken into account during designing the system of differential equations describing the dehydroxylation process. The residual squares sum was used as an objective function in a parameter optimization procedure that employed the simplex method of Nelder and Mead.

The best model for the first step of the dehydroxylation is a second-order reaction with the apparent activation energy of 153.3 kJ/mol and preexponential factor 7.24×10^6 s^{-1}. The best model for second reaction step is a first-order reaction with the activation energy of 273.1 kJ/mol and preexponential factor 2.29×10^{14} s^{-1}, but, according to Fisher's test, some other models for the second step fit experimental data equally well with similar values of the activation energy and preexponential factor.

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Simulation of phase transformation during heat treatment of Ti-6Al-4V alloy

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In this work, simulation of phase transformation processes during cooling of Ti-6Al-4V alloy is presented. Finite element analysis was employed for discretization of continua. In the calculation, the Newmark time integration method was used and thermal analysis was considered as transient. Since microstructure is composed of various phases, the linear mixed model of material properties was assumed. The Johnson-Mehl-Avrami-Kolmogorov (JMAK) model was used for simulation of anisothermal diffusion controlled metallurgical changes whereas Koistinen-Marburger law was used in simulation of diffusionless (non-isothermal) transformation. The results numerical analysis agree well with the experimental data.

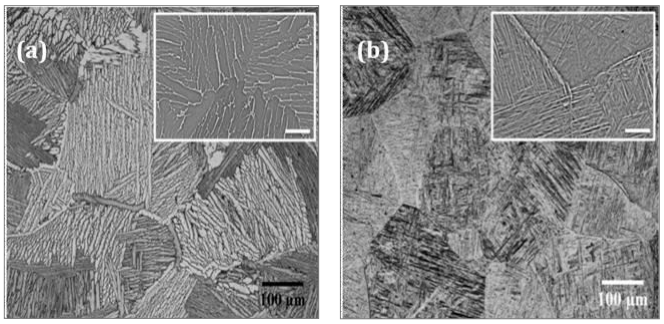

Figure 1 Optical micrographs of heat treated samples at 1040°C for 1h followed by (a) furnace and (b) water cooling in the XY direction.

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DC CONDUCTIVITY OF ILLITE AND KAOLIN AFTER VARIOUS FIRINGS

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Temperature dependences of the DC conductivity of illitic clay (80 % of illite) and kaolin (90 % of kaolinite) were measured in the temperature range of 20 °C – 450 °C, on green samples and on samples heated to 400 °C – 450 °C (Fig. 1, Fig. 2). The release of the physically bound water from illite green sample takes place in 3 stages - at 72 °C, 186 °C, and 298 °C. These three stages were confirmed also by DTG. The release of the physically bound water of green kaolin samples takes place in two stages – at 60 °C and 300 °C. In both materials, after heating to 400 °C, up to 220 °C, the dominant charge carriers are H^+ and OH^- ions with conduction activation energy (CAE) of 0.31±0.02 eV for illite and 0.32±0.02 eV for kaolin. At higher temperatures alkali metal ions, especially K^+ and Na^+, contribute to the DC conductivity with the CAE 1.12 eV for illite and 1.19 eV for kaolin. After heating to 450 °C, the DC conductivity of illite slightly increases and a higher CAE (1.22 eV) indicates that alkali metal ions are moving in a slightly more disordered structure, probably due to starting dehydroxylation at 450 °C. However the DC conductivity of kaolin is not changed after heating to 450 °C.

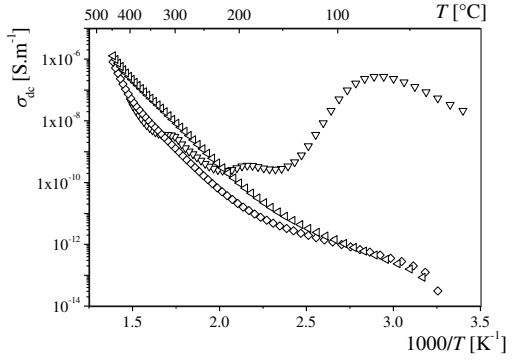

Fig. 1 - Temperature dependences of the DC conductivity of illite samples: green sample (▽), after heating to 400 °C (◇), after heating to 450 °C (◁)

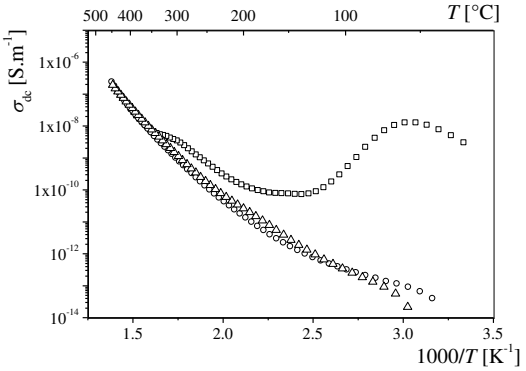

Fig. 2 – Temperature dependences of the DC conductivity of kaolin samples: green sample (□), after heating to 400 °C (○), and after heating to 450 °C (△).

The mechanism and products of hydration reaction in ternary blended Portland cement with metakaolin and blast furnace slag

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The development of ternary blended Portland cements using blast furnace slag (BFS) and metakaolin (MK) has taken growing importance nowadays [1-4]. It was proved that partial replacement of PC by BFS and MK could be perspective for construction materials in the future [2]. Both BFS and MK are being used very commonly as latent hydraulic and pozzolanic materials in mortar and concrete. They have showed influence in enhancing mechanical and durability properties of mortar and concrete [3]. The properties of BFS and MK as a pozzolanic materials have been reported previously [1,3]. The general scientific school is that BFS and MK react with CH in the presence of water to produce additional C-S-H products or C_4AH_{13}, C_2ASH_8 and C_3AH_6 [1-3]. Basing on calorimetric assessments, many studies have investigated the temperature dependence of the rate of hydration using different mathematical methods in order to elucidate the mechanism that governs a given reaction, and found that the temperature dependence can be described by an Arrhenius equation [4].

The present work has been undertaken to illustrate the role of metakaolin in the formation of ettringite during the hydration of Portland cement due the presence of gypsum. The course of hydration of two ternary blended cements PC-BFS-MK was studied at different temperatures 30°C, 40°C, 50°C and 60°C using conduction calorimeter, simultaneous TGA/DSC and X-ray powder diffraction. It was found out that the influence of supplementary materials on the hydration of Portland cement depends on temperatures. In the presence of calcium hydroxide and gypsum metakaolin has contributed to the formation ettringite at earlier period depending on mixture composition The kinetics of hydration reaction through activation energy values were established. High pozzolanic activity of MK can contribute to the increase of mechanical properties at earlier curing period, but it requires more water, that in return may lead to strength retrogression. Therefore, addition of BFS along with MK can improve flowability of fresh cement mixtures which is poorer due to presence of MK.

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Thermal curing of an epoxy-anhydride system modified with hyperbranched poly(ethylene imine)s with different terminal groups

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Epoxy resins are widely used in applications such as adhesives, coatings, electric laminates, encapsulation of semiconductor devices, matrix material for composites, structural components and cryogenic engineering because of their mechanical properties, adhesion and chemical resistance.

However, epoxy resins are inherently brittle due to their high cross-link density. To increase their toughness different modifiers such as rubber, thermoplastic and glass particles can be added, but they always limit the processability of the formulation. Hyperbranched polymers (HBP) are a new kind of polymers used as modifiers of epoxy resins to increase their toughness, but they maintain the processability of the formulation due to their highly branched dendritic structure, which is a key point in coatings applications [1-2].

In this paper, the influence of three hyperbranched poly(ethylene imine) polymers with different terminal groups (two of them with *t*-butyl terminal groups and the other one with phenyl groups) on the thermal curing of an epoxy-anhydride system has been studied. The synthetic procedure to prepare the polymeric modifiers is quite easy and it consists in reacting commercial poly(ethylene imine) with the corresponding isocyanate in chloroform solution at room temperature. The epoxy resin and the anhydride we selected are Epikote 828 and 4-methyl hexahydrophtalic anhydride, respectively. As initiator we have used N,N-dimethylbenzylamine [3]. The techniques employed in this study have been DSC (differential scanning calorimetry) and DMTA (dynamic mechanical thermal analysis). The kinetics of the thermal curing has been analyzed using isoconversional methods.

The addition of the hyperbranched polymers with *t*-butyl terminal groups hardly changes the thermal curing process of the epoxy-anhydride system, but if the poly(ethylene imine) with phenyl end-groups is added, the thermal curing of the system is decelerated.

In the systems studied, all the HBPs used decrease the glass transition temperature of the epoxy-anhydride system, acting therefore as plasticizers.

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Sequential UV/thermal processing of acrylate-epoxy clearcoats

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B-stage processing is a term used for one-pot thermosetting formulations that can be partially cured or pre-dried, after being applied to a substrate and then cured under heat and pressure. B-staging has processing advantages that can be exploited in assembly processes, especially the possibility of splitting the different steps of a process in a production line, in terms of time and location, thus helping to prevent manufacturing bottlenecks. However, in B-stage processing the pre-drying process has usually tight time and temperature constraints that make necessary a careful control to avoid over-drying leading to loss of properties such as adhesion and material waste. Alternative dual-curing procedures aim at eliminating the above drawbacks while keeping and even enhancing their processing advantages [1-3]. Further advantage comes from the possibility of tailoring the material structure and properties between both curing stages by changing the formulation composition. This represents a significant advantage over conventional B-stage, in which the material properties in the intermediate stage are kinetically controlled, depending on temperature/time and vitrification. This approach opens a new way for flexible processing, not just in terms of curing stageability but also in terms of the intermediate material characteristics (adhesion, flowing ability, rigidity,…). In addition, the latent character of the second curing stage ensures good storage stability between both curing stages.

In this work, the sequential UV/thermal processing of acrylate-epoxy clearcoats is studied. Mixtures of methacrylates/acrylates with different side chain and functionality, at least one of them bearing an epoxy group, are photocured to obtain a linear or cross-linked polymer that is subsequently post-cured at elevated temperatures to obtain the final cross-linked material. A combination of a radical photoinitiator and a cationic thermal latent initiator is used in order to permit sequential controlled curing. Different formulation compositions are examined in order to analyze the possibility of custom-tailoring the structure and properties between both curing stages and at the end of the process. The sequential UV-curing and thermal curing processes are studied with photoDSC, FTIR/ATR and DSC. The thermal-mechanical properties of the materials in the intermediate and final states are assessed with DMA, DSC and TGA. The potential application of this curing process is also illustrated.

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Thermal properties of calcium silicon oxynitride glasses

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Oxynitride glasses are a branch of high performance glasses, obtained by incorporation of nitrogen atoms into oxide glass network. [1-3]Oxynitride glasses have superior mechanical, rheological and optical properties as compared to their oxide glass counter partner [2-5]. Properties of these glasses can be tailored by changes in nitrogen content and additions of various alkaline-earth and or rare-earth elements. Ca- Si-O-N glasses containing high amount of nitrogen and modifiers have been prepared by melting the mixture of CaH_2, SiO_2 and Si_3N_4 powder in nitrogen atmosphere at 1600 – 1700°C. The glasses were characterized by X-ray powder diffraction, differential thermal analysis and scanning electron microscopy. The obtained glasses were found to be homogenous, and having colour opaque black[3]. These glasses show high values of glass transition temperature (1050°C), and crystallization temperatures ((1050°C) measured by differential thermal analysis. Generally the Ca-Si-O-N glasses thermal properties evolve approximately linearly with the nitrogen content. The viscosity increases significantly with the nitrogen content and reaches viscosity values close to reported values for rare-earth silica oxynitride glasses. The apparent viscosity activation energies are very high, ranging from 855 to 2170 kJ/mole. These nitrogen rich glasses can accordingly be classified as being both very refractory and very fragile.

Keywords: Oxynitride glass; Nitrogen content; Calcium content; thermal property; Glass transition temperature; Viscosity

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The Effect of Clay on Foaming and Mechanical Properties of Glass Foam Insulating Material

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Glass foam, which is insulator material, is produced from glass and foaming agents. Glass materials for this production are waste and used glass obtained from daily and industrial applications, generally. In addition, it is possible to produce novel glass for glass foam production. In terms of this, glass foam production is a type of glass recycling process for glasses. Glass material which softens at high temperatures allows releasing these gases from the body. In glass foam production, there are some parameters such as viscosity of glass during foaming process. If its viscosity is low, the gases obtained from decomposition of foaming agent can expose, suddenly, and gas bubbles and pores fall, otherwise, these gases can't expose because of high viscosity. Apart from glass, many different materials which vitrify have been investigated in the literature [1-3].

Clay is common raw material for many traditional ceramic products [4]; it is defined aluminium silicate mineral including chemically bonded water. The natural material clay exposes to some changes depending on increasing in temperature, between 25°C and 800°C, some compounds such as atmospheric water, carbon, organic materials, and sulphur burn off. Sintering temperature for clays are ranged from 900°C to 950°C depending on composition. Vitrification stage begins for clay above these temperatures. The melted materials promote further melting, as well as compacting and strengthening the clay body. This stage is known as mullite formation. It acts strengthening thanks to its high hardness and needle-like crystal structure. These crystals bring about interlocking and more strengthening. The basic theory of the current study bases on both foaming and mechanical properties of glass foam material.

In this study, the main composition was prepared by using soda lime glass and dolomite as a foaming agent, $CaMg(CO_3)_2$. The clay powder obtained commercially was mixed to the main composition, in different concentrations, varying from 10% to 30 wt.%. The mixtures were shaped by one axial pressing. The differential thermal analysis (DTA) was used for determination of glass transition temperature and the pellets were heated according to DTA results. Furthermore, heating microscopy was employed for high temperature behaviours of the mixtures. The study was characterized by scanning electron microscopy (SEM), X-ray diffraction analysis (XRD) and comprehensive strength test. The porosity and bulk density were measured for foaming capability of the mixtures. The results showed that clay addition has a positive role on mechanical properties of glass foam.

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The glass-ceramic sealant material obtained from basalt for SOFC

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The solid oxide fuel cells (SOFCs), which are electrochemical devices having green technology, produce electricity with a reaction of a fuel and air [1], these operate at elevated temperatures (700°C–900°C) with various fuels such as coal. Utilization of coal can play an important role in terms of power generation future, with much less environmentally harmful emissions than conventional coal combustion [2]. Because of this, utilization and spreading of SOFC are significant step to provide clean environment. There are a lot of studies about improvement of SOFC in the literature [3-4]. But, there are some problems about utilization of SOFC as a commercial product; one of these is sealant problem of SOFC systems. SOFC component interconnect materials connecting the cells for multiple cells is stainless steel, generally. It provides electrical connection between anodes of one individual cell to the cathode of another one, multiple SOFC are combined into high-performance cell stacks for power generation on a large scale. A sealant material is necessary to resist harsh environments and high operating temperatures of SOFC between metallic interconnect parts. In recent years, glass-ceramic systems have been investigated to provide required sealing performance for these [5]. Thermal compatibility between glass-ceramic sealant and interconnector is very important parameter; some phases forming in interface at high temperature can cause thermal mismatch effect. Especially, glass-ceramic systems including BaO and SrO oxides are suitable, but $BaCrO_4$ and $SrCrO_4$ phases forming with Cr in stainless steel interconnector bring about thermal mismatch [6].

In this study, volcanic rock basalt was used for glass-ceramic production as sealant material for SOFC. Crushed, milled and sieved basalt powders were modified by some additives. Modified mixture was melted in alumina crucible and cast into water and graphite mould. Thus, glass granules and bulk parts were produced. These granules were milled, and exposed to heating microscopy and differential thermal analysis (DTA). Some parameters such as glass transition and softening temperature were determined by these analyses. These powders were applied on the Crofer APU 22 interconnector material, and heat treatment was carried out. The interface characteristics between glass-ceramic layer and interconnector were investigated by using X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). The results showed that the glass-ceramic obtained from basalt has convenient effect for future of SOFC.

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Thermal analysis of AlMg1SiCu matrix composite materials reinforced with MWCNTs

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The present research is conducted to understand in more details the solidification pathway of the AlMg1SiCu based composites with multiwalled carbon nanotubes by a thermal derivative technique via one thermocouple thermal analysis method and dilatometry test. The liquidus and solidus temperatures, the dendrite coherency point DCP and linear expansion coefficient are characterized. AlMg1SiCu alloy reinforced with multi-walled carbon nanotubes (MWCNT) composites have been prepared by mechanical milling in the planetary mill up to 50 hrs [1]. The thermal analysis of melting and solidification cycles was carried out using the Universal Metallurgical Simulator and Analyser (UMSA). Analysis of powder compacts in the solid state was also made. Expansion of examined composite materials as a temperature function was measured by using DIL805A/D dilatometer. Changes of sample linear dimensions and the coefficient of linear thermal expansion and diagrams of this coefficient as a temperature function during heating and cooling cycle of AlMg1SiCu-based composites were registered. Microstructural evaluations were characterized by optical microscopy, X-ray diffraction, scanning and transmission electron microscopy. The experimental results prove that multi-walled carbon nanotubes react with aluminum alloy and form Al4C3 phases with needle shape. The reaction temperature for carbide formation depends on the milling time and heating rate during. The peak temperature of the reaction of carbon nanotubes and aluminum is found to depend on the heating rate during the continuous heating. This characterization will lead to a better understanding concerning the formation of cast microstructures and defects and will help to widen the application aluminium based composite.

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Formation of $SrTiO_3$ in mechanically activated $SrCO_3$ – TiO_2 system

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Strontium titanate ($SrTiO_3$) that has perovskite structure [1] takes attention because of its electrical, dielectric, piezoelectric, semiconducting, superconducting and optical properties [2]. $SrTiO_3$ could be fabricated by the solid state reaction between Sr carbonates or hydroxides and TiO_2. Before the annealing phase, oxide co-prepetition, sol-gel route, thermal decomposition of oxo-salts and hydrothermal methods could be applied as additional process for an intimate mixing to achieve homogenous starting powder [3].

In this study, mechanical activation process was used for intimate mixing as well as produce finely ground particles, increased surface area and improved chemical reactivity of materials. Strontium carbonate and TiO_2 powders were mixed at stoichiometric ratio of $SrTiO_3$ and followed by mechanical activation for 30 and 120 min.

Disappearing, intensity decrease and shifting of the XRD peaks realized with mechanical activation due to amorphization. Amorphization was also demonstrated by FT-IR analysis in where shift of band centres as well as decrement of transmittance related to CO_3 were observed. High temperature XRD analysis showed that 1300°C wasn't enough to form $SrTiO_3$ for non-activated mixture whereas structure only composed of $SrTiO_3$ at 1000°C for activated ones. The reason of this phenomenon was investigated by DTA-TG analysis. Tendency to lower temperature of the endothermic peaks with increment in mechanical activation time was detected and decomposition reaction was started as heating starts. The mass losses were detected as 21.36%, 20.23% and 19.76% at the end of the thermal analysis for non-activated, 30 min and 120 min respectively related decomposition may occurred during mechanical activation.

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Synthesis, characterization, thermodynamic properties and phase transitions of $CsMPO_4$ (M = Ni, Co, Mn) crystals

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Interest in β-tridymite structure type phosphates $CsMPO_4$ (M − divalent metal with a tetrahedral coordination), containing cesium in a high concentration and possessing chemical and radiation stability, is conditioned by an opportunity to use them as ceramic for ^{137}Cs γ-radiation sources of commercial and medical applications.

As it is known [1], cesium containing phosphates with a β-tridymite structure have four polymorphs with analogous frameworks and different unit cell symmetries (two monoclinic with space groups $P2_1$ and $P2_1/a$; and two orthorhombic with space groups $Pna2_1$ and $Pnma$). An increase in temperature is often accompanied by phase transitions with an increase in symmetry: $P2_1 \rightarrow P2_1/a \rightarrow Pna2_1 \rightarrow Pnma$; and the phase transformations between two monoclinic forms frequently occur below room temperature [2].

In the work the data of the thermodynamic properties for the crystalline phosphates $CsM^{II}PO_4$ (M^{II} = Ni, Co, Mn) with β-tridymite structure type are reported. The samples were synthesized by the co-precipitation method. The phase purity of the sample was checked by powder X-ray diffraction. The homogeneity and chemical composition of the sample were confirmed by electron microprobe analysis. The heat capacities of the phosphates were measured using adiabatic and differential scanning calorimetry in the temperature range 6–650 K. Phase transitions of phosphates $CsMPO_4$ (M = Ni, Co, Mn) were discovered. The temperature dependence of the heat capacity of crystalline $CsMnPO_4$ showed that for the phosphate two phase transitions were found at temperatures (6.9 and 127) K. They correspond to the order–disorder transition and the transition between monoclinic and orthorhombic modifications of $CsMnPO_4$, respectively. Three phase transitions were found at temperatures (311, 481 and 512) K for the $CsCoPO_4$ phosphate. They correspond to the transitions between monoclinic and orthorhombic modifications of $CsCoPO_4$ ($P2_1 \leftrightarrow P2_1/a$; $P2_1/a \leftrightarrow Pna2_1$; $Pna2_1 \leftrightarrow Pnma$). The investigation of samples by high-temperature X-ray powder diffraction and measurement of temperature dependence of the magnetic susceptibility of $CsMnPO_4$ crystalline phosphate allowed us to describe their nature. The transition functions (temperatures, enthalpies and entropies), $C^{\circ}_{p,m}/R$, $\Delta_0^T H^{\circ}_m/RT$, $\Delta_0^T S^{\circ}_m/R$ and Φ°_m/R were calculated over the range of T = (0 and 650) K from experimental data. Thermodynamic properties of all researched cesium containing β-tridymite structure type phosphates $CsM^{II}PO_4$ (M^{II} = Zn, Mg, Ni, Co, Mn), including literature data, were compared.

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Thermophysical properties of the complex phosphates $M_{0.5+x}Mg_xZr_{2-x}(PO_4)_3$ (M – Cd, Pb)

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Complex phosphates, containing zirconium and metals in oxidation state +2, belonging to $NaZr_2(PO_4)_3$ (NZP) type structure, are of particular research interest as materials with controlled (often, low) thermal expansion [1]. This property of NZP phosphates along with their high melting temperatures and chemical resistance makes them suitable for application as high-tech ceramics with thermal shock resistance.

The present study is devoted to the NZP phosphates $M_{0.5+x}Mg_xZr_{2-x}(PO_4)_3$ (M – Cd, Pb; x = 0, 0.5) thermophysical properties (thermal expansion and thermal conductivity) investigation. The compounds were synthesized by sol-gel method. Starting reagents were $Cd(NO_3)_2$, $Pb(NO_3)_2$, $Mg(NO_3)_2$, $ZrOCl_2$ and $NH_4H_2PO_4$ aqueous solutions. The reaction mixtures were dried at 90°C and thermally treated at 600−700°C in air access. The compounds were characterized by methods of X-ray diffraction, IR spectroscopy and electron microprobe analysis. The results have shown that the synthesized compounds are single-phase and belong to the NZP type structure.

There are many data on thermal expansion of $M_{0.5}Zr_2(PO_4)_3$ compounds [1]. Thermal expansion of the $MMg_{0.5}Zr_{1.5}(PO_4)_3$ (M – Cd, Pb) compounds was studied in the present investigation by X-ray diffraction studies in the temperature interval 25−800°C. The obtained thermal expansion coefficients values show, that $CdMg_{0.5}Zr_{1.5}(PO_4)_3$ belong to middle-expanding compounds: $\alpha_a = -3.2\cdot10^{-6}\ °C^{-1}$, $\alpha_c = 13.9\cdot10^{-6}\ °C^{-1}$, $|\alpha_a - \alpha_c| = 17.1\cdot10^{-6}\ °C^{-1}$, $\alpha_{av} = 2.5\cdot10^{-6}\ °C^{-1}$. $PbMg_{0.5}Zr_{1.5}(PO_4)_3$ thermal expansion coefficients and anisotropy are close to low-expanding materials: $\alpha_a = 1.9\cdot10^{-6}\ °C^{-1}$, $\alpha_c = 2.6\cdot10^{-6}\ °C^{-1}$, $|\alpha_a - \alpha_c| = 0.7\cdot10^{-6}\ °C^{-1}$, $\alpha_{av} = 2.1\cdot10^{-6}\ °C^{-1}$. This fact is may be explained by significant distortions of its structural framework at room temperature connected with incorporation of large Pb^{2+} ions in the structural cavities. So the further expansion of the structure in heating is suppressed by the bridge PO_4 tetrahedra that connect the skeletal framework fragments.

The thermal conductivity of the $M_{0.5+x}Mg_xZr_{2-x}(PO_4)_3$ ceramic samples was measured by the laser flash method in the temperature range 25−300°C. The obtained values satisfactorily agree with the data on the thermal conductivity of high-density NZP ceramics (0.6–1.4 W/(m·°C)). On the whole, the obtained results illustrate the possibility to develop new types of NZP ceramics capable of resisting thermal shocks and possessing the required level of thermophysical parameters.

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Synthesis and morphology YSZ nanopowder precursor

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Nowadays YSZ is of great importance in many applications, like electrolytes for solid oxide fuel cells (SOFCs) and oxygen sensors, refractory materials for high temperature furnaces as well as protective coatings for metals.

This study is dedicated to the synthesis of nanosized YSZ using sol-gel method from poorly soluble compounds containing active oxygen.

The goal is the development of techniques for the synthesis of zirconium hydroperoxide with a certain content of stabilizing additives; studying of the mechanism of processes in solid phases during heating of peroxide precursors.

For the synthesis of solid solutions ZrO_2 -Y_2O_3 was used zirconium and yttrium nitrate, ammonium carbonate, hydrogen peroxide.

Characterisation of the obtained materials was carried out using techniques such as X-ray diffraction, Infrared spectroscopy, thermogravimetric analysis. The powder morphology was evidenced by Scanning Electron Microscopy. Phase transformations in the system ZrO_2 -Y_2O_3 were installed. The mechanism of interaction in solution was determined.

Polyurethane/carbon nanotubes composites designed for in friction systems transmitting the drive in extreme load conditions used in transport machines and equipment

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In friction systems transmitting the drive in extreme load conditions used in transport machines and equipment, materials in many mines are subjected extreme loads, but also

they work in the environment of significant dust rate, at varying temperatures ranging from -40 ºC to +50º C and often under conditions of elevated humidity. So far, these machines and transport equipment worked in cycles. Currently, due to the need to increase coal mining is done in continuous mode. Cyclic mechanical loads and, consequently, thermal, do not cause such a rapid process of consumption of materials and total destruction, compared to continuous mode. Now, on tire wheels working in these friction systems polyurethane elastomers are most often used. Therefore, there is a need for a new group of polyurethane materials, composites and / or composite structures. On these materials expected their users, among others, in coal mines. One way to improve the thermal properties seem to add to the polyurethane carbon nanotubes.

This work refers to the preparation and characterization of polyurethane composites with carbon nanatubes to be used in friction systems transmitting the drive in extreme load conditions used in transport machines and equipment. The subject of the study were three series of composites. One made of a commercial polyurethane with different amounts of carbon nanotubes. The second and third polyurethane prepared on Warsaw University of Technology with varying amounts of nanotubes. In a second series, the filler was stirred in the polyol with a mechanical stirrer, and the third with the calender. Their properties were compared with the pure polyurethane.

The resulting material were tested for the required characteristics for this application such as high wear resistance, mechanical and thermal properties. The properties and structure of the manufactured PUR were characterised using the following techniques: Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMA), thermogravimetric analysis (TGA) and electron scanning microscopy (SEM). Also evaluated were the strength properties, wear resistance, hardness, resilience, density, abrasive wear in pair of polyurethane and steel. Also performed flammability tests of materials on the cone calorimeter, oxygen index was determined and defined flammability class test Ul-94.

Influence of used chain extender on properties of polyurethanes designed for in friction systems transmitting the drive in extreme load conditions used in transport machines and equipment

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In friction systems transmitting the drive in extreme load conditions used in transport machines and equipment, materials in many mines are subjected extreme loads, but also they work in the environment of significant dust rate, at varying temperatures ranging from -40 ºC to +50º C and often under conditions of elevated humidity. So far, these machines and transport equipment worked in cycles. Currently, due to the need to increase coal mining is done in continuous mode. Cyclic mechanical loads and, consequently, thermal, do not cause such a rapid process of consumption of materials and total destruction, compared to continuous mode. Now, on tire wheels working in these friction systems polyurethane elastomers are most often used. Therefore, there is a need for a new group of polyurethane materials, composites and / or composite structures. On these materials expected their users, among others, in coal mines. One way to improve the thermal properties may be the development of a new composition of polyurethane materials. In this work it was decided to investigate the effect of different chain extenders and their ratio on the properties of materials.

This work refers to the preparation and characterization of polyurethane materials with different chain extenders to be used in friction systems transmitting the drive in extreme load conditions used in transport machines and equipment. The subject of the study were materials with ethylene glycol, glycerol, DCDA and epoxy resin E1 used as chain extender. Two series of materials were made. One with glycol and glycerol used in different contents. The second with DCDA and E1 in different proportions.

The resulting material were tested for the required characteristics for this application such as high wear resistance, mechanical and thermal properties. The properties and structure of the manufactured PUR were characterised using the following techniques: Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMA), thermogravimetric analysis (TGA) and electron scanning microscopy (SEM). Also evaluated were the strength properties, wear resistance, hardness, resilience, density, abrasive wear in pair of polyurethane and steel. Also performed flammability tests of materials on the cone calorimeter, oxygen index was determined and defined flammability class test Ul-94.

Crystallization behaviour of ZrO_2-$3Y_2O_3$-xSrO precursor powders synthesized by coprecipitation process

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Crystallization behaviours of ZrO_2-$3Y_2O_3$-xSrO precursor powders have been studied. The zirconium oxide chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$), yttrium nitrate ($Y(NO_3)_3 \cdot 6H_2O$) and strontium nitrate ($Sr(No_3)_3$) using as the initial materials. Differential thermal analysis (DTA), X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), nano beam electron diffraction (NBED) and high resolution TEM (HRTEM) were utilized to characterize the crystallization behaviour of ZrO_2-$3Y_2O_3$-xSrO precursor powders. The activation energies of tetragonal ZrO_2 (t-ZrO_2) crystallization were 585.3, 255.2, 207.9 and 310.0 kJ/mol with SrO content for 1, 2, 3 and 4 mol%, respectively, by a non-isothermal method. The growth morphology parameter (n) and growth mechanism index were close to 2.0, showing that t-ZrO_2 had a plate-like morphology. The crystalline size of t-ZrO_2 increased from 26.9 to 27.2 nm for 3Y-PSZ precursor powders with x mol% SrO calcined at 923 K for 120 min. The crystallize size of t-ZrO_2 increased from 26.6 to 26.9 nm when the ZrO_2-$3Y_2O_3$-2SrO precursor powders calcined at 773 to 923 K for 120 min.

Synthesis and Characterization of Li_2TiSiO_5 Obtained by Melting and Solid-State Reaction

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In this work, the synthesis and obtaining of the Li_2TiSiO_5 compound was investigated by two different routes: (i) solid-state reaction of a mixture of Li_2SiO_3 and TiO_2 nanoparticles and (ii) melting of a stoichiometric mixture of Li_2CO_3, SiO_2 and TiO_2 nanoparticles. The melted (1550 °C/2h) products (Li_2SiO_3 and the stoichiometric mixture) were poured out into water. After cooling process, the solidified products were milled so that powders with particle sizes lower than 53 µm were obtained. Subsequently, the obtained powders were heat-treated at different temperatures (900-1000 °C) and times (60-120 min) and then subjected to thermal (DIL and DSC) and crystallographic (XRD) analyses in order to investigate the physical-chemical reactions and the resulting structure. The results showed that it is possible to obtain the Li_2TiSiO_5 compound for both synthesis routes but, apparently, the melting route seems to be more appropriated to obtain high content Li_2TiSiO_5 ceramic materials.

Thermal analysis of some composite powders used for spot welding electrodes

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Materials based on Cu/Cr respectively Cu/W represents one of the classes of materials used for welding electrodes, engine commutators, high temperature solenoid coils, slip rings, pistons and nozzles for plastic presses, points of oxygen lances, moulds for continuous casting plants and heat exchangers [1]. The presence of Cr and W in the composition of copper alloys increase their mechanical properties (hardness, tensile strength). The conductivity of copper –chromium alloy is about 80% of pure copper [2]. Due to lower solubility between Cu-Cr and lack of the solubility between Cu-W, this type of materials are suitable for technologies specific to powder metallurgy. One of these technologies is mechanical alloying/mechanical milling which consists in mechanical welding of powder particles when these are caught between the grinding balls and the vials.

For the experimental work four types of mixtures ($Cu_{98.5}Cr$, $Cu_{97}Cr$, $Cu_{93.5}Cr_{1.5}W$, and $Cu_{92}Cr_3W$) were prepared by mechanical milling for 5 respectively 10 hours.

The resulting samples were subjected to thermal analysis (differential scanning calorimetry - DSC) and were characterized by morphological (scanning electron microscopy-SEM), structural (X-ray diffraction-XRD), compositional (energy dispersive X-ray spectroscopy-EDX) point of views.

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Effect of milling time on the thermal behaviour of W/Cu composite powders

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The paper presents experimental research on the thermal behaviour of six mixtures based on W/Cu powders processed by high energy ball milling. The mixtures used in the research were W_xCu_{100-x} (where x is in the range of 55-80 % wt.). The milling process was carried up to 20 hours and samples were prelevated from 5 to 5 hours. The as prepared samples have been investigated from morphiological (scanning electron microscopy-SEM), structural (X-ray diffraction-XRD), compositional (energy dispersive X-ray spectroscopy-EDX) and thermal (differential scanning calorimetry - DSC) point of views.

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Poster Session 3

Thermochemistry & (Bio)Calorimetry, Polymers, Bio(macro)molecules & Biocomposites and Functional compounds

Physicochemical properties of dry native and modified hyaluronan

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Hyaluronan (HYA) is an anionic, unbranched and non-sulphated polysaccharide of glycosaminoglycan class (composed of repeating disaccharide units of β-1-3-D-*N*-acetylglucosamine and β-1-4-D-glucuronic acid. So far, mostly its solution behavior has been widely studied, but the information about the structural dynamics in solid state is scare. Currently, there is a trend to modify chemically native HYA, which improves its broad application potential mainly in drug delivery, but also in biomedical engineering, biomedicine and cosmetics.

With this respect, phase transitions in dry native or modified HYA and interactions of HYA chains within themselves have not been intensively studied yet [1]. We assume that shedding a light onto these processes might be crucial for further broadening of both native and modified HYA applications. In particular, it is important for improving drying procedures, designing of specific applications of native HYA [1-2], better understanding behavior of modified HYA used as a carrier for encapsulated pharmaceuticals (or cosmetic enhancers/antioxidants) [3] or spinning nanofibers [4].

The almost only hint to phase transitions in dry HYA is about 20 years old [5] and indicates some phase transitions in dry HYA. In this work, we try to explain the phase transitions in dry native and derivatized HYA utilizing classical DSC and temperature modulated DSC as well as thermogravimetry – mass spectrometry (TGA-MS) in order to better understand the processes of their physicochemical aging and degradation.

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Applying thermal analysis for the investigation of new coordination polymers based on 1,4-bis((1H-imidazoyl-1-yl)methyl)benzene, di- or tri-carboxylate ligands with Co(II), Ni(II), Zn(II)

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The metal-organic frameworks (MOFs) also known as coordination polymers are of great interest being widely studied during the past few decades due to their numerous applications such as catalysis, gas storage and separation [1]. Research into MOFs has been motivated by the prospect of discovering new structures with enhanced functional properties such as high thermal stability that will make these materials eligible in technical processes involving heating. A suggestive method for this purpose is thermal analysis.

A series of new coordination polymers have been synthesized and thermogravimetric characterized: $\{[Zn_2(BIB)_2(PDC)_2]\cdot 9.5H_2O\}_n$ (**ZnP**), $\{[Co(BIB)_{1.5}PDC]\cdot 4H_2O\}_n$ (**CoP**), $[Ni_2(BIB)(TCA)(OH)]_n$ (**NiP1**), $[Ni(BIB)(HIMDC)]_n$ (**NiP2**), $[Zn(BIB)_{0.5}(HIMDC)]_n$ (**ZnP2**), where BIB = 1,4-Bis((1H-imidazoyl-1-yl)methyl)benzene, PDC = 2,6-pyridinedicarboxylate, TCA = 1,3,5-tricarboxylate, HIMDC = monoprotonated imidazole-4,5-dicarboxylic acid.

TG trace for **ZnP** and **CoP** allowed to identificate the number of water molecules in the external sphere of the complexes. One interest was to see the effect of water removal from channels within the structures - in the absence of the guest molecules the compounds are thermally stable up to 200 - 230 °C.

Higher thermal stability was observed for **NiP1, NiP2** and **ZnP2**: 425 °C, 375 °C and 360 °C, respectively. Such high values are relatively rare in the literature for inorganic polymers. This property is important for reaching practical implementations of these compounds being a clue for good stiffness, rigidity, robustness and structural integrity estimation.

In order to assess the aforementioned applications for the compounds, further sorption measurements are on the way.

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Low-temperature calorimetry and thermodynamic functions of natural chalcanthite

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Natural crystalline hydrate of copper sulfate $CuSO_4 \cdot 5H_2O$ is one of the basic end products of metamorphism of copper minerals, and it often occurs in oxidation zones of deposits and mine workings, especially in a dry climate. Due to its high solubility, this mineral is a source of copper ions in the geochemical migration of elements.

This paper presents the results of studies of the thermodynamic functions of natural chalcanthite. The research of the heat capacity of the sample of natural chalcanthite was conducted by adiabatic calorimetry over the temperature range of 4.2-320 K. The experimental part of the research was carried out on a low-temperature thermophysical installation produced by LLC "Thermax" (Moscow). The measurement accuracy of the heat capacity of a standard sample – copper of the brand OFC is ± 1.43% at 5 K, ± 0.75% at 10 K, ± 0.23% at 40 K and less than 0.11% for the temperature range from 90 to 298.15 K [1]. Thermodynamic functions of the compound – change enthalpy ($H_{298.15}-H_0$) and standart entropy $S^0_{298,15}$ were obtained based on the measurements of the heat capacity $C_p(T)$ of the sample.

Natural sample of pentahydrate copper sulfate of chalcanthite $CuSO_4 \cdot 5H_2O$ (the deposit Kosmurun, Chingiz Ridge of Central Kazakhstan) was used as an object of measurements. The correspondence of the sample under study to the mineral of chalcanthite was confirmed by the methods of X-ray diffraction, infrared and Raman spectroscopy and electron probe microanalysis.

The experimental data on the heat capacity of the sample were smoothed by the method of approximating spline polynomials. The deviation of the experimental points regarding the smoothed values was within ± 2.0% at 5-20 K, ± 0.5% at 20-70 K, ± 0.2% at 70-320 K.

On the experimental curve of the temperature dependence of the heat capacity of natural chalcanthite there are no visible signs of a phase transition associated with crystallization of water, which we observed in the synthetic sample. The absence of free water indicates a high structural perfection of the natural sample. Below 5.5 K was registrated anomal behaviour in $C_p(T)$ associated with the end of phase transition.

Based on the experimental data on the heat capacity of a natural chalcanthite, the thermodynamic functions, the standard values of which are: $C_p^\circ{}_{(298.15)} = 288.0 \pm 0.4$ J/mol·K, $S^0_{298.15} = 295.2 \pm 0.8$ J/mol·K, $(H_{298.15}-H_0) = 46.35 \pm 0.09$ kJ/mol have been calculated over the whole temperature range.

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Study of dehydration processes of natural chalcanthite by thermogravimetric analysis and differential scanning calorimetry

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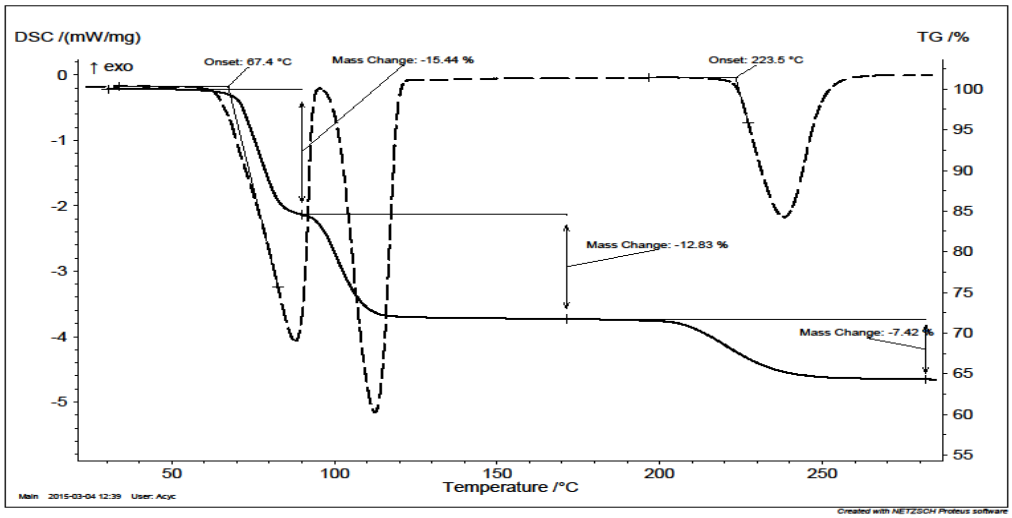
Chalcanthite $CuSO_4 \cdot 5H_2O$ is a typical mineral of the oxidation zone of copper-sulfide ore deposits. Its synthetic analogue (bluestone) is widely used in agriculture as well as in the chemical and paint industries. The bluestone dehydration process was investigated by thermal analysis previously, but there are no data on its thermochemical characteristics in the literature. The sample from copper-sulphide deposit Kosmurun (Chingiz Ridge of Central Kazakhstan) was selected to investigate. Diagnostics of mineral was made by X-ray, FTIR-spectroscopy, Raman-spectroscopy and X-ray microprobe analysis methods.

Dehydration process of mineral was studied using thermoanalytical systems NETZSCH TG 209 F1 and NETZSCH DSC 204 F1 (Germany) in a stream of nitrogen (20 ml/min) with a heating rate of 10°/min in the range from room temperature to 300°C, the sample weights were 3-4 mg. The DSC curve (fig.) showed three endothermic effects associated with the three stages of the removal of water: at temperatures of 67-95°C 2.2 moles of water were removed; at 95-125°C 1.8 moles of water were removed and the remaining 1 mole of water was removed at 223-265°C. The sum of thermal effects corresponding to the first and second stages was measured as 235±11 kJ/mol. The measured third thermal effect was equal to 77.0±3.0 kJ/mol.



The selectivity of imidazolium based ionic liquids for aromatics from aliphatic-aromatic mixtures

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In petrochemical industry, aromatic compounds are obtained almost exclusively from reformed naphtha. These aromatic components are separated from the aliphatic hydrocarbons usually through liquid extraction, since these hydrocarbons have boiling points in a close range and several combinations form azeotropes [1].

Ionic liquids (ILs) have unique properties such as low vapor pressure at ambient pressure, excellent thermal and chemical stability and favorable solvating properties. Therefore, ILs has been considered as promising solvents to replace traditional organic solvents, and in recent years, it has attracted the attention of researchers on liquid extraction of aromatics from aliphatic hydrocarbons instead of organic solvents. Moreover, the regeneration costs of ILs are lower than organic solvent such as sulfolane which has a high boiling point of 287.3 °C. In this work, some imidazolium based ILs, which are scarcely studied for the extraction of aromatics: [BMIM][Tf_2N], [BMIM][PF_6], [EMIM] [Tf_2N] and [OMIM][BF_4] was tested and compared their selectivity with conventional organic solvents. In addition, some thermo-physical properties were determined for the related binary mixtures.

For this purpose, the selectivity (*S*) of ILs to aromatics was analysed from the experimental LLE data at 298.15 K and atmospheric pressure. Thermo-physical properties were also studied. The LLE data were correlated by using the non-random two-liquid (NRTL) model for all the systems. The reliability of the experimental tie-line data was ascertained by using Othmer-Tobias correlating equations. The thermo-physical properties were correlated well with Redlich-Kister polynomials.

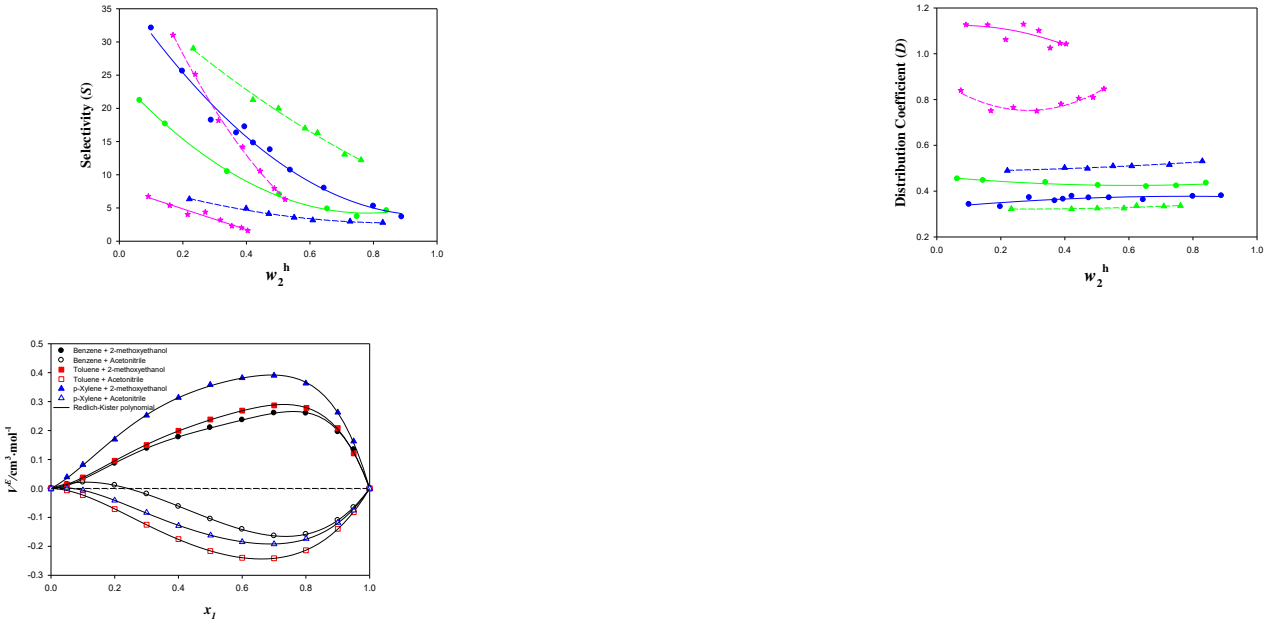

Fig. 1. A) Selectivity b) Distribution coefficients C) Excess molar volumes for some binary mixtures containing different solvents for aromatics

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Determinations of the phase behaviour and thermos-physical properties for developing of phosgene free benign synthetic process

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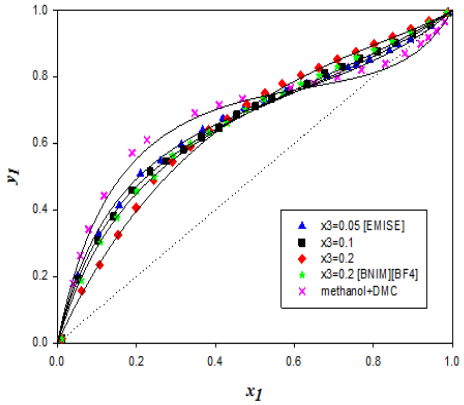
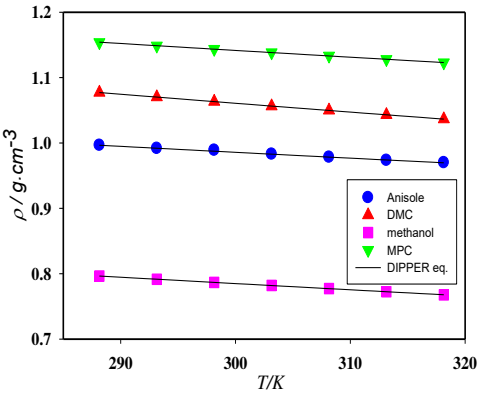
Polycarbonate (PC) is particular group of thermoplastic polymer, which widely used as an engineering plastic in various applications, i.e., electronic appliances, office equipment, and automobiles, etc. Traditionally, PC is produced using very toxic phosgene as an intermediate [1, 2], and this process cannot be avoided the formation of undesired salts and used a large amount of solvent. Many attempts have been made for non-phosgene PC manufacturing process. The main focus has been a route that produces diphenyl carbonate (DPC) via dimethyl carbonate (DMC), which then reacts further with bisphenol-A (BPA) to form PC. In this process, DMC reacts with phenol and BPA by trans-esterification, Methylphenylcarbonate (MPC), DPC methanol to be produced. However, to date, relatively very few investigations of the phase equilibria and thermos-physical properties have been reported for this non-phosgene DPC synthetic process. [3]

In the present work, therefore, the binary and ternary phase behavior and mixture properties were analytically determined for the intermediate components, i.e., MPC, methanol, anisole, phenol, etc. that may be encountered in the environmentally friendly DPC synthetic process. The measured phase behavior was correlated with activity coefficient model: non-random two-liquid (NRTL) and/or Universal Quasi-Chemical (UNIQUAC) models, while the thermo-physical properties were correlated with the Redlich –Kister polynomial and the Daubert and Danner equation, etc.

In addition, thermos-physical properties, such as density, refractive indices, kinematic viscosity for the reaction intermediates were determined and compared with the estimated values from linear, Goletz, Heller equation, etc. The Figures are examples of determined vapour-liquid equilibria for DMC+MeOH+ILS and densities for some intermediates.





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Effect of molecular weight of poly(acrylic acid) on the interaction between tetradecyltrimethylammonium bromide and poly(acrylic acid)

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Isothermal titration calorimetry (ITC) and surface tension measurement were applied to study the interactions between oppositely charged tetradecyltrimethylammonium bromide (C_{14}TAB) and poly(acrylic acid) (PAA) with the molecular weight ranging from 1800 to 450000 g/mol. Both ITC and surface tension measurement were performed by titrating C_{14}TAB aqueous solution into 0.05wt% PAA aqueous solution at 25 ^{o}C. Thermo-histogram of ITC exhibits an exothermic peak due to the formation of PAA/C_{14}TAB complex. The driving force is simply the electrostatic attraction between opposite charged PAA and C_{14}TAB. When the C_{14}TAB concentration reaches the saturated concentration, PAA is saturated with bound C_{14}TAB molecules. And when the C_{14}TAB concentration further increased up to the second critical micelle concentration, the C_{14}TAB free micelle started to form. The PAA molecular weights would also affect the result. In addition, the surface tension was measured to investigate the adsorption and complexation at the solution interface. Based on the results of titration of C_{14}TAB into PAA solution with six different molecular weights ranging from 1800 to 450000 as well as the surface tension data, it was found that when the PAA molecular weight larger than 25000 g/mol, they show the tendency as the above-mentioned, but there is a different mechanism in low molecular weights PAA/C_{14}TAB system (1800 and 5000 g/mol), C_{14}TAB started to form free micelles before the saturated concentration. The interaction of C_{14}TAB and PAA is independent of PAA molecular weight when the PAA molecular weight is larger than 250000 g/mol.

Water adsorption and thermal decomposition properties of polysaccharide from pulsed light irradiated white *Flammulina velutipes*

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White *Flammulina velutipes* (white enoki mushroom) is one of the favorite ingredients for Asians that is normally eaten with or added to soups in a hot pot with the other food. Food irradiation by pulsed light can confirm hygienic quality and extend the shelf life [1,2]. Comparisons were made of fruiting body and its base by various irradiated times of **pulsed light**, and then the polysaccharide of ingredients was contrasted, from which could be learned the reliable irradiation pulses and the favorable site of white *Flammulina velutipes*. Polysaccharide was prepared by hot water extracted of the fruiting body and its base of white *Flammulina velutipes* [2], which was irradiated at 0, 10, 30, 50, and 80 pulses by pulsed light. Interestingly, the polysaccharide content was in the range of 72.7 to 77.9 mg g^{-1} of fruiting body and 49.3 to 57.0 mg g^{-1} of its base with pulsed light (0-80 pulses), respectively; along with increasing pulsed light irradiated pulses, the polysaccharides' molecular weight distributions were not increased. Differential scanning calorimetry (DSC) was used to determine the enthalpy of endothermic and exothermic of the polysaccharide of white *Flammulina velutipes* [2]. We developed a novel approach to thermal decomposition and **water adsorption** that includes the moisturizing characteristics, heat decomposition properties, and storage conditions of the polysaccharide of white *Flammulina velutipes*, such as the kinetics of endothermic and exothermic reaction, which could be applied to a design during cosmetics processing, heat treatment, and **storage conditions**.

Keywords White *Flammulina velutipes* (white enoki mushroom). Pulsed light. Polysaccharide. Water adsorption. Storage condition

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Insight on thermal behaviour of some complexes with a bischelate Schiff base derived from tolidine

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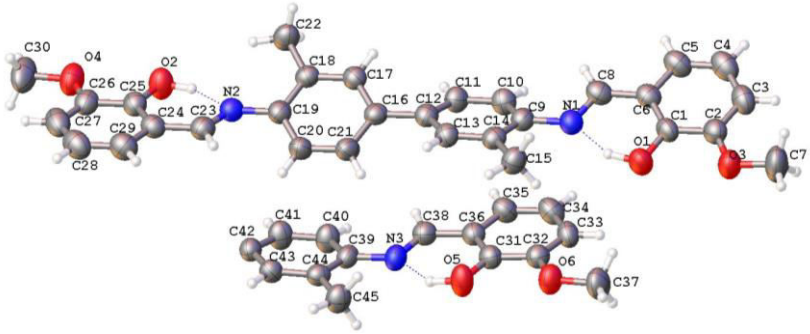
The increasing incidence of pathogenic microorganisms' resistance imposes the development of new drugs. One of the strategies developed in this field take into consideration a different mechanism of action for complexes in comparison with organic species. From this point of view, the multidentate Schiff bases are attracting ligands and many of their complexes exhibit a good antimicrobial activity, in most cases enhanced in comparison with that of free ligand. Furthermore, some complexes of this type present interesting properties such magnetic, electrochemical, luminescent and catalytic [1]. Some of these species were studied also concerning thermal behaviour [2].

In order to develop new metallo-antimicrobials a series of complexes of type $[M_2LCl_4]$ (M: Ni, Cu, Zn, Cd), L: *N,N'*–bis–(3–methoxy–salicyliden)–*o*–tolidine, Schiff base derived from o-tolidine and o-vanillin [1+2] condensation) were synthesized. The ligand was also isolated and full characterised by single crystal X-ray diffraction.



The complexes features have been assigned from microanalytical, ESI-MS, IR, UV-Vis-NIR, NMR and magnetic data at room temperature. All these investigation account for a square-planar stereochemistry for Ni(II) and Cu(II).

The *in vitro* preliminary screening of the antimicrobial activity performed against Gram positive (*S. aureus, B. subtilis*), Gram negative (*P. aeruginosa, E. coli, Enterobacter spp.*) and *C. albicans* reference strains indicates an overall good activity for Cd(II) complex.

Complexes display a similar thermal behaviour. Processes as hydrochloric acid endothermic elimination as well as oxidative degradation of the Schiff base were evidenced according with TG and DTA curves profile. The final product of decomposition was metal (II) oxide as powder X-ray diffraction indicated.

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Spectral and thermal characterization of some new complexes with 2-(iminopyridyl)-3-butanone as potential antifungal species

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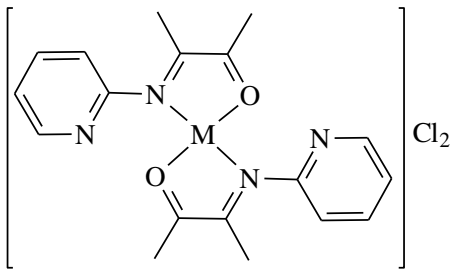
The complexes with Schiff bases incited a great interest due to their structural diversity as well as biological involvement. Complexes with such ligands have many applications such structural models for metal–enzymes, involvement in biological redox processes like dioxygen activation, hydrogen peroxide decomposition, or several hydrolytic processes. Moreover, there are many studies concerning antibacterial, antifungal, antimicrobial, anticonvulsive, anti–HIV, anti–inflammatory and antitumor activity of these complexes [1]. Some complexes with such ligands presented also an interesting thermal behaviour [2].

A novel series of complexes of the type $[M(ipb)_2]Cl_2 \cdot nH_2O$ (M: Co(II), n=0; Cu(II), n=1.5 and Zn(II), n=1; ipb: 2-(iminopyridyl)-3-butanone have been synthesized via template condensation of 2,3-butandione and 2-aminopyridine. The complexes were formulated as mononuclear species:



The features of complexes have been assigned from microanalytical, IR, UV-Vis, EPR and magnetic data. Electronic spectra of Co(II) and Cu(II) complexes are characteristic for tetra-coordination. The IR spectra display the characteristic band of azomethine and indicate the chelate behaviour of ligand.

The *in vitro* screening indicates a good activity against *Candida albicans* strains both planktonic and biofilm embedded.

The thermal analyses in air have evidenced process as water elimination as well as fragmentation and oxidative degradation of Schiff base. Anhydrous species display a similar thermal behaviour. The water elimination up to 160°C is an indicative of its crystallisation nature while the residue was metal (II) oxide as powder X-ray diffraction indicated.

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[2] I. Alan, A. Kriza, R. Olar, N. Stanica, M. Badea, J. Therm. Anal. Calorim., 111 (2013) 1163

Synthesis, spectral and thermal studies of the sodium salts of some Ru(III) complexes with quinolone antibiotics

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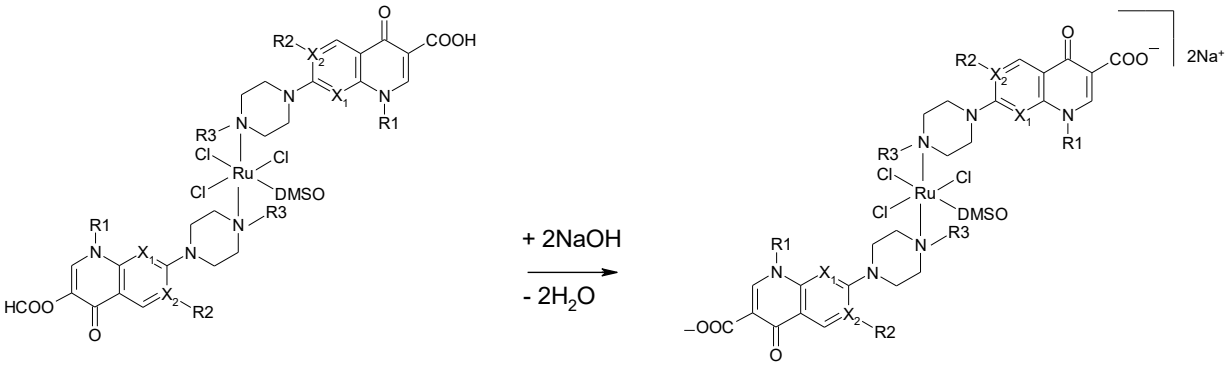
Solubilisation by salt formation is an effective method to increase the solubility of slightly soluble drugs, applied especially for the development of liquid formulations for parenteral administration. In the present study, this strategy is applied for new Ru(III) complexes with quinolone antibiotics, valuable for biological application such as anticancer activity. The parent compounds, formulated as $RuCl_3(HL)_2(DMSO)m(H_2O)_n$ (HL: pipemidic acid, norfloxacin, ciprofloxacin, ofloxacin, levofloxacin, enrofloxacin, enoxacin) were transformed in their corresponding soluble sodium salts (scheme 1) with general formula $Na_2RuCl_3(L)_2(DMSO)_m(EtOH)_n(H_2O)_p$. The sodium salts have been characterised by elemental analysis and some spectrometric methods (IR, UV-Vis). The thermal behaviour of the newly synthesized salts was studied by simultaneous TG/DTG/DTA analysis and it was evidenced a higher thermal stability comparing to that of the parent compounds.



Scheme 1 The general scheme for synthesis

Thermal behaviour of some biologically active species based on complexes with a triazolopyrimidine pharmacophore

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The triazolopyrimidine derivative complexation to transitional metal ions has received considerable importance having in view their variable bonding modes, structural diversity and promising biological implications. Our interest in such complexes study arise from their wide range of biological activities evidenced for triazolopyrimidine derivatives such as anti-inflammatory, analgesic, cardiovascular, antimalarial, antiviral, cytostatic as well as antimicrobial [1].

Having in view these aspects, we extended this field in one-pot synthesis of new complexes with formula $ML(CH_3COO)_2 \cdot nH_2O$ ((**1**) M: Co, n=4.5; (**2**) M: Ni, n=3.5; (**3**) M: Cu, n=0.5; (**4**) M: Zn, n=0; L: 5-phenyl-7-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine). The complexes were characterized by elemental analyses, ESI-MS, IR, UV-Vis-NIR, NMR, EPR spectra, magnetic susceptibility at room temperature as well as thermogravimetric analysis.

The modifications in the IR spectra of complexes are in accord with the condensation process and indicate the triazolopyrimidine coordination as monodeprotonated species. The electronic and EPR spectra together with magnetic moments indicate an octahedral stereochemistry.

The *in vitro* preliminary screening of the antimicrobial activity was performed against some Gram positive, Gram negative and fungal both reference and clinical multidrug resistant strains. The complexes exhibited an improved antimicrobial activity in comparison with the ligand, both on planktonic and biofilm embedded cells. The Cu(II) complex exhibits both cytotoxicity on HT 29 tumor cell line and anti-inflammatory activity.

The thermal decomposition investigated in air confirmed the proposed formulas for complexes and provided information concerning the modifications at heating and also the thermodynamics effects that accompany them. The thermal transformations are complex according to TG and DTG curves including dehydration, acetate into carbonate transformation, fragmentation and oxidative degradation of triazolopyrimidine derivative. The final product of decomposition was the most stable metal oxide as powder X-ray diffraction indicated.

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Selective, High Affinity Inhibitors Synthesized for the Cancer Associated Protein Carbonic Anhydrase IX

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Carbonic anhydrase IX is highly expressed in tumor tissues. It acidifies the cancerous environment and promotes metastatic invasiveness. Its selective inhibition could potentially be used as a treatment of solid hypoxic cancers.

A series of fluorinated benzenesulfonamides with substituents on the benzene ring were designed and synthesized. CAIX was purified from mammalian cell cultures. All other CAs were purified from bacterial cells. Binding studies were performed using the fluorescent thermal shift assay and isothermal titration calorimetry. The inhibition of the CA isoforms was determined by the stopped-flow CO_2 hydration assay.

Because several CA isoforms did not crystallize, including CAIX, multiple amino acid CAII mutants were created to mimic the CAIX active site. This chimeric protein was referred to as chCAIX in the study. X-ray crystallographic structure of the compounds bound to CAII and the chCAIX were determined.

Several compounds exhibited strong, selective binding and inhibition of CAIX. Three fluorine atoms increased affinity in a significant manner by withdrawing electrons and lowering the pK_a of the benzene sulfonamide group. Bulky ortho substituents were able to fit in a hydrophobic pocket that is found in the CAIX active site but not in CAII, for example.

In the analysis of the data it was important to find a balance between affinity and selectivity for potential drug leads.

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Thermal characterization of chocolate

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The aim of this work was to determine the temperature interval in which chocolate can exist in both melted and solid states.

Chocolate is unique substance usually made of cocoa butter, cocoa powder, cane sugar, soybean lecithin, milk powder if not dark and also some flavouring. It is well known that is in solid form at room temperature and liquid at body temperature, which is not the result of simple crystallization and melting. Its main ingredient cocoa butter is polymorphic and can crystallize into six polymorphic forms, which influence on stability and different physical characteristics such as gloss, hardness and of course, melting point [1-2].

In our work we report on using several DSC technics to determine the interval between two melting points (chocolate hysteresis) in the several commercial affordable chocolates. We also investigate the characteristics of raw materials and their influence on the shape of the DSC melting curve. Depending on the conditions of crystallization, a variety of melting points can be observed.

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Glass transition temperature of emulsion pressure sensitive adhesives with modified glucose

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Since their introduction in 19th century, pressure sensitive adhesives have been widely used in many fields. They are capable of bonding to a variety of surfaces with the use of a light pressure. There are three basic applicative adhesion properties which determine adhesive properties: peel strength (the ability to resist removal by peeling), tack (the ability to adhere quickly) and shear resistance (the ability to resist flow when shearing forces are applied). The balance between these three interrelated properties is usually tailored according to the end use of the PSA [1, 2]. Tack, peel strength and shear resistance are strongly dependent on the emulsion particle size distribution, polymer gel fraction, polymer molecular weight distribution and copolymer composition. The glass transition temperature affects the adhesion properties by determining the softness of the PSA, which is needed for an appropriate flow of the adhesive during the film formation process. In the PSA industry, T_g is normally tailored via the copolymerization process via the selection of different monomers [3, 4].

PSAs were synthesized using n-butyl acrylate, modified glucose (butyl polyglucoside maleic acid ester, BGMAH), anionic and non-ionic surfactants, ammonium persulfate and distilled deionized water.

The samples of obtained emulsions were coated on a glass plate and dried in a vacuum dryer at 120 °C for 2 h. The glass transition temperature of the polymer was determined by differential scanning calorimetry (DSC) using a Mettler Toledo DSC 1 instrument and by dynamic mechanical analysis (DMA) using a Mettler Toledo DMA 861e instrument.

In DSC thermograms of copolymers two glass transition temperatures were evident; the lower T_g value was observed between -47 and -45 °C and the higher one around 84 °C. Smaller endothermic peaks occurred between 100 and 130 °C. DMA analysis of the copolymer with 10 % of BGMAH has showed two very broad glass transitions followed by a melting. On the other hand, DMA analysis of the copolymer with 25 % of BGMAH has showed four glass transitions.

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Thermal degradation of polydimethylsiloxane as a function of molecular weights

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Thermal properties of polysiloxanes are one of the technically most important advantages compared to other polymeric materials, since their applicability exhibits wide temperature range [1]. The main purpose of the proposed study is to prepare polydimethylsiloxane (PDMS) samples with different molecular weight and to observe the effect of molecular weight on the thermal stability of PDMS from TGA experiments in both, inert and oxidative atmosphere. Depolymerization under high temperature in inert atmosphere may be explained by three mechanisms proposed in the literature, known as unzipping mechanism, random scission mechanism and external catalyzed mechanism (presence of ionic and polar impurities or additives). In contrast, thermal degradation in the presence of oxygen obviously differs in comparison to inert atmosphere. Since the degradation follows the radical mechanism, along with the cyclic oligomers, other volatile products are also formed, which leads to silica as an end product [2, 3]. PDMS samples with different molecular weights were prepared by anionically initiated ring-opening polymerization (AROP) in emulsion. Thermal stability of PDMS samples was assessed by thermogravimetric analysis (TGA). The investigated temperature range was from 25 up to 700 °C.

The degradation of PDMS in oxygen atmosphere started at lower temperature than in the case of nitrogen atmosphere, when sample was established to the same heating rate. Furthermore, the exothermic nature of PDMS degradation in oxygen atmosphere and endothermic in inert atmosphere was confirmed by DSC analysis. At higher temperature, the molecular weight of PDMS affected the shape of TGA curve drastically, when measurements were performed in nitrogen atmosphere. The lower the molecular weight, the better the thermal stability of PDMS. Mentioned phenomena can be observed in the broader temperature interval of degradation with increased molecular weight. The predominant mechanism at lower molecular weights is unzipping mechanism, since the amount of –Si-OH end molecules and consequently the number of reaction sites involved in unzipping mechanism is higher than in the case of higher molecular weights. However, when the molecular weight increased, the temperature interval became narrower. The observed behaviour could be attributed to the increased probability of random vaccination of polymer chains at higher molecular weights, caused by intramolecular and intermolecular redistribution reactions. In the oxygen atmosphere the obtained TGA curves for samples containing polymer of different molecular weights were similar. The PDMS degraded in the same temperature interval regardless of its molecular weight.

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Investigation of the Diels–Alder reaction between furan containing benzoxazine and *N*-phenylmaleimide

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Recently, much attention has been given to the synthesis of polymer materials with self-healing ability, since recent trends in material design demand materials that can repair breaks and microcracks, which occur as consequence of operation and utilization. One of heavily investigated concepts of self-healing is based on the thermally reversible Diels–Alder reaction, mainly between furan and maleimide moieties. Current aim of our investigation was to characterise Diels–Alder (DA) and retro Diels–Alder (rDA) reaction between *N*-phenylmaleimide [1] and furan containing benzoxazine [2].

Starting compounds were synthesised according to the literature procedures [1] and [2]. Afterwards reactants were grounded in mortar in stoichiometric amount, and optimal temperature of 70 °C for DA and 140 °C for rDA reaction were determined with non-isothermal differential scanning calorimetry (DSC). During the DSC investigation it was identified that DA reaction initiates as soon as reactants start to melt, and that there is no clean temperature boundary between DA and rDA reaction. It was also noted that peak for rDA reaction further extends into exothermic peak which represents polymerization of benzoxazine moiety. In search of a clean peak boundary of DA and rDA reaction on DSC thermogram, we have shifted from normal DSC analysis towards the analysis with alternating differential scanning calorimetry (ADSC) [3], by which we were able to determine peaks for DA and rDA reactions.

DA reaction quantification was performed on samples of reactants which were heated isothermally at 70 °C for 1, 3, 6, 12 hours, and were afterwards analysed by ^{1}H NMR. In the case of rDA reaction quantification, reactant sample which was previously heated isothermally at 70 °C for 3 hours was picked as a standard. This standard mixture was further heated at 140 °C for 1, 3, 6, 12 hours, and quenched afterwards in an ice bath, and then analysed by ^{1}H NMR.

Products, as a result of DA reaction, were determined by heating the sample mixture at 70 °C for 24 hours. Afterwards, the obtained reaction mixture was separated by column chromatography. By analysing separated samples with ^{1}H NMR spectroscopy it was observed that the reaction led towards two isomeric products, namely *endo* and *ekso* DA adduct.

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Thermal analysis of ambroxol in Flavamed tablets

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Thermal methods of analysis, alone or in combination with other techniques, are frequently used to study the forced degradation of drugs, to provide informations of drug thermal stability, purity, confirmation of structures of compounds, etc [1–3].

In this study, simultaneous thermogravimetry and differential thermal analysis (TG/DTA) were used to examine kinetics of thermal degradation of ambroxol hydrochloride (AMB) within the standard ambient of commercial Flavamed tablets. Ambroxol hydrochloride (AMB), (1s,4s)-4-((2-amino-3,5-dibromocyclohexyl)methylamino) cyclohexanol hydrochloride, is semi - synthetic derivative of vasicine obtained from Indian shrub *Adhatoda vasica*. It is a metabolic product of bromhexin and acts physiologically as a broncho secretolytic and an expectorant drug [4].

TG/DTA was performed in nonisothermal regime (β = 10, 30 and 50 °C min^{-1}) in inert atmosphere (N_2) with gas flow rate 70 cm^3 min^{-1} .

The decomposition was studied from the kinetics point of view. The kinetics analysis of TG data was performed by isoconversional and model fitting methods. The Flavamed tablets degradation proceeds in six stages, where the third stage was found to be the that when active compound (AMB) degradation happened. The energy of activation for third stage of decomposition obtained by isoconversional methods amounted to 137.9 kJ mol^{-1} (Expanded Friedman), 137.3 kJ mol^{-1} (Modified Coats-Redfern) and 137.6 kJ mol^{-1} (Kissinger). The best fit of experimental data to a recation model was obtained by means of a Reaction order model (Ea = 138.5 kJ mol^{-1}, A= $5.153 \cdot 10^{12} s^{-1}$, n = 0.760), and a four-parameter Sestak-Berggreen model (Ea = 137,1 kJ mol^{-1} , A= $4.376 \cdot 10^{12} s^{-1}$, n = 0.872 and m = 0.0856)

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Application of Isothermal Titration Calorimetry in Evaluation of Protein-Nanoparticles Interactions

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Nanoparticles offer a number of advantages over small organic molecules for controlling protein behaviour inside the cell. Protein binding to the surface of nanoparticles depends on their surface characteristics, composition, and method of preparation.[1]

Because proteins are on the brink of stability, they may experience interactions with some types of surfaces that are strong enough to cause denaturation or significantly change their conformations with concomitant loss of their biological function. Structural changes in the protein may cause exposure of new antigenic sites, “cryptic’ peptide epitopes, potentially triggering an immune response which can promote autoimmune disease.[2]

Mechanistic details of protein structural changes at NP surface have still remained elusive. Understanding the formation and persistence of the protein corona is critical issue, however, there is no many analytical methods which could provide more information about protein structural changes caused by interactions with nanoparticles. Fluorescence spectroscopy is most extensively used in protein conformational studies so far.

The possibility of using isothermal titration calorimetry in the study of protein structural changes upon adsorption on nanoparticle surface is investigated. We compared results obtained from different studies based on ITC application on nanoparticle-protein interactions with results obtained with different analytical tools.

The data illustrate that ITC is a versatile tool to monitor conformational changes in proteins.

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Thermal characterization of bis(3-chloropyridazine-6-hydrazone)-2,6-diacetylpyridine and its complexes with Co^{III}, Ni^{II}, Cu^{II} and Zn^{II}

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Natural and synthetic derivatives of pyridazine are widely used as active principles of pharmaceutics. Due to the heteroatoms, pyridazines have good coordination abilities forming also bi- or multinuclear complexes with transition metals. Coordination to transition metal ions may either improve or worsen the activity of biologically active compounds.

The thermal properties of biologically active compounds are of general interest in their characterisation [1]. In this paper the thermal characteristics of biologically active complexes of bis(3-chloropyridazine-6-hydrazone)-2,6-diacetylpyridine (Hp_2DAP) with Co^{III}, Ni^{II}, Cu^{II} and Zn^{II} of composition $[Co_2(\mu\text{-}Hp_2DAP–2H)_2(\mu\text{-}O_2)]\cdot 4H_2O$ (1), $[Ni(Hp_2DAP–2H)]$ (2), $[Cu(Hp_2DAP–2H)]\cdot H_2O$ (3) and $[Zn(Hp_2DAP–2H)]\cdot H_2O$ (4) are determined and discussed in detail. Beside the thermal stability and mechanism of decomposition of the complexes, thermal properties offer important structural information on the compounds.

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Synthesis, thermal analysis, and spectroscopic and structural characterizations of tetranuclear nickel(II) cubane-type clusters with 2-hydroxybenzaldehydes or 2-hydroxyphenones

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High-nuclearity Ni(II) complexes are known to attract an intense and continuous interest due to their biomimetic activity (models of metal-containing sites) [1], properties of single molecule magnets (SMM) [2–4], and provide structural diversity in cluster constructing [5]. Considerable efforts in this area have been devoted to the synthesis of the cubane-type Ni_4O_4 clusters using suitable chelating ligands, which may simultaneously serve as bridging and terminal ligands to the Ni(II) ions.

Three novel tetranuclear nickel(II) cubane-type clusters with the general formula $[Ni_4(L)_4(\mu_3\text{-}CH_3O)_4(CH_3OH)_4]$ (L = the anion of 2-hydroxybenzaldehyde or 2-hydroxyphenone derivatives) were synthesized and characterized by single-crystal X-ray diffraction analysis, IR and UV–Vis spectroscopy. The crystal structure of each compound contains the core $[Ni_4O_4]$, where each Ni(II) atom is surrounded by two oxygen atoms from the chelated anions of the ligand (L) and by the μ_3-CH_3O oxygen atom that bridges three Ni atoms of the cubane core. The coordination sphere is completed with one methanol molecule thus making approximately octahedral geometry. Simultaneous TG/DTG–DTA techniques were used to analyze their thermal behaviour under inert atmosphere, with particular attention to determine their thermal degradation pathways, which was found to be a multi-step decomposition accompanied by the release of the ligand molecules. Finally, the kinetic analysis of the decomposition processes was performed for the first degradation step of complexes and Kissinger–Akahira–Sunose (KAS) isoconversional method was applied.

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Thermal properties of cytotoxic Pt(IV) complex with EDDA-type ligands

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Ever since cisplatin's use as chemotherapeutic drug was established [1, 2], a great number of transition-metal complexes were synthesized in order to overcome its side effects. Beside standard characterization methods, thermal behaviour of some compounds was additionally determined using standard thermal techniques (TG, DSC).

The non-isothermal decomposition of cisplatin is primarily confirmed defining it as thermally unstable compound in the temperature range 450-500 ºC [3]. Following the example of cisplatin, the thermal degradation of Pt(IV) complex with *O,O'*-di-*n*-butyl-(*S,S)*-ethylenediamine-*N,N'*-di-2-(3-cyclohexyl)propanoate dihydrochloride was investigated as it showed remarkably high cytotoxicity toward U251, C6, L929 and B16 cell lines.

In this work thermal analysis (TG and DSC) of the studied Pt(IV) complex was carried out in the temperature range from 30 ºC to 600 ºC with the heating rates of 5, 8 and 12 ºC min^{-1}.

TG curve indicates complex's thermal stability up to 175 °C when the beginning of its decomposition takes place. The first step occurs in the temperature range between 150-225 °C and represents a fast mass loss originating from all four chloro ligands. DSC profile shows a broad peak in the same temperature region with T_{max} at 202 ºC. Next two steps present a radical mass loss generally consisted of organic, bulky moiety and is accompanied with the corresponding endo-effects in DSC curves. The elimination of organic ligand appears over a large temperature range (230-396 °C) leading to a constant mass value. Thus, the final mass residue, detected at 418 ºC, originates from elemental platinum.

Furthermore, obtained DSC curves were used for evaluation of activation energy for the first decomposition step. The standard isoconversional methods (KAS and FWO) were employed for activation energy calculations. The values of the activation energy were determined for the conversion degree range $0.8 < \alpha < 0.2$ and equal 122.0 and 121.3 kJ mol^{-1}, respectively. Noticeable decrement of activation energy values implies on non-single step process.

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Thermal and color properties of leucodye-based thermochromic composite with dodecanol solvent

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Thermochromic properties originate in interactions of the matter with light that could include reflection, absorption or emission of light [1]. The research of such materials has made a tremendous progress in the last decade in designing thermochromic systems by physical or chemical interaction of their components.

Our research considers the leucodye-developer-solvent composites which show thermochromic change by absorption of visible light. Such materials are commonly coloured in the solid state and transform into a colourless liquid when heated. Even though change of colour is related to phase change of the composite, thermal analyses have been shown in the literature so far only for a few thermochromic systems [2-5]. The temperature of the colour change depends by large extent on the used solvent, but the molar ratio of other compounds used is also important. Moreover, the preparation procedure may influence the thermochromic effect to certain extent, but this phenomenon was not studied enough in detail yet.

Leucodye-based thermochromic systems are more deeply coloured in the solid state if the same solution of the three components is cooled more rapidly, i.e. when it is quenched. To analyse this effect, we have measured the thermal and colorimetric properties of a composite based on 1-dodecanol solvent and spirolactone leucodye (crystal violet lactone, CVL) which was cooled in liquid nitrogen or in icy water. Two molar ratios of the composite were considered, one of them gives completely colourless material in the liquid state while the other still retains some colour after liquefaction. Differential scanning calorimetry (DSC) was used for thermal analysis. Temperature dependent colour was measured during cooling and heating using CIELAB colour space. DSC and colorimetric measurements were made on the same temperature region with the same heating and cooling rates. Comparison of temperature dependent colour with DSC curves gives relations between thermal properties and thermochromic colour change of the composites. This enables to analyse some details of the thermochromic effect. The influence of different molar ratio of the components used in the composite and of the cooling ways applied at its preparation on the thermochromic effect was also shown.

The presented research provides new information on the mechanisms taking part behind thermochromic effect in leucodye-based thermochromic systems. This information is important for the scientific and practical purposes.

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Thermal properties of novel lanthanide(III) complexes with N-donor ligands

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Lanthanide coordination compounds have been studied extensively in recent years due to their interesting luminescent properties, which have lead to their applications in electroluminescent devices, analytical tools and medical imaging. The optical properties of lanthanide-based complexes also make them promising materials for increasing the solar cell efficiency by exploring the UV part of the solar spectrum. Unfortunately, their large-scale application is limited by some drawbacks, a major one being the limited stability at elevated temperatures. Thermal analysis is well suited for performing analysis of thermal stability of those types of compounds.

We report on the synthesis of 7 novel lanthanide complexes, prepared using various ligands: complexes with nicotinic acid [1] with the general formula $Ln_2[(NIC)_6(H_2O)_4]$ (Ln = Yb, Gd, Nd; NIC = nicotinic acid, C_5H_4NCOO), with dipicolinic acid [2] with the general formula $Na_3[Ln(DPA)_3]\cdot 14H_2O$ (Ln = Ho, Dy; DPA = dipicolinic acid, $C_5H_5N(COO)_2$)) and with dipicolinic acid and 2 - aminobenzothiazole with the formula $(ABT)_3[Eu(DPA)_3]\cdot 5H_2O$ (Ln = Eu, Tb). All new compounds were characterized by standard methods like chemical analysis, IR spectra, and magnetic measurements, while the structures were determined using single - crystal X-ray analysis.

The thermal stability of all complexes was measured by TG measurements with main emphasis on the complexes with Eu and Tb, which appear to be the most promising luminescent compounds. Both complexes decompose during several, partly overlapping stages. The obtained final decomposition products depend on the used atmosphere: in nitrogen flow, oxosulfides Eu_2O_2S and Tb_2O_2S were obtained while oxides (Eu_2O_3 and Tb_2O_3) were obtained in air flow or oxygen atmosphere. The measured temperature losses were in good agreement with values calculated from empirical formulas obtained by crystal analysis.

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DSC as a tool for determination of extremely low thermal conductivities of aerogels

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Many instruments are nowadays available to determine the thermal conductivity of materials. One of them is DSC, which was first proposed by Hakvoort and van Reijen [1]. In this method, the melting behaviour of a pure metal (e.g. indium) on top of a cylindrical sample or disk is measured. During heating, the metal reaches its melting point and the temperature remains constant while the metal melts. The temperature difference between lower end surface of the disk and the heat flowing into the disk are measured by the DSC and the thermal conductivity is calculated from the temperature difference and the heat flow. The research work presented in the paper describes this method for measuring the thermal conductivity of novel advanced materials – organic aerogels. Aerogels are materials with outstanding properties, high porosity, large surface area and low density. They are used in many application, like thermal insulators, capacitors, pharmaceuticals, food additives etc..

Polysaccharide aerogels (pectin, alginate, xanthan and guar) were first prepared by the novel process of ethanol-induced coagulation. Those alcogels were supercritically dried to retain the structure of the wet gel. Such dry materials, aerogels, were then measured by the HPDSC1 to determine their thermal conductivity. Aerogels were prepared in the form of disks with a height of 0.5 to 1.5 mm. The sample was then placed directly on the sensor and the crucible was placed at the top of the sample. Crucible was filled with 80 mg of indium. The sample was heated from 153 to 162 °C, 0.5K/min.

Ultralow thermal conductivity was observed for all samples. Thermal conductivity of high-methoxyl pectin was determined to be 28±0.2 $mWm^{-1}K^{-1}$, xanthan 30±0.2 $mWm^{-1}K^{-1}$, alginate 88±0.3 $mWm^{-1}K^{-1}$ and guar 95±0.3 $mWm^{-1}K^{-1}$. The lowest thermal conductivity was observed for low-methoxyl pectin aerogels. The conductivity is promising (20-24 $mWm^{-1}K^{-1}$) nevertheless it could be improved, for instance by making pectin-silica composites. Polysaccharide aerogels have been until now mainly used for pharmaceutical or biomedical applications. Those results on thermal conductivity show another possibility for using those materials as super-insulators.

DSC is thus not only a great method to determine the nature of the materials (amorphous, crystalline) and their degradation, but according to those results also the method for the precise determination of thermal conductivity of insulating materials.

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Decomposition pathway of aqueous glycolato-Ti(IV) precursors: an elaborated spectroscopic and thermogravimetric study

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An increasing interest for low temperature processing of oxide films requires fundamental insights into the underlying mechanisms of precursor decomposition and phase formation. To gather part of this knowledge, the thermo-oxidative transformation of a precursor towards the oxide can be investigated by means of spectroscopic (FTIR) and hyphenated thermogravimetric analyses (TGA-EGA).

In this work, we study aqueous glycolato(-peroxo)-Ti(IV) solution-gel precursors towards TiO_2 formation. Glycolic acid is the smallest α-hydroxy acid available. Although intrinsically having a low carbon content, the precursor decomposition and phase formation process is not as expected based on the global carbon content inside the precursor.

Varying the glycolic acid to Ti(IV) ion ratio, it is possible to influence the temperature window of decomposition. Moreover, the large exothermic contribution for a 4 to 1 glycolic acid:Ti(IV) ratio precursor allows to lower the total decomposition by 150°C compared to the a 1:1 ratio. The oxide formation path is also different for the different excesses, leading to different TiO_2 polymorphs at a fixed temperature. This indicates that a lower carbon content does not necessary result in earlier precursor decomposition or phase formation, stressing the importance of elaborated hyphenated thermogravimetric studies in general.[1]

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Colorimetric and thermal analyses of reversible thermochromic composites using crystal violet lactone as a colour former

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Three component leuco dye based thermochromic systems usually exhibit reversible colour change that is dependent on their component ratios [1–3]. The colour change is driven by interaction of a colour former and a developer in an environment formed by a co-solvent. The phase change of the co-solvent then determines the temperature at which the colour change appears [4]. However, in some complexes, a lower colour-change temperature than the melting point of the solvent was reported [3]. In our previous research [1–3], 1-alcohols with even carbon number were used. At the low temperature, alcohols have a crystalline structure that can be β-form or γ-form. Both crystalline phases transform to a solid α-phase [5] called also rotator phase [6, 7]. The solid–solid (rotator–crystal) phase transition exhibits a strong hysteresis comparing to solid–liquid phase transition [6]. On heating, the solid–solid and solid–liquid transitions of even alcohols are overlapped, whereas on cooling these transitions are clearly separated [7, 8].

In present study, our intention was to investigate how the colour change of thermochromic composites is connected with its phase transition. We have used crystal violet lactone as a colour former (molar ratio $x_{CVL} = 1$), bisphenol A ($x_{BPA} = 4$) as a developer and 1-tetradecanol as a co-solvent ($x_{TD} = \{60, 80, 100, 120\}$. The colour analysis was done by measuring the bulk thermochromic composites using i1Pro spectrophotometer. Phase transitions of pure co-solvent and thermochromic mixtures with varying concentration of the co-solvent were characterized by Pyris 1 Perkin Elmer instrument. The rate of temperature change during DSC measurements was 2 °C/min, which was similar to the rate during colour measurements.

The temperature at which the colour change stops (T_{DE}) is connected with the temperature of the solid–liquid transition of the thermochromic composites. However, these temperatures do not match. For the lowest concentration of the co-solvent, the T_{DE} is slightly higher than the melting point of the composite, while with increasing concentration of the co-solvent the T_{DE} becomes lower. Similarly, the temperature at which the colouration starts (T_{CS}) is connected with the solid–solid transition upon cooling. Also in this case, the T_{CS} is higher than the corresponding DSC transition peak for the lowest concentration and lower for thermochromic composites having the largest concentration of the co-solvent. This indicates that the concentration of the co-solvent influences the shift between temperatures characterizing the colour change and the temperatures characterizing the phase transitions.

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Thermal decomposition of heavy rare earth butanoates

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Rare earth butanoates can find applications as precursors for the manufacture of functional thin films, in particular in the field of high-temperature superconductivity. In this contribution, we present a detailed study of the conversion of heavy rare-earth butanoates ($RE(C_3H_7CO_2)_3$ RE = Er, Tm, Yb and Lu) to sesquioxides upon heating in a flow of argon gas.

Using a variety of techniques including simultaneous TG-DTA, evolved gas analysis, in-situ high energy (synchrotron) X-ray diffraction and hot-stage microscopy, it was possible to observe the formation of liquid crystalline and isotropic liquid states prior to decomposition. The main decomposition stage results in the formation of oxycarbonate compounds with release of a symmetrical ketone and carbon dioxide. Final decomposition is taking place with carbon dioxide release only.

The differences between the thermal behaviour of these heavy rare earth butanoates and previously studied light rare earth butanoates [1,2], in particular the absence of a detectable metastable intermediate product during the main decomposition stage, are highlighted. Further comparisons are made with the known behaviour of other heavy rare earth carboxylates such as propionates [3,4] and valerates [5].

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TA-MS and FTIR study of Mg^{2+} and glycine modified Ca-hydroxyapatite

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Calcium hydroxyapatite, (CHAp) is majority of the inorganic components of human bones and teeth. Bone is a biological nanocomposite, which organic part composed primarily of collagen. Collagen is tertiary protein, in which in sequences of amino acids every third position is glycine (Gly). Synthetic CHAp is known to be one of the most important implantable material due to its biocompatibility, bioactivity and osteoconductivity coming from the analogy to the mineral components of natural bones. Therefore interaction of Gly with synthetic hydroxyapatites has particular importance. Most of natural bio-apatites are non-stoichiometric because of the presence of minor constituents such as different cations (Mg^{2+}, Zn^{2+}, Na^{+}, Sr^{2+} etc.). Even on the level of traces these cations, introduced into structure of CHAp, change their physical and chemical properties [1, 2] which can play an important role in their interaction with biomolecules of living tissues.

In this research, the interaction of glycine with Ca- and Ca-Mg- apatites was studied and the role of Mg^{2+} in these interactions was evaluated. The Ca and Ca-Mg apatites were precipitated in aqueous Gly solutions. Thereafter, the TG/DTA combined with EGA/MS to follow the evolution of H_2O, CO_2, NH_3 and CH_4 as well as FTIR spectroscopy and XRD analysis were used to determine the composition of solid materials before and after thermal treatment. The obtained results were compared with the thermal decomposition data of mechanical mixtures of pure Ca- and Ca-Mg-apatite with glycine.

It was shown, that the thermal decomposition of Gly in both precipitates is similar, but occur at higher temperature than in the mechanical mixture of Gly and CHAp. Ca-Gly starts to decompose at 315 ˚C and Ca-Mg-Gly at 323 ˚C. FTIR analysis confirmed that for both samples obtained at 300 ˚C the absorption bands corresponding to Gly remain unchanged.

It is worth noting that the evolution of gaseous products is quite different for the two samples. The evolution of CH_4 in the Ca-Gly sample takes place in the temperature range of 350 - 700 ˚C in three stages; for the Ca-Mg-Gly sample, evolution of CH_4 proceeds in one step at 525 - 650 ˚C. The evolution of NH_3 follows very similar trend for both samples. The higher decomposition temperature of Gly showed that both samples are interaction products of Gly and apatite, but not mechanical mixtures of constituents. The results obtained also support supposition that the presence of Mg^{2+}in the system leads to more efficient interaction of glycine with apatite.

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Physical structure and stability tests of novel diketopyrrolopyrroles for organic solar cells

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The current trend in the organic electronics is the so-called "renaissance of color" - the developing of novel monomer dye structures such as diketopyrrolopyrrole (3,6-diphenyl-2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione) derivatives (DPP), isoindigo, benzodifuranones, etc., which are being modified and coupled to serve as the active materials themselves or as building blocks of them. The diketopyrrolopyrrole pigments are playing now a major role in organic electronics [1],[2]. Stability of DPP materials is a crucial issue for their further utilization, even if it would be a non-electrical one [2],[3],[4].

We have already examined the pyridyl substituted DPP isomers and it has been found, that the 4-pyridyl derivatives are more stable than the 2-pyridyl ones [5]. Further, the *N*-alkyl substituted derivatives of the staple DPP have been studied, with the result, that alkyl substituted DPPs show lower thermal stability, while the stability is increasing with the length of the alkyl chain, but is lowered, when the substitution is symmetrical [2]. Recently we have found, that morpholinyl and piperidyl DPP derivatives generally showed high thermal stability and evaporation onsets slightly lower than the degradation onset and seem to be suitable for thin layer vacuum deposition [6]

Compared to our previous results, we continue in thermal analysis of novel synthesized stilbene–triphenylamine [7] and *N*,*N*′-dinitrophenyl-substituted [8] DPP derivatives.

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Thermal melting of protein bets sheet crystals

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The remarkable stability that makes silk useful in garments and surgical sutures has impeded efforts by scientists to study its thermo-physical properties. Here, we use fast scanning chip calorimetry and report the first reversible thermal melting of protein beta-pleated-sheet crystals, exemplified by silk fibroin. Heating nanogram-sized samples at 2000 K/s, allowed us to avoid thermal decomposition, and demonstrate that beta-pleated-sheet crystals melt to become random coils, helices and turns. We establish that following melting silk can be recrystallized into beta-pleated-sheets, and remelted.

The similarity between thermal melting behavior of beta-pleated-sheet crystals and crystals of synthetic polymers is confirmed. Significance for controlling beta-pleated-sheet content during thermal processing of biomaterials is envisioned based on these findings. Demonstration of reversible thermal transitions in silk, the most beta-pleated-sheet-enriched and stable protein, suggests important new insights can also be gained with the broader range of proteins where beta-pleated-sheets serve as critical control points in structural transitions.

Thermogravimetric stability of HDPE reinforced with lignocellulosic fibers

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Due to the increasing environmental awareness, natural fiber composites are becoming more prevalent in use. A recent study, referring to the widespread use of natural fiber based composites, mentions that in 2010 their total global shipments topped a value of US$ 289.3 million, while the market is expected to grow to US$ 531.3 in 2016 [1]. Overall, natural fibre composites are seen as potential materials for many engineering applications, since they exhibit low density, low specific weight, ease of shaping, low energy consumption, good thermal and insulation properties along with acceptable strength, toughness and stiffness. However, much remains to be done in terms of the poor compatibility between hydrophilic fibers and hydrophobic matrices, the high moisture absorption and the degree of dispersion of the fibers into the matrix.

The aim of this study is to compare a series of unmodified HDPE-based composites regarding their thermal stability by means of Thermogravimetric Analysis (TGA). The aforementioned composites, containing 10, 20 and 30 wt% of kenaf, hemp, ramie and flax as fillers, were prepared by melt mixing.

Mass loss curves of all the composites lie in the region between neat HDPE and the corresponding fiber, while a gradual shift of the total curves towards lower temperatures is displayed with increasing fiber content, influencing negatively their thermal stability. Nonetheless, each composite's thermal performance depends mainly on its fiber's distinct chemical composition. Generally, fibers contain cellulose, hemicelluloses, lignin, pectin and waxes, while the properties of each constituent contribute to the overall properties of the fiber [2]. Hemicellulose is responsible for the moisture absorption and the least thermal resistance, whereas higher cellulose content of fibres enhances the thermal stability of composites. Indeed, ramie-based composites -the fiber with the lower content in hemicelluloses and the greater content in cellulose- exhibits the highest onset degradation temperature.

Acknowledgement:

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Study of UF resins for particleboards strengthen with MWCNTs modified with amino-groups on their surface

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Carbon nanotubes are minuscule allotropes of carbon having sizes to the scale of nanometres. The product types include single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT). Carbon nanotubes enabled nanotechnology to become one of the most sought-after technologies and have made a huge impact on a wide range of applications. Today, carbon nanotubes are the fastest growing segment in nanomaterial technology market across the globe. The global CNTs market's revenue was estimated to be worth $926.3 million in 2012, which is expected to reach $2,398.4 million by 2018, growing at a CAGR of 15.5% from 2013 to 2018.

In this study, MWCNTS modified to their surface with amino groups were used as reinforcing materials of typical urea-formaldehyde (UF) resins. The amino-MWCNTS were prepared by the Aristotle University of Thessaloniki, while the new resins were synthesised by CHIMAR HELLAS S.A. The modified MWCNTS were added during the synthesis of the resin, at the level of 1%w/w under vigorous blending. This resin was evaluated against a typical UF resin (control). The resins were compared for their adhesive strength via their application in the lab production of particleboards having density of 680kg/m^3 and prepared according to the industrial practice.

It was found that the experimental resin had properties close to that of control. In particular, the use of amino groups-modified MWCNTS resulted in resins having somewhat higher pH, buffer capacity and gel time, but lower water tolerance. The maximum curing temperature of the experimental resin was also slightly shifted to lower values than the control while both resins were losing mass practically with the same rate according to Thermogravimetric Analysis (TGA) studies.

The particleboards were firstly conditioned and then subjected to tests for the evaluation of their mechanical properties, dimensional stability (thickness swelling) in humid conditions and formaldehyde content according to the relative European standards. It was found that amino modified MWCNTS improve the internal bond while leave all other properties practically at the same level of the control UF resin. Such panels are suitable for the manufacturing of furniture and other interior applications.

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Conformation and polymorphism in iodinated contrast media

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One of the challenging issues in drug development is given by the kinetics of interconversion among the several conformational species and, therefore, the conformational changes that can occur during their solubilization; in particular, hindered rotations give rise to metastable conformational isomers in solution (atropisomerism). Among all examples, the non-ionic iodinated contrast media (NICM) [1] are particularly relevant since are widely used for diagnostic purpose. Despite the high concentration, required to provide satisfying quality images, the NICM solutions are characterized by a relatively low osmolality and viscosity, in a state of an apparent oversaturation [2]. A peculiar aggregation at the border-line between supersaturation and primary nucleation has been proposed. Thermodynamic and spectroscopic investigations carried out so far put in evidence that both intermolecular association and conformational phenomena with a balance of polar and non-polar interactions govern the solution properties of NICM [3,4].

New results are presented on the investigation on some solid state properties of iopamidol contrast media by differential scanning calorimetry (DSC), X-ray diffraction (XRD) and Raman spectroscopy. Raman and X-ray diffraction experiments identified the crystallographic structures of three different polymorphs: anhydrous, monohydrate and pentahydrate. The comparison of the structural, spectroscopic and calorimetric results aim at providing potential guidelines for the implementation of atropisomerism phenomenon in the case of contrast media. The major interest for the more general applications in pharmaceutical field is understanding whether atropisomeric molecules may co-crystallize with some solid state disorder or one form only is selectively crystallized from the solution mixture of atropisomers.

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Isothermal dehydration of biological systems by DSC

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The state of water and its physical changes in natural and model systems during isothermal dehydration has been investigated, by means of a novel microcalorimetric set-up. The new application of the DSC technique has been recently developed in order to provide information about the thermodynamics and the kinetics of water evaporation in isothermal conditions. Under quasi-thermodynamic conditions and fixed boundary terms, the apparent water activity is determined during dehydration, namely as a function of the water fraction of the sample [1, 2, 3].

The experimental parameters controlling the dehydration in isothermal condition have been investigated. A calibration curve with $CaCl_2$ has been identified to correlate heat flow and water activity. The technique allows to distinguish the dehydration behavior of model samples of aqueous solutions and gels, on the basis of their capability of binding water.

An extension of the technique to a wide range of substrates such as vegetable thin tissues and cell monolayers is presented and discussed. The actual value of this novel experimental approach is the determination of the “apparent” water activity values for a wide range of systems over the full range of water content and within a short experimental time-window (from minutes to few hours).

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Composite Biomaterials based on Pectin and Coffee Ground

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The low performance of environmentally friendly biopolymers from renewable resources like chitosan, chitin, cellulose, starch, pectin, etc. is hindering their use in some applications such as, for example, packaging. However, they are the most important and interesting candidates to be considered alternative to plastics in several applications.

One of the most used strategy to enhance the performance of a polymeric material is the use of particles as fillers. As a general feature, even these fillers have to be sustainable, biocompatible, green, available at low cost, etc. For this reason, we prepared and characterized biocomposites based on pectin and coffee grounds (Fig. 1).

They are interesting materials for many reasons, not least because they are also edible and therefore useful for food packaging.

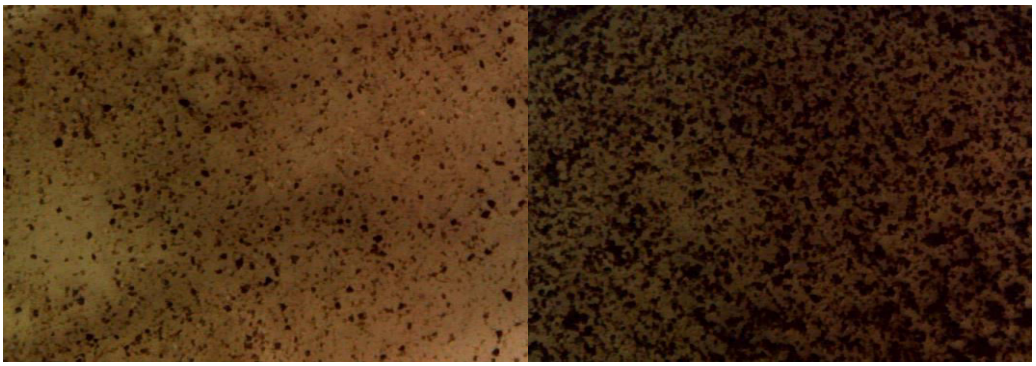

Figure 1. Optical micrographies (x230) of the biocomposite *films* at 9% w/w (left) and 38% w/w (right).

The nanocomposites were studied through thermal stability, dynamic mechanical analysis, wettability and the optical microscopy.

The "pectin-coffee ground" hybrid films were subjected to curing for thirty days at 55±3% of Relative Humidity, 25±1°C under UV irradiation.

The collected parameters allowed us to deduce that these films are very promising. In particular, the Young modulus of the hybrid "Coffee 9%" is much better than that of pristine pectin. The ultimate tensile strength and the fracture strain are improved by adding 9% w/w coffee ground to the pectin film. Also, the hydrophobicity of the hybrid films is enhanced as well as the resistance to atmospheric agents.

Thermal Decomposition of Metal N,N-Dialkylcarbamates: TG-FTIR and X-Ray Diffraction Studies

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N,N-dialkylcarbamates represent a class of compounds of relatively recent acquisition; they contain the $[O_2CNR_2]^-$ ligand which is uninegative and substantially planar, due to extensive charge delocalization. The preparative aspects of these compounds have been reviewed extensively [1].

Most of the metal *N,N*-dialkylcarbamates are thermally robust compounds but in some cases, as for carbamates of high valent transition metal cations, reduction of the metal is observed on moderate heating depending on the nature of the R group on nitrogen [2].

In this work thermogravimetric analysis coupled to IR spectroscopy has been used to investigate the thermal stability and the decomposition products of *N,N*-dialkylcarbamates of zirconium(IV), hafnium(IV) and niobium(IV), $M(O_2CNR_2)_4$. DTA and TG techniques were in fact successfully used to describe the thermal behaviour of alkali, alkaline earth metal and silver carbamates [3].

We found that the $Nb(O_2CNR_2)_4$ compounds are less stable than the corresponding Zr(IV) and Hf(IV) derivatives and the thermal stability is in the order R = Et > ^{i}Pr > Me; *i.e.*, *N,N*-dimethylcarbamates being the less stable of the series.

The thermal decomposition generally starts with loss of CO_2 below 100°C and it continues with a main decomposition step in the temperature range 200-300°C with the evolution of CO_2 and amines. On increasing the temperature, *N,N*-dimethyl- and *N,N*-diethylcarbamates produce *N,N*-disubstituted formamides or tetralkylureas during the main decomposition step.

N,N-diisopropylcarbamates and $Hf(O_2CNEt_2)_4$ show the simplest degradation pattern due to the high volatility of these mononuclear species which readily sublime in vacuo). Formation of volatile species accounts the low values of the residual mass obtained at 600°C.

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Energetics and structural insights on the *o*-hydroxyacetonaphthone isomers

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The formation of intramolecular hydrogen bonds (IMHB) in organic compounds provides them biological interactions and photophysical properties with a multiplicity of applications in various scientific and technological fields. The *o*-hydroxyacetonaphthone isomers (structural formulae presented in Fig. 1) present a close proximity and orientation of the carbonyl oxygen towards the hydrogen of the hydroxyl group, enabling the formation of an IMHB [1]. Generally, upon photo-excitation of these compounds a fast acid-base reaction can occur via the IMHB resulting in a tautomeric transformation from the ground state enol form to an excited keto form. This process is known as excited state intramolecular proton transfer (ESIPT). Compounds displaying ESIPT phenomena are drawing considerable attention due to their unique properties which facilitate novel optoelectronic applications, particularly focusing on chemical sensors, fluorescence imaging, proton transfer lasers, and organic light-emitting diodes (OLEDs); furthermore, they are also used as fluorescence probes on microenvironments of biological systems.

Energetic and structural studies regarding the isomers 1'-hydroxy-2'-acetonaphthone and 2'-hydroxy-1'-acetonaphthone were performed based on both experimental and computational research. The massic energy of combustion and the vapour pressures at different temperatures were measured by static bomb combustion calorimetry and Knudsen mass-loss effusion techniques, respectively. For the computational studies, the G3(MP2)//B3LYP method was used, since it is an appropriate theoretical procedure for this class of compounds. The combination of experimental and computational data enabled the determination of the enthalpies, entropies and Gibbs energies of sublimation and formation of these compounds, both in the crystal and gas phase. The IMHB energetics *o*-hydroxyacetonaphthone isomers and their corresponding tautomeric structures will be also analysed.

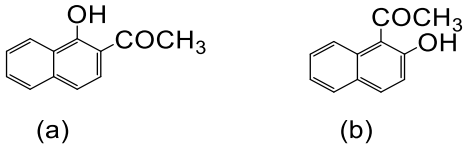

Figure 1. Structural formulae for 1'-hydroxy-2'-acetonaphthone (a) and 2'-hydroxy-1'-acetonaphthone (b).

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Properties of pure and modified starch materials

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Starch is a carbohydrate with occurs in plants only and it is storehouse of energy. This is a supplementary material and it is collected in this form by plants in a photochemical carbon dioxide adsorption. The physical properties of starch, chemical reactivity and susceptibility to enzymes do not depend only on external factors (the weather, soil quality and fertilization) but also on the weather conditions during harvest, drying and storing of grains. These properties also depend on internal factors (the ratio of amylase to amylopectin, humidity, trace protein, lipid and mineral salts contaminants). The physical properties of starch, chemical reactivity and susceptibility to enzymes do not depend only on external factors (the weather, soil quality and fertilization) but also on the weather conditions during harvest, drying and storing of grains. These properties also depend on internal factors: the ration of amylase to amylopectin, humidity, trace protein, lipid and mineral salts contaminants.

The aim of this study was to investigate the physicochemical properties of selected samples of pure starch and subjected to extrusion process. Commercial starch containing 0.26% ash, 0.02 % proteins and 0.03 % fat with the moisture 19.5% has been extruded The atomic force microscopy (AFM) has been used for obtaining the pictures of the sample surfaces and to determine the fractal coefficients. Thermogravimetry data were used for the calculation of adsorption capacity and desorption energies (energetic heterogeneity) of adsorbed liquids on starch surfaces. The Q-TG and Q-DTG curves were obtained by means of programmed liquid thermal desorption in quasi-isothermal conditions which were further used for determination of desorption energies and desorption heats, statistical number of liquid monolayers and adsorption capacities [1].

Sorptomatic measurements were used for estimation specific volumes and specific surface areas, total pore volumes, means radius of pores together with volumes distribution against pore radiuses. Low-temperature adsorption-desorption isotherms of nitrogen and fractal coefficients have been estimated, too. Geometric heterogeneity of samples as their cracks, roughness of the surface, coarseness and porosity has bees described using nitrogen method whilst energetic heterogeneity was described using programmed thermal desorption technique. It was allowed to assess and estimate total heterogeneity of the starch and their extrusion products. Based on these data the character and physicochemical properties of surface of examined samples was deduced.

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Synthesis and Thermal Behaviour of Triblock Semifluorinated n-Alkanes

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A series of semifluorinated long chain alkanes of the general formula: $H(CH_2)_m(CF_2)_6(CH_2)_mH$, abbreviated as $H_mF_6H_m$, where m = 12, 14, 16, 18 and 20, have been synthesized in two steps, by radical addition of 1,6-diiodoperfluorohexane $I(CF_2)_6I$ to two equivalents of an appropriate terminal alkene $CH_2=CH(CH_2)_{m-2}H$, followed by subsequent deiodination.

Phase polymorphism of the synthetized compounds was investigated both upon heating and cooling, in the temperature range of 270-360 K, using differential scanning calorimetry (DSC). Additionally, polarized optical microscopy (POM) was applied in order to identify the phases and characterize of the phase transitions on the base of their textures.

In the investigated temperature range the compounds exhibit rich phase polymorphism, including different types of liquid crystalline phases (e.g. smectic A, smectic B and smectic E). From DSC results it can be concluded that for compounds with m = 16, 18 and 20 all phase transitions (crystalline ↔ smectic, between smectic phases, smectic ↔ isotropic) shift toward higher temperature with increasing the length of the hydrocarbon chain. The phase situation for compounds with m = 12 and 14 is slightly different. However, for all the investigated compounds it can be observed that the longer hydrocarbon chain, the higher temperature of the phase transition to the isotropic phase. No metastable phases were observed.

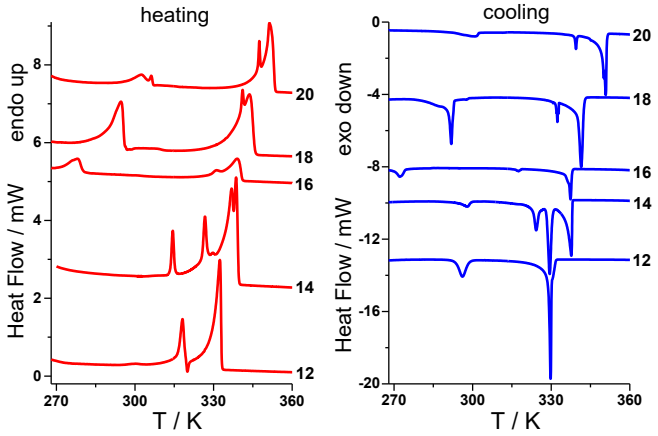

Fig. 1 DSC curves of $H_mF_6H_m$ (m = 12, 14, 16, 18 and 20) samples registered during heating and cooling with a scanning rate of 2 $Kmin^{-1}$

Calorimetric investigation on wax precipitation in diesel fuel modified by gemimi surfactants

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Nowadays, several research are devoted to improve the properties of fuel which determine long and efficient work of engine. The blocking problem in car engine caused by precipitation of long chained hydrocarbons at low temperatures is well-known and it can cause dangerous failure of facilitie s. Wax deposition can be prevented, delayed, or minimized by the use of different kind of dispersants or crystal modifiers which keep the wax nuclei from agglomerating and minimize the tendency of the wax to adhere [1].

In the last period of time the use of gemini surfactant as a fuel wax dispersant has evolved considerably, mainly due to their high efficiency in reducing the tendency of the wax to adhere and low cost [2].

In this work we presented the influence of different additives from gemini surfactants group on wax deposition in diesel fuel. In our work we used the DSC technique to study wax solidification and the interaction between gemini surfactants additives and waxes. The measurements were done in the temperature range 253.15-308.15K. We analysed the effect of different additives, differ with structure and aggregation ability, on diesel fuel behaviour at low temperature.

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Application of differential scanning calorimetry to optimisation of transport conditions for perishable food

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There is no doubt, that conditions of transport and storage for perishable food is one of the most important factor to preserve the food in a good condition. One of the most urgent need of the transport sector concerns the research and development of new thermal insulation materials which allow to make the transport process the more efficient.

Different heat capacities of various group of perishable products and their temperature dependences play a key role in the optimisation of transport conditions. In spite of the fact, mentioned factors are often not taken into consideration in choosing the thermal insulation parameters for a truck freezer.

The main aim of the work was the investigation of the influence of the thermal dependences of heat capacity for perishable food on choosing thickness and type of insulating material. Mentioned parameters of insulating material are crucial because they determine stream of heat transfer through the walls of the body depending on the difference of temperatures outside and inside the body.

For that reason the heat capacities for different group of perishable products within 253.15–288.15K temperature range were investigated by means of Differential Scanning Calorimetry. On the basis of the result obtained, we created the algorithm which allows to select the optimal parameters of insulation materials used in cooling trailers construction.

Study of thermal properties of photoluminescent dimethacrylate derivative of naphthalene-2,7-diol

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In recent years, the development of polymeric-based photoluminescent materials is observed. Such materials can be used as information displays, in electrophotography, lighting, X-ray intensification and scintillation or for solar energy conversion. [1,2] Naphthalene derivatives are often used as a luminescent material due to their unusual properties such as intense fluorescence, strong π-stacking and good physico-chemical stabilities. [3] Therefore, naphthalene derivatives have been applied e.g. as luminophores in optical devices [4], polymeric light-emitting diodes (PLEDs) [5] or organic semiconductors [6].

In this article, synthesis and thermal properties of photoluminescence copolymers are presented. The copolymerization of 2,7-(2-hydroxy-3-methacryloyloxypropoxy)naphthalene (2,7-NAF.DM) [7] with different commercial vinyl monomers such as: 2-hydroxyethyl methacrylate (HEMA), butyl acrylate (AB), divinylbenzene (DVB), styrene (ST) was performed. As a initiator α,α'-azoiso-bis-butyronitrile (AIBN) was used. The influence of the crosslinking agent's used on the physico-chemical properties of the obtained copolymers were examined. ATR spectra were used to characterise chemical structure of the materials. Thermal stabilities and degradation behaviours of the obtained copolymers were studied by means of differential scanning calorimetry (DSC) and thermogravimetric (TG/DTG), in inert and oxidative atmospheres.

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Copolymerization and thermal study of the new methacrylate derivative of 2,4,6-trichlorophenole

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PMMA is a commercially available polymer which is the most used in the optical fiber technology. Polymeric optical fibers (POFs) have some good properties such as low cost, high ductility, large core-diameter and easy handling characteristics. Besides, relatively low glass transition temperature (T*g*), high water absorption and limit of its usability for optical electronic applications are the main disadvantages of PMMA [1].

The mentioned drawbacks of PMMA cause that there is still a need for new polymers with increased transparency and processability. Already designed polymers include polysiloxanes [2], fluorinated polyimides [3] and perfluorocyclobutane aromatic ether polymers [4]. Therefore, the synthesis of the new halogenated compounds were carried out.

2,4,6-Trichlorophenyl methacrylate (TClPhMA) (Fig 1.) was synthesized by reaction of methacryloyl chloride with 2,4,6-trichlorophenol in the ice bath condition. The obtained monomer was extracted by chloroform and purified on chromatography column. Spectroscopic studies (FT-IR, ^{1}H-NMR, ^{13}C-NMR and GC-MS) were investigated.

Next, the obtained new monomer (TClPhMA) was copolymerized with commercially available monomers such as: methyl methacrylate, styrene, divinylbenzene and 2-hydroxymethyl methacrylate. The copolymers were obtained by bulk polymerization. The thermal properties of the copolymers were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

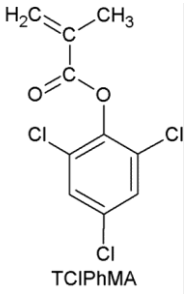

Figure1. Chemical structure of the 2,4,6-trichlorophenyl methacrylate (TClPhMA)

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Interaction between new platinum(II) complex with tris(2-carboxyethyl)phosphine and biomolecules

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Since antitumor activity of *cis*-$[PtCl_2(NH_3)_2]$ (*cis*-DDP) was first discovered by Rosenberg [1] very intense investigation of platinum-based antitumor chemotherapeutics begun. Platinum compounds are very effective in the treatment of ovarian and testicular cancers and in combinations with other antitumor agents are used in the therapy of many carcinomas, e.g. bladder, small lung, head and neck tumors.

The subject of the research was newly obtained platinum(II) complex with tris(2-carboxyethyl)phosphine (TCEP): *cis*-$[PtCl_2(TCEP)_2]$. Synthesis and properties of this compound was reported earlier [2]. In this study, the interaction of platinum complex with biomolecules (phospholipids, albumin and DNA) was investigated with the help of calorimetrical methods (DSC, ITC) and spectroscopy. Additionally the effect of *cis*-$[PtCl_2(TCEP)_2]$ on plasmid DNA was investigated using single-molecule fluorescence technique and time-correlated single photon counting fluorescence correlation spectroscopy (TCSPC-FCS) [3].

Microcalorimetric experiments demonstrated that *cis*-$[PtCl_2(TCEP)_2]$ slightly increases the phospholipids main phase transition temperature and decreases cooperativity in all model lipid/compound systems. These results together with results of fluorescence spectroscopy suggest that investigated complex slightly interacts with lipids and locates itself mainly in the hydrophilic part of the lipid bilayer, which would be different comparing to the *cis*-DDP which enters cells by passive diffusion and forms stable adducts with DNA [4].

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The use of a DSC in the Institute of Agricultural Engineering of Wrocław University of Environmental and Life Sciences is gratefully acknowledged. This work was sponsored by the statutory activities of the Department of Physics and Biophysics of Wrocław University of Environmental and Life Sciences.

Influence of cytotoxic butyltin complexes with 2-sulfobenzoic acid on the thermotropic phase behavior of lipid model membranes

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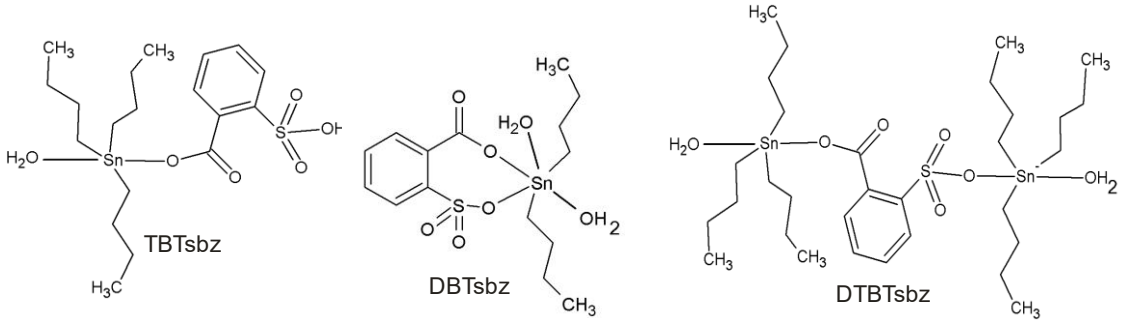
In the previous study we showed that butyltin complexes with 2-sulfobenzoic acid: TBTsbz, DBTsbz and DTBTsbz (commonly referred to as BTsbz) are very active cytostatic agents against tumor cells and antibacterial agents against Gram-positive and Gram-negative bacteria [1].



The aim of this study was to investigate relationship between the biological activity of those complexes and their thermal effects related to lipid model membrane. The effects of BTsbz on thermotropic phase transition of phospholipids were studied by means of differential scanning calorimetry (DSC) and steady-state fluorimetry. These combined methods allow us to track the changes caused by butyltin complexes in different regions of the phospholipid bilayer.

We analyzed the effect of the BTsbz on temperatures of the main transition (T_m) and pretransition (T_p) in the phospholipid phase of the bilayer. All investigated compounds change the thermotropic properties of lipid model membranes. Obtained results show that these complexes slightly change T_m and very much reduce transition's cooperativity. Probably BTsbz concentrate in the hydrophilic area of the lipid bilayer and do not penetrate of the acyl chain region of the bilayer.

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This work was sponsored by the statutory activities of the Department of Physics and Biophysics of Wrocław University of Environmental and Life Sciences. The use of a DSC in the Institute of Agricultural Engineering of Wrocław University of Environmental and Life Sciences is gratefully acknowledged

Thermodynamic properties of phase transitions in $[Ni(DMSO)_6](ClO_4)_2$ and its deuterated analogue

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The differential scanning calorimetry (DSC) measurements performed for non-deuterated $[Ni(DMSO)_6](ClO_4)_2$ in the temperature range of 298-530 K indicated very rich and interesting phase polymorphism of this compound (solid line in Fig. 1) [1]. The crystallization by cooling of this compound undergoes in a specific way because some of its phases can be very easily supercooled, and become the metastable phases. It was concluded from the enthalpy changes values, that some of these phases are so called: "orientationally dynamically disordered crystals" (ODDIC) and the other phases are more or less ordered.

The $[Ni(DMSO\text{-}d_6)_6](ClO_4)_2$, was synthetized and next characterized using DSC, for researching which of the observed phase transitions are connected with a change of the reorientational dynamics of the DMSO ligands. On the basis of the obtained results we can conclude that in the deuterated analogue all observed phase transitions are slightly shifted towards higher temperatures (dash lines in Figs. 1 and 2). We can also noticed that the high temperature phase transition is connected with a large change of the entropy value (more than 20 $Jmol^{-1}K^{-1}$), what can suggest existence of a rotational phase (plastic crystal) in this state.

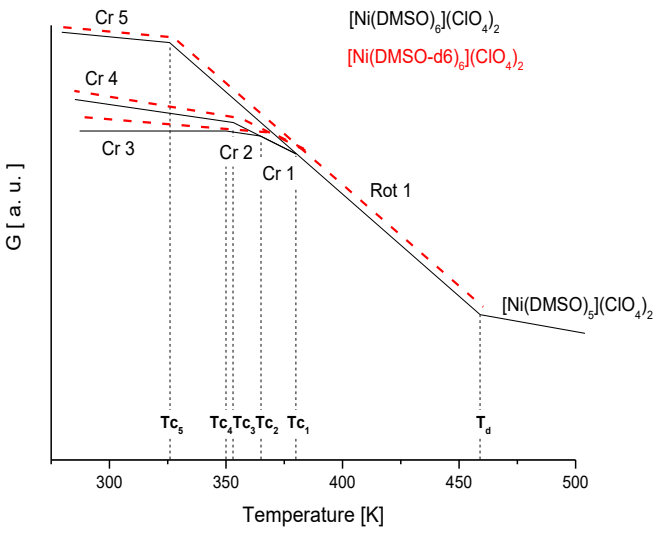

Fig. 1. Scheme of temperature dependence of the free enthalpy G of $[Ni(DMSO)_6](ClO_4)_2$ and its deuterated analogue

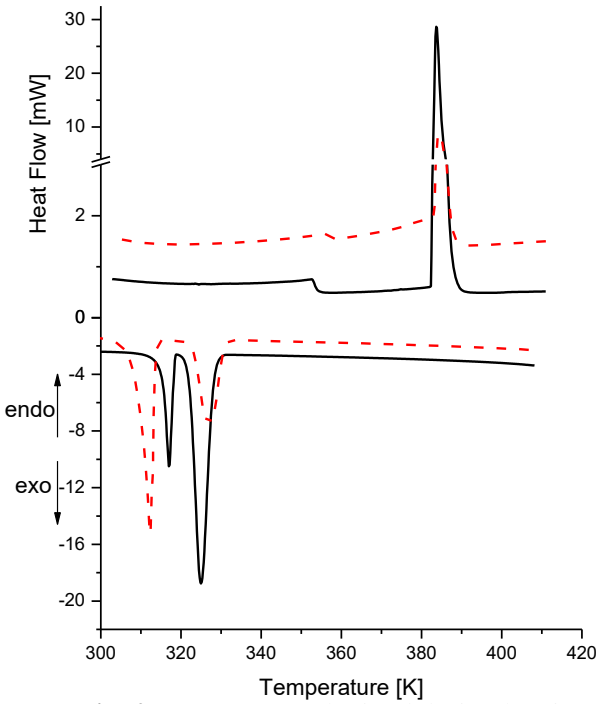

Fig. 2. DSC curves obtained during heating and cooling of $[Ni(DMSO)_6](ClO_4)_2$ and its deuterated analogue

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Thermoanalytical data supported by multivariate analysis as an efficient strategy for detection of incompatibilities between ingredients of solid dosage formulations

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Incompatibilities between active pharmaceutical ingredients and excipients are the reason for degradation of a drug substance, which so decreases its quantity that proper therapeutic effect cannot be obtained. Furthermore, the products that appear as a result of chemical reactions can be dangerous due to potential toxic effects. According to this, the objective of this work was to evaluate the utility of two mostly used multivariate techniques, principal component (PCA) and cluster (CA) analyses as an efficient strategy for detection such incompatibilities, which sometimes occur during the preformulation stage of a solid dosage forms (tablets, capsules, granules, powders).

The physical and chemical incompatibilities between selected active pharmaceutical ingredients (acetazolamide, piroxicam, and hydrocortisone) and excipients (magnesium stearate, methylcellulose, mannitol, lactose, meglumine, chitosan, polyvinylpyrrolidone, starch, and β-cyclodextrin) were tested by the thermoanalytical and spectroscopic techniques. The binary physical mixtures of active pharmaceutical ingredients and excipients at the mole or mass ratios of 9:1, 7:3, 1:1, 3:7 and 1:9 were prepared by mixing adequate quantities of both substances in porcelain mortar. For detection of physical and chemical interactions in the active pharmaceutical ingredient – excipient mixtures, thermogravimetry (TG), differential scanning calorimetry (DSC), IR spectroscopy and X-ray powder diffraction (XRPD) techniques were used.

Graphical interpretation of the results showed that in the PCA plot, both substances alone, and their physical mixtures do not create clear clusters. All samples are located along PC1 axis, beginning from the single substance located at the most negative value of PC1, through the following mixtures with gradually diminishing concentration of the first substances, and increasing content of the second one, until the second substance located close to the most positive values of PC1. In the CA dendrogram the lack of interaction between both substances is identified by two large clusters, from which one groups excipient and physical mixtures with high concentration of excipient. The second cluster is an active pharmaceutical ingredient and mixtures with high content of this substance.

The investigation performed with the use of selected active pharmaceutical ingredients and excipients showed that PCA and CA proved their role as an efficient tool in the interpretation of the data recorded in thermoanalytical methods. Based on multivariate analysis it is possible to detect incompatibilities between active pharmaceutical ingredient and excipients, and the obtained data concur highly with the results of DSC, IR and XRPD analyses.

Green rigid polyurethane foams from rapeseed oil-based polyol

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Polyurethane foams are commonly used in a variety of industries *e.g.* furniture, automotive, construction, and cosmetics industry [1,2]. According to statistics published in 2013, the global market for polyurethane foams amounted to 40.1 billion dollars in 2012 and is estimated to grow to 61.9 billion dollars in 2018 [3]. The high demand for this type of materials generates the need for the introduction of renewable raw materials as a replacement for petrochemical polyols, both for economic and environmental reasons [4].

The aim of the study was the determination of the influence of the rapeseed oil-based polyol content on the properties of obtained rigid polyurethane foams as well as the evaluation of the obtained products with respect to industrial applicability. The selection of the optimal product was based on the optimisation of the renewable substrate content and the application properties in order to develop a valuable environmentally-friendly material.

Rigid polyurethane foams were fabricated using the rapeseed oil-based polyol and the petrochemical polyols, which were tested using differing weight ratios. Investigation of the thermal degradation was performed using thermogravimetric analysis techniques and differential scanning calorimetry was used to determine the phase-transition temperatures and the thermal effects. Chemical composition of rigid polyurethane foams was examined by IR absorption spectrosopy. Dimensional stability, apparent density, water absorption, friability and changes in aging were determined in accordance with International Standards.

Acknowledgement:

The study has been financed by the National Research and Development Centre within the framework of the project EPURNAT PBS1/B5/18/2012.

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An interesting route for mononuclear into polynuclear zinc complex conversion

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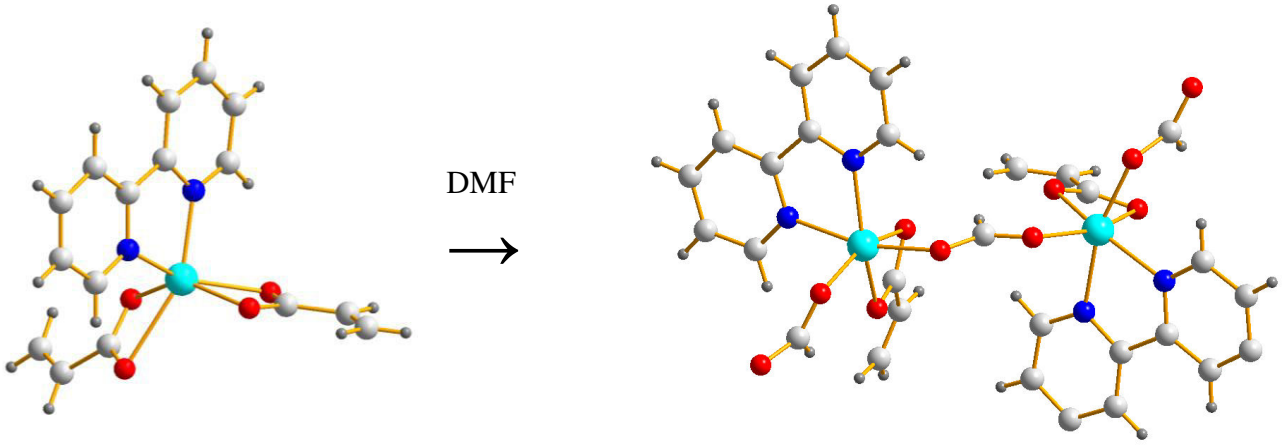
It is well known the ability of zinc ion to catalyse a lot of chemical or biochemical reactions. This fact is due to the special position of zinc in the first-row transition metals, having the 3d orbitals full occupied. This electronic configuration confer it a high stability, being unable to participate in redox reaction but rather functions as Lewis acid. Moreover, the zinc ion has no strereochemistry preference, its crystal field stabilisation energy being zero.

The results of this research are based on catalytic activity of zinc ion from a mononuclear complex, [Zndipy(acr)$_2$] over dimethylformanide, which was converted to formate ion. The reaction occurs in the presence of melamine and the obtained carboxylate ion coordinates as bridge leading to a polynuclear complex. The new compound was characterized by elemental analysis, IR and UV-Vis spectroscopy and thermal studies.



Synthesis, thermal analysis and biological characterisation of some new nickel (II) complexes with acrylate and benzimidazole

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In context of our current research work concerning synthesis of complexes with acrylate as ligand, we have investigated the use of benzimidazole derivatives as ligands as well. Therefore, we report herein the synthesis, thermal behavior, structural and biological characterization of four new coordination compounds with acrylate (acr) accompanied by benzimidazole (HBzIm), 2-methylbenzimidazole (2-MeBzIm), 5-methylbenzimidazole (5-MeBzIm), 5,6-dimethylbenzimidazole (5,6-Me_2BzIm) of type: $[Ni(HBzIm)_2(acr)_2]\cdot 3H_2O$ (**1**), $[Ni(2\text{-}MeBzIm)_2(acr)_2(H_2O)]\cdot 1.5H_2O$ (**2**), $[Ni(5\text{-}MeBzIm)_2(acr)_2(H_2O)]$ (**3**) and $[Ni(5,6\text{-}Me_2BzIm)_2(acr)_2]$ (**4**).

Their chemical formulation was achieved on results provided by chemical analysis and thermal analysis data, the coordination modes of the ligands were assigned by FTIR measurements, the octahedral geometry of Ni(II) in complexes were assigned on the basis of NIR-UV-Vis spectra and magnetic moments measurements. The biological assays were performed on several microbial strains, and the cytotoxicity was evaluated on HeLa cellular lines. Biological investigations indicated that Co(II) complexes were more active than Ni(II) ones against *Candida albicans 1760, Enterococcus faecium E5, Bacillus subtillis ATCC 6683, Escherichia coli ATCC 25922.*

Thermal decomposition of $C_6H_{10}Ge_2O_7$

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$Ge_2C_6H_{10}O_7$ raised a high interest as a dietary supplement, as a drug with anticancer and other activities [1-3]. It was synthesized in 1967, and proved to have a very low toxicity [4].

Due to its effectiveness as an addition to MgB_2 superconductor [5], a new application of $Ge_2C_6H_{10}O_7$ is anticipated. Understanding the thermal behavior of the addition presents a great interest, as it is used in sintering of MgB_2 up to 1150 ^oC.

In this work we studied the thermal behavior and phase transformations of $Ge_2C_6H_{10}O_7$, based on differential scanning calorimetry and thermo-gravimetric analysis (DSC-TGA, SDTQ600, TA Instruments, in argon, 10 ^oC/min). We also employed X-Ray Diffraction (XRD, Bruker-AXS D8 ADVANCE, $Cu_{K_{\alpha 1}}$ radiation, λ = 1.54056 Å) and Fourier Transform Infrared Spectroscopy (FTIR, JASCO 4200, 350-4000 cm^{-1}) for sample characterization.

The results show a complex decomposition of $Ge_2C_6H_{10}O_7$, in 5 stages, preceded by a reversible transformation, without mass loss, at ~192 ^oC. XRD and FTIR data of our samples, taken at room temperature, support our proposed transformation/decomposition scenario.

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Application of thermal analysis methods for damage assessment of leather in an old military coat belonging to History Museum of Braşov - Romania

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The scope of this work has been the assessment of the hydrothermal stability, crystalline zone deterioration and thermo-oxidative deterioration of the leather samples from the military coat from 16^{th}-17^{th} century located in the History Museum of Braşov-Romania. In this purpose, the differential scanning calorimetry (DSC) and thermogravimetry/derivative thermogravimetry (TG/DTG) methods have been employed. The hydrothermal stability is characterized by shrinkage temperature determined by DSC analysis of leather samples in water excess. The damage of crystalline zone of leather samples has been determined by DSC analysis in nitrogen flow. The thermo-oxidative damage of investigated leather samples has been characterized by the rate of the first thermo-oxidation process put in evidence in TG/DTG curves recorded in static air atmosphere. The qualitative damage for each leather sample and each kind of deterioration has been evaluated using the criteria resulted by thermal analysis of a large number of collagen-based materials (pure collagens, new and old parchments and leathers) [ ].The obtained results could facilitate the choice of the restoration and conservation procedures applicable for the investigated military coat.

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Synthesis, structure, TG+FTIR analysis and solid-state conversion to ZnO of new coordination compounds constructed from Zn(II), Bis-Tris and divergent N-donor ligands

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A series of new Zn(II) coordination compounds were synthesized from zinc(II) nitrate, Bis-Tris amino-alcohol (Bis-Tris = 2,2-Bis(hydroxymethyl)-2,2',2''-nitrilotriethanol) and divergent N-donor ligands, such as pyrazine, 4,4'-bipyridine, 1,2-Bis(4-pyridyl)ethane, 1,2-Bis(4-pyridyl)ethylene, 2-phenylazopyridine and 3,6-Di(4-pyridyl)-1,2,4,5-tetrazine. The structures of the compounds, as revealed by single-crystal X-Ray diffraction, are similar and are made of binuclear zinc(II) molecules, in which the divergent N-donor ligand acts as a spacer that links two $[Zn(BT)]^{2+}$ units. The obtained compounds were characterised using coupled TG+FTIR technique in synthetic air, that gave information regarding the thermal stability and the volatile products formed on the thermal decomposition of the compounds. The specific FTIR bands of solvents (MeOH, EtOH, $CHCl_3$) were observed in the first mass loss of the compunds, while the main decomposition process was accompanied by the evolution of CO_2, NH_3, H_2O, N_2O and NO. The decomposition of the compounds is complete at 500–600 ^oC, leading to formation of ZnO in expected amounts. The ZnO structures generated upon calcination in air of the compounds were investigated using SEM analysis. Aggregates of ZnO crystallites with asymmetric hexagonal shapes and dimensions from few tens to few hundreds of nanometers were observed.

Influence of glycerin on denaturation temperature of chrome- and vegetable-tanned leathers

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The denaturation (or shrinkage) temperature is of great importance in the leather industry. Usually it is determined by observing the length variation of the sample which is immersed in water and heated. For chrome-tanned leathers the shrinkage temperature is above 100 ºC and these tests are conducted either in pure glycerin or in a 75% glycerin-water solution. The aim of our study was to see whether glycerin affects the denaturation temperature of leather's collagen as compared to the true hydrothermal conditions. For this, samples of chrome-tanned leathers were analyzed by DSC measurements while immersed in pure water, glycerin–water solutions of different concentrations (25, 50, 75, 90%) and pure glycerin, in pressure-tight crucibles. The denaturation temperature, T_d, of chrome-tanned leathers has shown an increase from ~110 ºC(in pure water) to ~116 ºC (in 75 – 90% glycerin solutions) and a slight decrease in pure glycerin. Quite interestingly, for vegetable-tanned leathers measured in similar conditions, an opposite behavior was observed, namely a decrease in T_d of the same magnitude up to 75% glycerin, followed by a slight increase in pure glycerin. These results indicate that glycerin alters the denaturation process of leather's collagen protein. A possible mechanism for this phenomenon was proposed.

Investigation of thermal-induced decomposition of iodoform

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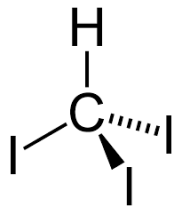
Iodoform (CHI_3, IDF) is the tri-iodo-substituted methane. It is a volatile yellow crystalline solid, with a specific sweetish penetrating odor. It is occasionally used as a disinfectant, especially in dentistry. The chemical structure of IDF is presented in Figure 1.

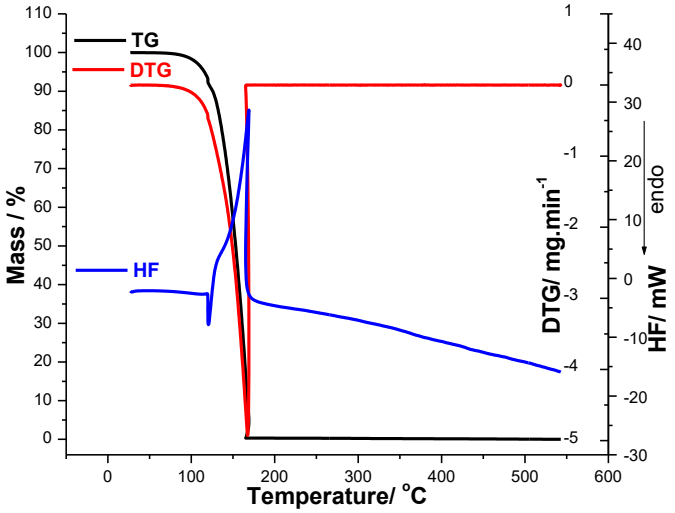
Iodoform was obtained in our laboratory through haloform reaction, namely the halogenation of dimethyl ketone in the presence of a base, and later purified according to literature [1].

In order to determine the thermal stability of IDF, thermogravimetrical analysis was carried out up to 550 ºC in dynamic air atmosphere, at a heating rate of 10 ºC min^{-1}. IDF showed an increased thermal stability (due to the considerable molar mass and the presence of three voluminous moieties – iodine atoms) up to 95 °C, then a well-defined decomposition begins and later followed by melting at 120 °C.

The kinetic study was carried out using the TG data in air atmosphere for the first step of IDF decomposition, corresponding to β = 5, 7, 10, 12 and 15 °C·min^{-1}, respectively. The kinetic triplet was determined according to Kissinger-Akahira-Sunose, Flynn-Wall-Ozawa, Friedman and NPK methods.



(a)



(b)

Figure 1. Structure of IDF (a) and thermoanalytical curves obtained in air at β=10 °C·min^{-1} (b)

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Simple and mixed oxide systems undispersed and dispersed in SiO_2, obtained by thermal decomposition of Zn(II), Mg(II) and Al(III) carboxylates

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This paper presents the synthesis of simple and mixed oxide systems undispersed and dispersed in hybrid silica gel obtained by thermal decomposition of Zn(II), Mg(II) and Al(III) carboxylates.

Simple metal oxides range from essentially ionic compounds with the electropositive elements to covalent compounds with the non-metals. The knowledge of the metal oxide chemistry implies fundamental relationships between the reactivity of oxide compounds and their chemical compositions, crystal structures, and properties [1,2].

The obtaining of the carboxylate precursors is based on the redox reaction between 1.3-propanediol and zinc, magnesium and aluminum nitrates. By thermal decomposition of this carboxylates, corresponding simple or mixed metal oxides are obtained. Metallic carboxylates can be directly synthesized within hybrid silica gel, which by decomposition at low temperature lead to simple or mixed oxide systems dispersed in silica matrix [3]. By adequate thermal treatment, nanocomposites with specific properties are obtained.

The formation of carboxylate compounds in hybrid silica gel pores was evidenced by thermal analysis and Fourier transform infrared spectroscopy (FT-IR). The oxide systems and the nanocomposites were characterized by X-ray diffractometry (XRD), FT-IR and scanning electron microscopy (SEM. Due to their optical, photocatalitic and adsorbant properties, the synthesized compounds are of a great interest for different potential applications.

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Acknoledgement:
This work was partially supported by the strategic grant POSDRU/159/1.5/S/137070 (2014) of the Ministry of National Education, Romania, co-financed by the European Social Fund-Investing in People, within the Sectoral Operational Programme Human Resources Development 2007-2013.

Search of interaction indicators in binary mixtures of Pravastatin sodium with pharmaceutical excipients

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Pravastatin sodium (PRV, Figure 1) is an inhibitor of 3-hydroxy-3-methylglutaryl coenzyme (HMG-CoA), mainly used nowadays as a hypolipidemic agent [1]. It was found that reduces the risk of death by decreasing the possibility of heart attacks [2]. Other studies revealed that PRV decrease the risk of acute ischemic strokes and transient ischemic attacks [3]. Currently, PRV is formulated in solid dosage form with content of active ingredient between 10 and 80 mg. This study presents the instrumental analysis (TG/DTG/HF, FTIR) of interaction indicators in binary mixtures of PRV with eight different pharmaceutical excipients, with different roles in the final pharmaceutical formulation. The obtained results from spectroscopic investigation at ambient temperature, were correlated with the ones obtained under heating between 30 and 500 °C and the temperature-induced intreactions between the components were established.

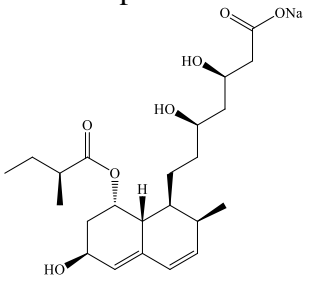

Figure 1. Structure of PRV

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Is oxo group a stabilising or destabilising moiety in pentacyclic triterpenoid structure?

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Betulonic acid is a semi-synthetic derivative which can be obtained by chemical modification of natural products like betulinol and betulinic acid, with the aim to modulate the biological properties is an area of current interest [1,2].

This study discuss the thermal stability of betulonic acid in comparation with already-published data obtained in similar conditions for precursors, such as betulin and betulinic acid [3], which were previously investigated in our research group. The obtained results by employing isoconversional methods and as well the modified NPK method allowed an objective interpretation of the importance of chemical structure over stability.

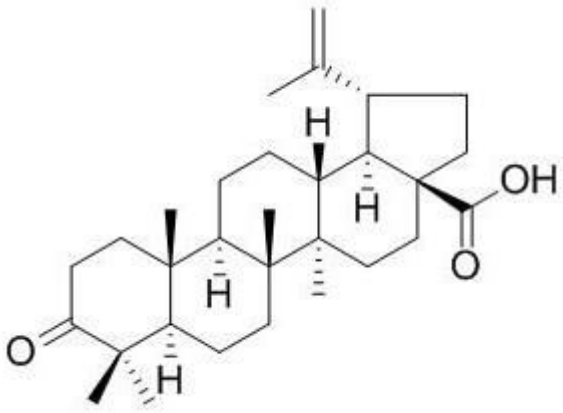

Figure 1. Structure of betulonic acid

Acknowledgements:

This work was supported by a grant from the University of Medicine and Pharmacy "Victor Babeş" Timişoara (Grant PIII-C1-CFI-2014/2015-03 to I.L., A.F.; L.S and C.S.).

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Stoichiometry of a thermochromic complex by TMDSC

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Multicomponent systems are the most important group of materials used as reversible thermochromic systems. Usually, this type of mixtures consists of a color former, a color developer and a solvent and the thermochromic transition takes place at the melting point of the solvent. Interactions between the color former and the developer and the competition between different equilibria established in this type of mixtures determine some of their critical properties, such as: the decolorisation rate, the color contrast and stability, hysteresis, etc. [1, 2].

One of the most important parameter to be studied in any of the thermochromic mixtures which could be imagined is the optimum ratio between the color former and the developer. As already established during the last years the formation of supramolecular complexes of weak acids (color developer) with leuco dyes (color former) is the main cause of the thermochromism and it was found that as the mole fraction of color developer increases the formation of a more intense colored mixture can be observed [3, 4].

Our work deals with the study of thermochromic properties of Crystal Violet Lactone (CVL) – Phenolphthalein (PPht) mixtures in 1-tetradecanol based on calorimetric analysis correlated with optical investigations by means of visible and infrared spectroscopy. Therefore, several mixtures of components in different proportions were analyzed and the results confirm that the maximum contrast was obtained when the molar ratio between color former and developer was established at 1:2.5. Structural data obtained from FTIR-ATR spectra confirm thermal measurements obtained by Temperature Modulated Differential Scanning Calorimetry (TMDSC) which show that at this particular ratio, the maximum coordination number is obtained and consequently the highest color intensity will be recorded. The method takes into account all the processes which take place at the transition temperature which involve besides the melting of the solvent accompanied by polymorphic transitions, the dissolution of each component into the solvent, formation of hydrogen bonds and the existence of π-π interactions between the components and opening of the lactone ring and aromaticity [5].

The results are in perfect agreement with diffuse reflectance data obtained on thermochromic mixtures when the law of continuous variation states is applied for the chemical equilibrium of CVL-PPht mixture in order to predict the stoichiometry of the colored complex.

Using a TMDSC technique we were able to separate the complex processes into more easily interpreted components. The Total Heat Flow signal contains the sum of all thermal transitions, just as in standard DSC. The Reversing signal, the heat capacity component, contains phase transition: glass transition, melting transitions, while the Nonreversing signal, the kinetic component, contains kinetic events: dissolution, reactions, decomposition etc.

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Thermal behaviour of some novel biological active complexes with a triazolopyrimidine pharmacophore

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Triazolopyrimidine derivatives are interesting having in view their similarity with DNA purine nucleobase. These kind of species exhibit a large spectrum of biological effects such as analgesic, anti-inflammatory, antimicrobial, antiviral, antitumor and cardiovascular [1]. Furthermore, for complexes with such ligands antimicrobial [2] and antitumor activity was evidenced [3].

In order to modulate biological activity new species of type $M(pmtp)Cl_2 \cdot nH_2O$ (M: Co, n=2; M: Ni, n=3; M: Cu, n=1; M: Zn, n=0; pmtp: 5-phenyl-7-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine) were synthesised by one pot condensation. Chemical analysis, IR, UV-Vis-NIR, EPR spectroscopy and magnetic data at room temperature provided useful information concerning the molecular formula, stereochemistry and the ligand coordination mode.

The *in vitro* screening of the antimicrobial properties were performed against Gram positive (*S. aureus*, *B. subtilis*), Gram negative (*E. coli*, *K. pneumoniae*, *P. aeruginosa*), both reference and clinical multidrug resistant strains. Cobalt(II) and zinc(II) complexes were the most active, with minimum inhibitory concentration (MIC) in the range 62.50-125 $\mu g\ mL^{-1}$. The complexes ability to inhibit the microbial biofilm adhesion on inert substratum was also assayed.

In order to evidence the modifications at heating and also the thermodynamics effects that accompany them the thermal behaviour of these derivatives was investigated in synthetic air by thermal analysis (TG, DTA). The nature of the gaseous products formed in each step was evidenced by simultaneous TG/DSC/EGA measurements. Processes as water and chloride elimination, fragmentation and oxidative degradation of the triazolopyrimidine derivative were observed during the thermal studies. The final residue was the most stable metallic oxide as X-ray powder diffraction indicates.

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Insight on thermal behaviour of new complexes of Ni(II), Cu(II) and Zn(II) with a bismacrocyclic ligand as biological active species

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Bismacrocyclic complexes have received special attention concerning their great kinetic and thermodynamic stability as well as antiviral, antimicrobial and cytostatic activity [1]. Furthermore, such complexes containing two metal centres in close proximity were studied as mimics for metallospecies involved in important biochemical processes concerning oxygen activation such as carriers or enzymes [2]. Some complexes with polyaza bismacrocyclic ligands presented an interesting thermal behaviour [3].

A multi-component reaction involving metal ion, amines and formaldehyde have been used for the preparation of decaaza bismacrocyclic complexes $M_2L(CH_3COO)_4 \cdot nH_2O$ ((**1**) M: Ni, n=2.5; (**2**) M: Cu, n=1; (**3**) M: Zn, n=10; L: 1,3-bis(N,N-1,3,6,9,12-pentaazacyclotridecane)-benzene ligand resulted from 1,3-phenylenediamine, 3,6-diazaoctane-1,8-diamine and formaldehyde one-pot condensation). Elemental analyses, ESI-MS, IR, UV-Vis-NIR, NMR and EPR spectra, magnetic susceptibility at room temperature as well as thermogravimetric analysis provided data concerning the complexes features. The ligand behaves as bischelate resulting in square planar or octahedral stereochemistry.

The *in vitro* screening of the antimicrobial activity were performed against Gram negative (*E. coli*, *E. cloacae*, *P. aeruginosa*, *P. mirabilis*, *K. pneumoniae*), Gram positive (*S. aureus*, *S. epidermis*, *B. subtilis*, *E. faecalis*), and fungal (*C. albicans*, *C. krusei*), both reference and clinical isolates multidrug resistant strains. The overall antimicrobial potency of complexes is enhanced in comparison with free ligand, regarding both planktonic and biofilm embedded pathogenic strains. The complexes exhibit a low cytotoxicity on HCT 8 tumor cells.

The thermogravimetric curves (TG, DTG, DTA) evidenced in air processes as water elimination, acetate into carbonate transformation as well as oxidative degradation of the bismacrocyclic ligand. The powder X-ray diffraction data indicate MO (M: Ni, Cu, Zn) as final product.

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Synthesis, thermal behaviour and physico-chemical properties of Fe-P-O-OH hydroxyphosphates

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Iron phosphates are a huge family of compounds with a very rich crystal chemistry. Moreover, the presence of mixed valence for iron can induce interesting properties and they are considered as promising materials for numerous applications such as catalysis [1,2], Li insertion [3-5] etc. In this context, we have chosen to study the influence of the oxidation state of the transition metal on the structure and magnetic properties of iron hydroxyphosphates. We report here the synthesis by hydrothermal method of the mixed valent iron oxide barbosalite $Fe_3(PO_4)_2(OH)_2$ and its thermal behaviour under different atmospheres.

$Fe^{2+}Fe_2^{3+}(PO_4)_2(OH)_2$ crystallizes at room temperature in the monoclinic $P2_1/n$ space group with a complex structure characterized by a dense 3D framework of FeO_6 octahedra and PO_4 tetrahedra [6]. The compound has been prepared by hydrothermal synthesis at T=220ºC for 72h in a 60 ml Teflon-lined steel autoclave, starting from $FeCl_2.9H_2O$, $FeCl_3$ and $(NH_4)_2HPO_4$. The sample was checked by room temperature X-ray diffraction and found to be single phase, well crystallized and the SEM images indicates that the product consists of octahedral microcrystals of approximately 10μm diameter.

Thermogravimetric analysis of this hydroxyphosphate were performed under various atmospheres, evidencing significant differences in its thermal behaviour. The TGA performed in air up to 500°C shows a transition from barbosalite to lipscombite phase [7], whereas $Fe_3(PO_4)_2(OH)_2$ compound adopts a different TG behaviour in vacuum or argon, characterized by several structural transitions and accordingly magnetic phase transitions. These results will be discussed in relation to the structural information obtained by XRD, TEM analysis and infrared spectroscopy.

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The estimation of thermal endurance for some heteropoly acidic catalysts from thermogravimetric decomposition data

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The calculation of thermal endurance and the estimation of the catalyst lifetime at certain temperatures is a problem of high interest for the catalysts used in practice. In this purpose a standard method based on thermogravimetric data is used. The calculation of catalyst's lifetime with high degree of confidence needs reliable values for activation energy.

The activation energy values calculated with respect of [1] comply with such exactingness owing to its clear rules for: the sample shape, the experimental procedure and the calculation course based on Flynn-Wall isoconversional method (integral model-free). Also, the activation energies were calculated with Friedman isoconversional method (differential model-free) for checking, because this provides accurate values of activation energies compared with the integral model-free methods, which could give significant errors in the determination of the activation energy [2].

The tungstophosphoric acid, $H_3[PW_{12}O_{40}]xH_2O$ (H_3PW) and its Cs acidic salts, pure or doped with Cu, Fe, Ni, Co, Pd, Pt, Rh are ones of the most known compounds with application in catalysis. In this work the lifetime of H_3PW and some of its acidic Cs salts, pure and doped with Pd was determined according to [3]. The thermal decomposition of the H_3PW and some of its acidic Cs salts, pure or doped with Pd, occurs through the constitutional water release (the water formed of the protons and the oxygen from the $[PW_{12}O_{40}]^{3-}$) having as result the loss of acid centres (protons) and its catalytic activity at the same time [4,5].

The activation energy values calculated with respect of the Standard Test Method for Decomposition Kinetics by Thermogravimetry are reliable for the conversion range of $5 \leq \alpha \geq 20$, but the value for $\alpha=10\%$ is recommended for the calculation of the lifetime.

The Estimated Thermal Life of the H_3PW and some of its acidic Cs salts pointed out a very good thermal endurance at temperatures below 523 K. The Pd doping decreases the thermal endurance drastically in all cases.

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Green parts thermal debinding for alloplastic bone grafts

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The alloplastic bone grafts represent one of the most modern solutions for bone reconstruction [1]. The complexity of the bone grafts requires advanced molding technologies and the medium-pressure injection molding (MEDPIMOLD) provides technical and economical advantages (max. pressure 5 MPa, max. injection temperature 120 °C) in comparison with the classic injection molding (60-100 MPa respectively 220-250 °C).

The raw material to be injected is represented by the mixture (feedstock) between the wax-based binder system (40-60 % mass) and the biocomposite powder particles (balance). The binder system is made of paraffin, carnauba and bees waxes, ethylene vinyl acetate and stearic acid. The biocomposite powders mixture is made of hydroxyapatite (30-50 μm), titanium hydride (~ 100 μm), citric acid, calcium carbonate and ammonium bicarbonate.

The green parts obtained after the injection step were submitted to the thermal debinding in order to remove the binders and the brown parts obtained will pass to the sintering treatment. The aim of our research was to study the influence of the thermal debinding parameters (temperature and dwell time) on the thermophysical and micro/macro-structural properties of the brown parts, monitored by thermal analysis (TA), Fourier transform infrared spectroscopy (FTIR), optical microscopy and mechanical tests.

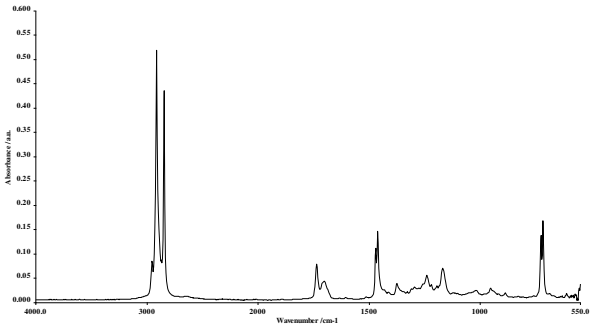

Fig. 1

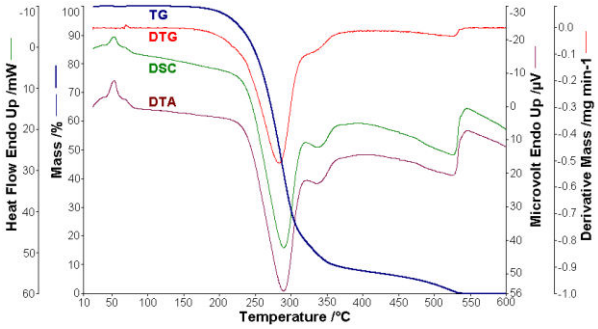

Fig. 2

Figs. 1 and 2 show the results of thermal analysis and FTIR spectroscopy of the mixture of binders used to prepare raw parts for alloplastic bone grafts. The binders decompose totally, in the air, to a temperature of 535 °C.

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Feedstock set-up of the biocomposite material for alloplastic bone grafts manufacturing

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In case of the small-sized bone reconstruction, specific grafts may have complex geometries. The powder metallurgy technology is one of the most recommended to elaborate small bone grafts made of hydroxyapatite (HAP) and titanium based composites [1].

The technological novelty of our research is the use of the medium-pressure injection moulding (MEDPIMOLD) to shape HAP-based biocomposite grafts. The raw material, named feedstock, represents the mixture between the wax-based binder system and the biocomposite powders. The binder system consists of the following components (% mass): paraffin wax (20-40), carnauba wax (5-15), bees wax (5-15), ethylene vinyl acetate-EVA (40-50) and stearic acid (2-7). The biocomposite powders mixture is made of (70-80) % HAP (30-50 μm), (15-25) % TiH_2 (~ 100 μm), citric acid (1-3) % and $CaCO_3$ and NH_4HCO_3 each of (1-2) %.

The feedstocks were studied and the ratio between the binder system and the biocomposite powders were: 1:1, 0.9:1.1 and 1.1:0.9.

The aim of this study is to investigate the influence of the feedstocks viscosity on the green parts properties: thermo-physical and micro/macro-structural properties by thermal analysis (TA), Fourier transform infrared spectroscopy (FTIR), optical microscopy (OM), and mechanical tests.

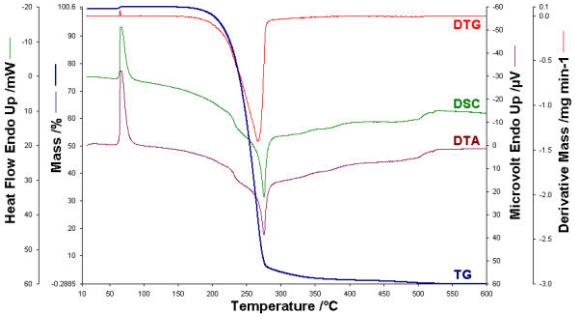

Fig. 1

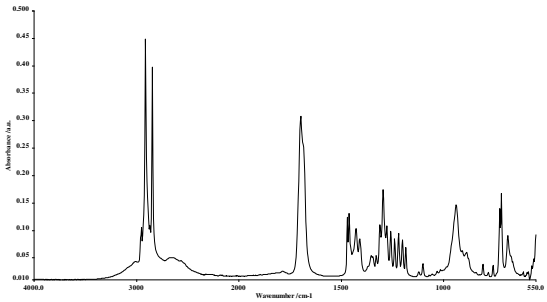

Fig. 2

In Fig. 1 are given the thermoanalytical curves of oxidative decomposition of one of the components of the feedstock to manufacturing biocomposite material for alloplastic bone grafts: stearic acid. As the other binders, stearic acid is decomposed totally at rather small temperatures.

Fig. 2 shows the FTIR spectra of the same stearic acid.

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Influence of the polyol on the thermal behaviour of different polyesters

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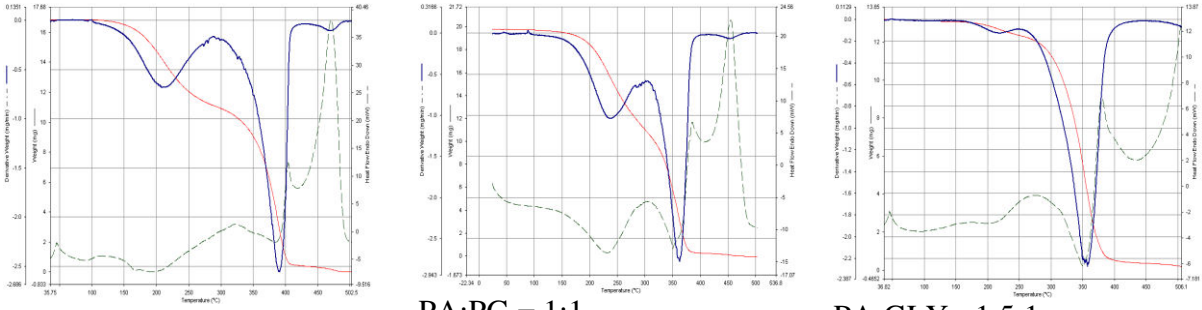
The large spectra of applications of polyester resins impose different mixtures of raw materials, regarding the acidic component, as well as the alcoholic ones. The most utilized polyesters are based on phthalic anhydride as acidic component, so that the variations of the working properties are especially due to the polyols [1-2].

The aim of this paper is to identify the influence of the alcoholic component, on the thermal behavior of phthalic type polyester. As reaction partner for the phthalic anhydride (PA) were selected monoethylene glycol (MEG), propylene glycol (PG), and glycerol (GLY) respectively, in PA:polyol molar ratio of PA:MEG = 1:1, PA:PG = 1:1 and PA:GLY =1.5:1. The polycondensation was performed without catalyst, at temperature until 220°C and an acidity index less than 20 mg KOH/g.

The thermal behavior was estimated by nonisothermal kinetic study using the TG/DTG/Heat Flow (see Fig. 1) data, processing by Friedmann, Flynn-Wall-Ozawa and modified NPK methods [3-5].



PA:MEG = 1:1 PA:PG = 1:1 PA:GLY =1.5:1

Fig. 1. TG/DTG/Heat Flow data of phthalic type polyester (in air with β=10°C/min)

The influence of the functionality and of the methyl group was estimated by comparison of the activation energy and the conversion function (by modified NPK method) obtained by the decomposition of the synthetized polyesters.

Acknowledgments:

This work was supported by POSCCE Grant nr. 12PO102418/5124/22.05.2014, SMIS 50328: “New energetic efficient technology for synthesis of polyester copolymers”

[1] P. Zhang et al., *Polym. Degrad. Stab.*, 94 (8)(2009), 1261-1266.
[2] D. Hansen, et al., *Mat. Res.*, 10 (3)(2007) 257-260.
[4] I. Ledeti et al., *J Therm Anal Calor,* **118(2)**, 2014, 1057-1063
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Thermal behaviour of some branched bicomponent phthalic base polyesters

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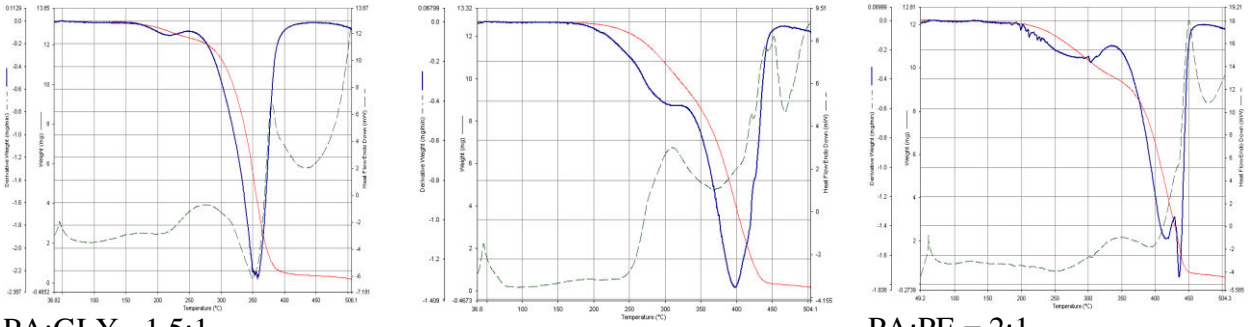
The thermomechanical properties of polyesters with phthalic anhydride (PA) as acidic component strongly depend on the molecular architecture of the polyol [1-2].

This work deals with the kinetic study of thermal behavior under nonisothermal conditions of three phthalic polyesters having glycerol (GLY), trimethylolpropane (TMP) and pentaerythritol (PE) as alcoholic component (see TG/DTG/Heat Flow curves in Fig.1)

The non-catalyzed synthesis were performed at molar ratio of PA:GLY =1.5:1, PA:TMP = 1.5:1 and PA:PE = 2:1 respectively, at temperature until 220°C and an acidity index less than 20 mg KOH/g.

The kinetic analysis was performed using Friedmann, Flynn-Wall-Ozawa and modified NPK methods [3-5]. The activation energy and the conversion function (by modified NPK method), was the principal criterion for estimation of the influence of the molecular structure (branched chain) on the thermal behavior of the synthetized polyesters.



PA:GLY =1.5:1 PA:TMP = 1.5:1 PA:PE = 2:1

Fig. 1. TG/DTG/Heat Flow data of phthalic type polyester (in air with β=10°C/min)

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[6] P. Albu et al., *J Therm Anal Calor,* **105(2)**, 2011, 685 - 689

Thermogravimetric study and lifetime estimates of cellulose

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This work shows different procedures to estimate the lifetime and thermal degradation behaviour of materials using thermogravimetric analysis [1-2]. Namely, cellulose is characterized by thermogravimetry (TG) [3]. Isothermal and nonisothermal tests at different heating rates were performed and kinetic models were applied to thermally characterize cellulose and estimate its lifetime due thermal aging [1-2]. Arrhenius based models and free kinetics models were implemented [1,3]. Also an alternative methodology inspired by the Time Temperature Superposition (TTS) [4] procedure is applied to TG isothermal data. In fact, a master curve is defined for an specific mass loss conversion (10, 20, 50 wt%) and the time to loss this amount of mass is measured depending on temperature. The lifetime estimates obtained by the different models are compared. An R software [5] library named TTS is performed to permit the thermal analysis community to apply the above mentioned techniques using free software.

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Bis[*N*-(quinoline-8-yl-aryl)benzenesulfonamide]-palladium(II) chloride: As catalysts for the oxidation of benzyl alcohol

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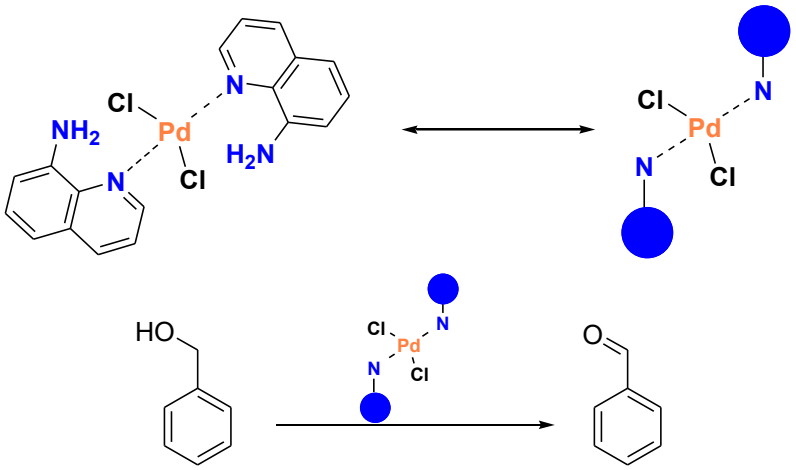
Erciyes University,Science Faculty Department of Chemistry, Kayseri/TURKEY

In general, sulfonamides are obtained from the reaction of sulfonyl chloride with primary or secondary amines in alkaline [1]. Sulfonamides and their derivatives have attracted the interest of many researchers' due to their importance in the development of coordination chemistry, their application in medicinal chemistry, catalytic fields, etc. [2]. For example, metal complexes containing sulfonamide ligands have been used as catalysts in various organic reactions [3].

Herein, *N*-(quinoline-8-yl-aryl)benzenesulfonamide were successfully synthesized by the reaction of 8-aminoquinoline and various benzenesulfonyl chlorides. A series of neutral coordinate Pd(II) complexes were prepared from the reaction of$PdCl_2$ and benzenesulfonamides. The synthesized compounds were characterized by TG/DTA, FT-IR, elemental analysis and NMR spectroscopy. The complexes were used as a catalyst in the oxidation reaction of benzyl alcohol to benzaldehyde in the presence of H_5IO_6 in acetonitrile. All complexes showed satisfactory catalytic activity.



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Thermochemical study of the styrene butadiene latex coagulation by calcium carbonate

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Traditional methods for producing polymer compositions are often associated with an inhomogeneous distribution of filler particles in the polymer, which leads to the formation of particle agglomerates and mechanical degradation.

Therefore, the actual problem is rubber filling at the latex stage. Using of chemically coagulated calcium carbonate both as a filler and a latex coagulant is of great interest. Calcium carbonate is a by-product of fertilizers manufacture.

Thermochemical study coagulation styrene-butadiene latex with calcium carbonate was carried out on a differential microcalorimeter.

Thermokinetic curves shows that with increasing mass of calcium carbonate the value of heat absorption increases and reaches its maximum during the period from 40 to 70 seconds. The total process time varies insignificantly and lies in the range from 6000 to 8000 seconds.

Thermal effects of latex coagulation with calcium carbonate were calculated according to the process energy values. Studies have shown that the interaction of the modified calcium carbonate with the latex is accompanied by heat absorption. This process can be considered as combination of the following basic interactions: latex with water, a hydrophobic chalk with water, latex particles together with hydrophobic latex and calcium carbonate. The endothermic effect of the process decreases with increasing mass carbonate filler. The data obtained can be used in the preparation of polymer compositions.

Thermal analysis of sugar cane bagasse ash and its potential use in clay products

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The current increasing industrialization, particularly in less developed nations, is placing an enormous pressure on the environment through the volume of materials consumed, the amount of waste sent for disposal and the amount of energy used. The ceramics industry, given the high volume of materials processed, stands as one of the largest consumers of natural raw materials but has also the capacity and potential to make significant contributions to solving problems associated with wastes. Clay-based materials show a natural forgiveness towards the incorporation of a variety of materials, including potentially hazardous industrial rejects or sub-products. Research work carried out over the past two decades has shown that the ceramics industry can incorporate different types of industrial rejects, without degradation of properties. Today, it is clear that some industrial wastes are similar in composition to the natural raw materials used in the ceramic industry, and often contain materials that are not only compatible but also beneficial in the fabrication of ceramics [1-3]. In Brazil, the growth of the sugar and ethanol production is leading to an increasing amount of wastes with high environmental impact. This work explores for the first time the effect of the incorporation of a sugar cane bagasse ash (SCBA) in a commercial clay material, in order to minimize the SCBA negative impact on the environment.

The results obtained (X-ray diffraction and fluorescence, thermal analysis, firing shrinkage, water absorption and mechanical strength) show the effect of the SCBA additions on the clay mixture behavior and suggest that the incorporation of the SCBA (10 wt. %) material into the clay mixture can constitute a valid route to the amelioration of the environmental concerns.

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Solid-state characterization and pharmaceutical compatibility between Citalopram and excipients using thermal and non-thermal techniques

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The selection of an adequate excipients for drug formulation should be based on its characteristics, compatibility and stability with other components [1]. The study of drug-excipient compatibility, recommended by the International Conference on Harmonization, represents an important step in the pre-formulation stage [2]. The aim of the present work was to evaluate the possible interactions between Citalopram hydrobromide (CIT) and some excipients using Differential Scanning Calorimetry (DSC) and powder X-Ray Diffraction (XRD).

Thermal analysis were carried out at a heating rate of 10 °C min^{-1} from 25 to 600 °C under nitrogen flow (50 mL min^{-1}) using a Mettler-Toledo TGA/ DSC 1 (simultaneous TG/DSC). The DSC curve of CIT presents an endothermic event at 182 °C (T_{onset} = 184.2 °C; ΔH_{fus} = 90.0 J g^{-1}) associated with the melting point as indicated in literature [3]. In this temperature range, TG/DTG curves did not show mass loss. The TG/DTG curves reveal that CIT is thermally stable up to 230 °C. Since the ΔH_{fus} for the CIT corresponds to 99.0 J g^{-1}, the value expected in a 1:1 mixture CIT-excipient is close to 44 J g^{-1}. Binary mixtures with hydroxypropylmethylcellulose (HPMC), magnesium stearate (MS), microcrystalline cellulose (MC) and starch present the same behaviour. Mixture with lactose monohydrate (LM) shown changes on thermal profile due to occurrence of Maillard reaction. The evaluation of the XRD pattern of 1:1 (m/m) mixtures between CIT/starch, CIT/MC, CIT/MS and CIT/HPMC, clearly shows the characteristics diffraction peaks, corresponding of a good crystallinity material. XRD pattern suggests that no interaction is present between individual components. CIT/LM mixture showed considerable increase in the intensity of the some peaks, however, the XRD still showing the same crystalline structure for CIT.

Based on our results, DSC provides indications that LM has presented interactions with CIT, nevertheless, without occurring any alteration in the crystalline structure of the molecule of CIT in this mixture, as observed by the XRD results.

The authors acknowledgement the financial support from CAPES, CNPq and FAPEMIG

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Characterization of Amitriptyline by Thermal Analysis

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Amitriptyline (AMT.HCl) is a tricyclic antidepressant and is chemically known as 3-(10,11-dihydro-5H-dibenzo[a,d]cycloheptene-5-ylidine)-N,N-dimethyl-1-propanamine hydrochloride [1]. The objective of this study was to characterize and evaluate the properties of the raw material pharmaceutical AMT.HCl using Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC).

Thermal analysis were carried out at a heating rate of 10 °C min^{-1} from 25 to 600 °C under nitrogen flow (50 mL min^{-1}) using a Mettler-Toledo TGA/ DSC 1 (simultaneous TG/DSC). The TG/DTG curve showed that AMT.HCl was thermally stable up to 165 C and then three mass loss stages could be observed. The TG curves showed that AMT.HCl has three characteristic thermal events, the first loss of mass occurs when the drug melts, between 165 and 196 °C (Δm = 0.9 %), a second stage of decomposition between 198 and 306 °C (Δm = 94.9 %), followed by a third and last degradation stage between 306 and 480 °C (Δm = 3.1 %), events determined by the first TG derivative.

The DSC curve showed a sharp endothermic peak between 193 °C and 200 °C (T_{onset} = 193,5 °C, T_{peak} = 196,1 °C, ΔH = 96,7 J g^{-1}) corresponding to the melting of the crystalline form of the drug according the literature [2,3] followed by the partially overlapped endothermic peaks up to 207 °C related to the thermal decomposition was also observed in DSC curve, corresponding with changes in TG curve.

These previous results obtained have enabled the determination of the physical and chemical properties of the drug, providing relevant information on the quality of raw material.

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The authors acknowledgment the CNPq, FAPEMIG and CAPES for the financial support.

Hydroxypropyl-beta-cyclodextrin:epiisopiloturin and epiisopilosin complexes: characterization by DSC, TG, DTA, NIR and MID

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Epiisopilosina and Epiisopiloturina are imidazole alkaloids found in the leaves of *Pilocarpus microphyllus* (jaborandi). Although it has been proven that these compounds have activity against Shistossoma mansoni - one of the major agents of the schistosomiasis disease - they have low solubility in water [1], which can lead to incomplete absorption. Thus, it is essential to consider the enhancement of their solubilities [2]. The formation of inclusion complexes with cyclodextrins has proven to be successful and has been extensively used to improve the solubility and bioavailability of lipid-soluble drugs[3]. The aim of this work was to obtain inclusion complexes of the alkaloids Epiisopilosina and Epiisopiloturina with hydroxypropyl-β-cyclodextrin (HPβCD) by using physical mixing (PM) and kneading (K) methods, where the complexes were characterized by thermal analysis (DSC, TG and DTA) as well by near-infrared (NIR) and mid-infrared (MID) spectroscopy. The physical mixtures were obtained by hand-mixing using mortar and pestle in an equimolar ratio (1:1) of epiisopiloturina: HPβCD and epiisopilosina: HPβCD. The same molar ratio was used to prepare the inclusion complexes by the kneading method, where 1g of each alkaloid was dissolved in 10 mL of methanol and then added to a wet paste obtained by dispersing 5.03g of HPβCD in 6 mL of EtOH:H2O (2:1). The mixture was subjected to kneading in a porcelain mortar for 30 minutes and dried in an oven at 60°C for 30 minutes. The DSC curve for the PM and K product of epiisopiloturina:HPβCD showed significant reduction of the melting enthalpy of the alkaloid (from 100 J.g $^{-1}$ to 9 J.g $^{-1}$ and from 100 J.g $^{-1}$ to 27.4 J.g $^{-1}$, respectively). In addition, a displacement of the melting peak attributed to the alkaloid was observed, with a reduction of 18°C in its melting temperature. Although no change was observed with the epiisopiloturina:HPβCD complex obtained by kneading, a slight reduction occurred with the PM (from 180.04°C to 172.01°C). However, the melting enthalpy decreased in both systems (from 51.14 J.g $^{-1}$ to 6.7 J.g $^{-1}$ and 5.1 J.g $^{-1}$, respectively). The NIR spectrum of the PM showed a displacement of the bands attributed to epiisopilosina (from 4335 cm^{-1} and 4776 cm^{-1} to 4255 cm^{-1} and 4973 cm^{-1}; from 5973 cm^{-1} to 5858 cm^{-1} and from 6111 cm^{-1} to 6176 cm^{-1}). In the K complexes, the bands at 4072 cm^{-1} and 5973 cm^{-1} were displaced to 4994 cm^{-1} and 5922 cm^{-1}, respectively, and a new band appeared at 6450 cm^{-1}. The spectrum of the epiisopiloturina:HPßCD complex, prepared PM, showed that the 5966 cm^{-1} band was shifted to 5648 cm^{-1}. Moreover, the bands at 6386 cm^{-1} and those in the region of 7843-9680 cm^{-1} disappeared. The complexes prepared by K showed that the 4233 and 4994 cm^{-1} bands were displaced to 4055 and 4443 cm^{-1}, respectively, and that the ones at 7695, 8287 and 9258 cm^{-1} disappeared. The correlation between the experimental and the theoretical spectra of epiisopilosina:HPßCD complex prepared by PM established the regions of lower correlation. The bands at 1024 and 1747 cm^{-1} were displaced to 1374 and 1513 cm^{-1}, respectively, while some bands appeared in the 3150-3313 cm^{-1} region. On the other hand, the spectrum of the complex obtained by K showed low intensity bands at 1408 and 1537 cm^{-1}, a displacement of the 1747 cm^{-1} band to 1711 cm^{-1} and the presence of the following bands: 2907, 3348, 3615 and 3731 cm^{-1}. The correlation between the epiisopiloturina:HPßCD complex prepared by both methods evidenced regions of greater interaction. The spectrum of the PM shows a shift of the 1020 cm^{-1} band to 1367 and 1441 cm^{-1}, a decrease in the intensity of the band at 1768 cm^{-1} and the presence of a broad band in the region of 3151-3340 cm^{-1}. However, the spectrum of the complex prepared by K showed the displacement of bands at 1020, 1523 and 1765 cm^{-1} to 1431, 1547, 1705 and 1747 cm^{-1}, as well as the appearance of the 2929, 3340 and 3615 cm^{-1} bands at varying frequencies.

Pre-formulation studies using thermal analysis for chocolate candies with tocopherol applied to pediatric cystic fibrosis

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The dose adjustment of medicines for pediatric patients is an usual practice at the hospitals [1]. The dose of tocopherol (vitamin E) is adapted for treatment of children with cystic fibrosis and associated to hipercaloric diets [2]. The aim of this work was to develop pre-formulation studies using thermal analysis to evaluate the characteristics of tocopherol incorporated into chocolate candies applied to therapy of pediatric cystic fibrosis. The chocolate candies without vitamin E (placebo) and with different doses of the vitamin (100, 400 and 1000 mg), in two chocolate bases (milk and white), were prepared by the solidification method and characterized in relation to average weight variation, relative standard deviation and yield. The thermal properties of pure vitamin and chocolate candies (placebo and with vitamin) were evaluated by differential scanning calorimetry (DSC) and thermogravimetry (TG) under atmosphere of nitrogen. The chocolate candies were obtained with acceptable values of average weight variation (< 5%), relative standard deviation (< 4%) and yield (from 75.52% to 88.64%). In the DSC curves of chocolate candies containing the vitamin had the disappearance of two endothermic peaks (250 and 290°C) and the displacement of one exothermic peak (350°C) of tocopherol at both chocolate bases. The increase of vitamin quantity into candy caused a reducing in melting enthalpy of chocolate and disappearance of first endothermic peak present on placebo candies. The TG curves of candies with tocopherol showed that the first and second step of weight loss were analogous to placebo candies and only the third step of weight loss was associate to the vitamin and occurred at higher temperatures, independent of the quantity of tocopherol or nature of chocolate base used. The results of thermal analysis suggest a favourable interaction with a thermoprotective effect of chocolate (milk and white) associate to the tocopherol on candies produced. Then, it was possible to obtain chocolate candies containing tocopherol of adequate manner and to use the thermal analysis as fast and useful tool in pre-formulation studies of a novel pharmaceutical preparation applied to treatment of children with cystic fibrosis.

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Thermal characterization of polyurethane foams with vegetal polyol and different chain extenders and glycerol as a crosslinker

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Organic compounds containing the functional urethane group (NHCOO) were first synthesized by Wurtz in 1848 from the condensation reaction between chemical structures containing functional groups such as isocyanates (NCO) and hydroxyl (OH), for example [1]. Among the synthetic polymers, the PU is one of the classes of polymers most used industrially. There is a wide variety of raw materials for production of macromolecular polymer with different structures and consequently different physico-chemical properties, and the use of vegetable oils are an renewable source excellent for the chemical industry and particularly for applications in polymer synthesis [2,3].

In this study, different polyurethane foams were synthesized from different formulations containing different amounts of polymeric 4,4'-diphenylmethane ***diisocyanate***, polyol derived from castor oil, dimethylcyclohexylamine as catalyst and triethanolamine, glycerol as a crosslinker, polyethylene glycol 400 (PEG 400) and propylene glycol as chain extenders, and water and pentane as blowing agents. The materials were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetry (TG) and differential scanning calorimeter (DSC). It also determined the density, the modulus of elasticity for ***compressive strength*** at a specific deformation of 10% and the water sorption capacity by the foam. The TG curves were obtained on a Shimadzu DTG-60 in dynamic N2 atmosphere, in alumina pans. The DSC experiments were performed on a Shimadzu DSC-60 in aluminum pans, in dynamic N2 atmosphere and the glass transition temperatures (Tg) was determined by ASTM D3418.

The formation of urethane linkage was confirmed in all materials, by FTIR. All synthesized foams showed low density, with values between 16.5 and 27.3 kg m^{-3}. Morphological analysis obtained by SEM showed cell size ranging from 351 to 578 µm. The foam containing a high amount of glycerol, which is a crosslinker, showed the highest density 27.3 kg m^{-3} and a lower water sorption capacity of 5.3 g water / g foam. However, foam containing PEG 400 as the chain extender had lower density and water sorption capacity, 16.5 kg m^{-3} and 12.5 g water / g foam, respectively. The TG curves showed initial degradation temperatures ranging 218 to 247 °C, and the DSC analysis showed glass transition temperature ranging from 10 to 47 ºC for the materials studied.

The authors thank CNPq, CAPES and FAPEMIG for financial support.

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Dependence of dehydration enthalpy on exchangeable cations of montmorillonite interlayer space from the Sakhalin Island

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The field of bentonites is located on east coast of the central part of the Sakhalin island. The sedimentary, igneous-sedimentary and igneous formations of cretaceous, paleogene and neogene age blocked by cover of friable quarternary deposits take part in geological structure of the territory.

Physical and chemical properties of bentonites directly depend on the content of montmorillonite, exchange - cationic capacity and composition of exchange cations in interlayer space. Ability alkaline bentonite clays (where Na^+ and K^+ cations prevail in exchange complex) repeatedly to swell in aqueous solutions is used for preparation of drilling muds. Cause of bentonite wide application in the industry are ability to plasticity and the bonding capacity arising for swelling of bentonites,.

The structure of exchange cations of montmorillonites under study is very unstable. According to the received data, the content of exchange cations of Ca^{++}, Mg^{++}, Na^+ and K^+ change largely. Na^+ cation is subject to the greatest fluctuations. Its concentration change from 0,43 to 67 mg*eq/100 g. On composition of exchange cations within field alkaline bentonites, alkaline-earth (with dominance of Ca^{++} and Mg^{++}) and the mixed type - alkaline and alkaline-earth (with approximately the same ratio of that and others) are allocated.

The method of thermal analysis was studied dependence of dehydration enthalpy on cation-exchange capacity and varieties of exchange cations. Researches were carried out on the F1 Jupiter STA 449 instrument («Netzsch», Germany) by heating rate 10 K/min in the closed crucibles in the air atmosphere. Samples weight – 40 mg. The data of thermal analyses was used to suggest the dependence of total area below DSC pattern (J/g) on cation exchange capacity and exchange cation varieties. The total area according to expended dehydration energy during thermal treatment of montmorillonite was found to be inversely proportional to the total value of exchangeable cation.

The part of the DSC pattern between 30° and 220° C was divided into three extremum groups by special program (NETZCH Peak Separation). The first group is below 100°, the second is about 100-130° and the third is about 120-170° C.

According to the double electric layer theory and to experimental data acquired by many researchers we could notice the following [1]. Water removal from the surface occurs at the temperature range below 100° C. The water is not from mineral interlayer space and wasn't included in the calculation of total area. Graphically it was detected that the total area depends on the quantity of monovalent exchangeable cations. With the increase of the number of monovalent exchange cations the dehydration enthalpy is decreased. This energy is expended to evacuate water molecules from interlayer space. Similar relation for divalent cations is not observed.

Work is executed with financial support of the Grant of the Russian Federal Property Fund No. 13-05-00765a, ONZ-5.

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Bionanosiderite research from ferruginous quartzite of the Kursk Magnetic Anomaly (KMA) by STA method

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The deposit is located in 10 km from Stary Oskol in the Belgorod region. The field is combined of Proterozoic slates of Kursk series, quartz porphyries, slates and the amphibolite of Mikhaylovsk series.

The synchronous thermal analysis (STA) was carried out on the instrument (STA 449 F1 Jupiter "Netzsch"). A scanning was proceeded with rate of 10 °C/minute into argon atmosphere with the closed by covers corundum crucibles.

On the differential scanning calorimeter (DSC) patterns a dissociation of siderite is fixed from 350 to 550 °C and accompanied by complex endothermic effect with three maxima. This phenomenon matched to existence in the samples of several generations of the mineral with a number of particle sizes and respectively a decomposition temperature. The beginning of endothermic effect is observed at 350 °C. After that there is some delay comes in its development owing to what on downward branch the change with maximum will be formed at 380 °C. The late peaks of dissociation are appearance of the most small-sized nano-dimensional mineral particles. The endothermic effect reaches the maximum development at 424.5 °C then there is the intensive exothermic reaction connected with formation of magnetic intermediate phases. The exothermic effect peaks at 500 °C then chokes with energetically opposite effect of dissociation of the most coarse particles of siderite. After achievement of maximum of endothermic effect at 520 °C, again there is iron oxidation to trivalent, causing exothermic effect to maxifg3wg3e3et3eTmum at 555 °C. Additional exothermic effect at 620-630 °C is connected with magnetite oxidation in hematite.

Availability of magnetite in test is fixed by means of thermogravimetric (TG) of curve which at 600oC shows increase in weight for 2.81 %, and also exothermic effect on curve DSK with maximum at 935oC. Proceeding from set of the qualitative information received on curve DSK and quantitative – on TG curve, the content of siderite (from 46 to 52 %) in studied samples on formula has been calculated:

$$C_{(сидерита)} = \frac{M_{FeCO_3}}{M_{CO_2}} d = \frac{116}{44} d$$, *where With – the content of siderite, %; M – molny weight of substance, d – fire losses, %.*

In the range of temperatures 702-930 ^{o}C the flattened exothermic effect with maximum is observed at 849 ^{o}C, connected with destruction of thermostable organic chemistry [2].

Thus, in the KMA ferruterous quartzites two generations of siderite which are cardinally differing on the morphology and kristallokhimichesky and physical characteristics are revealed. One of these generatsiya is for the first time the bionanosiderite found on KMA.

Work is executed with financial support of the Grant of the Russian Federal Property Fund No. 13-05-00765a, ONZ-5.

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Electrochemical and Thermal Stability of Chlorophyll

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The chlorophyll is a natural green pigment that is used as additive food and as dietary supplement having beneficial effects on the body [1]. The chlorophyll transformation is a very complex process that depends on many factors, such as: solvent nature, environment composition and pH, temperature, etc [2, 3]. The ethanol solution of commercialized product containing chlorophyll extracted from a mixture of plants with spirulina and seaweed has been electrochemically decomposed in presence of Cl^-. The UV-Vis spectra (Fig.1) indicate that the chlorophyll "*a*" is the main phase of the mixture that has a very low electrochemical stability.

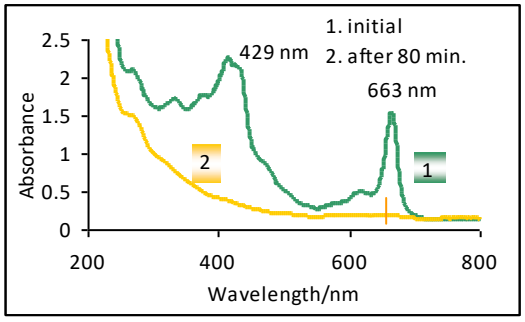

Figure 1. Diagram of chlorophyll electrochemical degradation

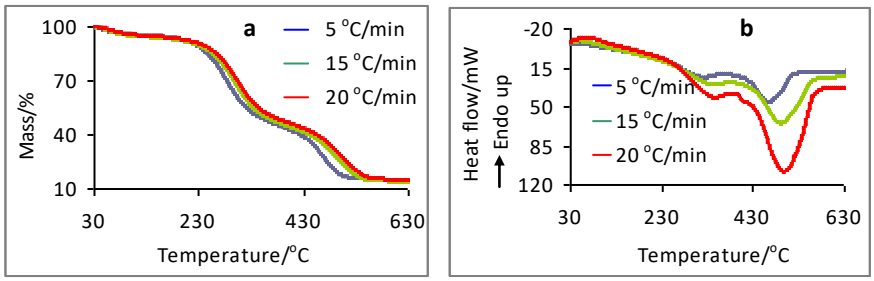

Figure 2. TG (a) and DSC (b) curves of chlorophyll

The thermal analysis (Fig.2) shows a gradual loss mass before 200°C, no more 8%. This suggests that no risks are involved, during the chlorophyll processing as additive food until 200°C. The following steps suggest breakdown of the porphyrin macrocycle remaining a residuum of 13.8% containing magnesium and/or its compounds.

Acknowledgements:
POSDRU/174/1.3/S/149155 Project - "The teaching staff of the education system - promoter of learning on all lifetime".

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UV-Vis Spectrophotometry and Thermal Decomposition of Vanillin Synthesized from Lignin (VSL)

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Vanillin is one of the most important flavouring materials, being known its applications in pharmaceutical and perfumery industry and its usage as additive food [1]. To ensure the quality of natural product commercialized as vanillin obtained from lignin it is important to verify its authenticity and purity to confirm the manufacturer information. Thus, the UV-Vis spectrophotometry and thermal analysis were used to identification the chemical constituents of the product commercialized as natural vanillin synthesized from lignin (VSL). By strategic depolimerization the lignin generates aromatic chemicals, vanillin being a lignin derived compound [2]. The TG curve was recorded from *RT* to 700°C, in nitrogen atmosphere with a temperature scan rate of 10°C/min (Fig.1).

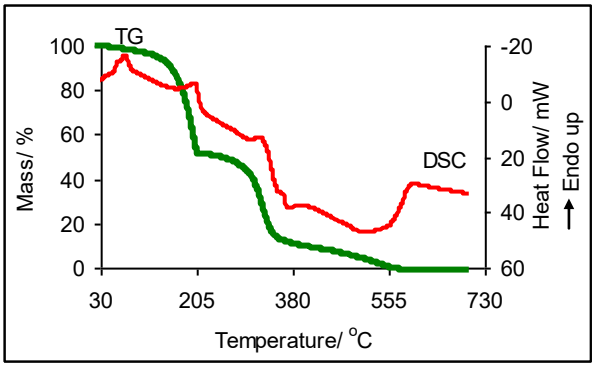

Figure 1. TG and DSC curves of VSL

In temperature range from *RT* to 150 °C the first decomposition step was observed with a mass loss of 8.9% which corresponds to adsorbed water and/or other compounds resulted from manufacturing process of vanillin. The following steps (two and three) between 150 °C and 360 °C can be assigned to vanillin releasing [3], the mass loss having a value of 79.6%. Finally, deeper degradation of the residue takes place with exothermic maximum levels at 375 °C and 510 °C observed on DSC curve (Fig.1).

Acknowledgements:

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Stigmasteryl derivative: thermal, spectral and liquid crystal behaviour

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Synthesis of stigmasteryl derivative (Fig. 1) was performed in benzene by direct esterification of *p*-(*p*-phenoxy-phenylsulfanyl)-butyric acid with stigmasterol in the presence of *p*-toluensulphonic acid.

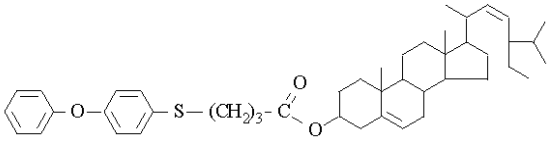

Fig. 1

Thermal behavior of the stigmasteryl derivative (Fig.2), was studied in the air, in the field of RT-600 °C, with the heating rate of 2 K/min. At 94 °C an exothermal effect occurs and at the 169.5 °C an endotherm effect. The compound is stable up to 202.8 °C. Between 202.8 and 314.5 °C lose mass of 80 %, and the remaining 20 % is lost between 314.5 and 515 °C.

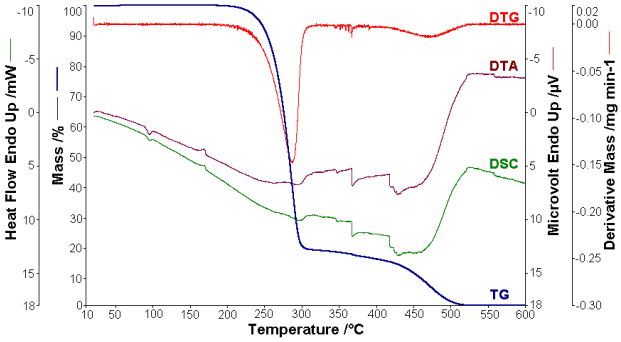

Fig. 2

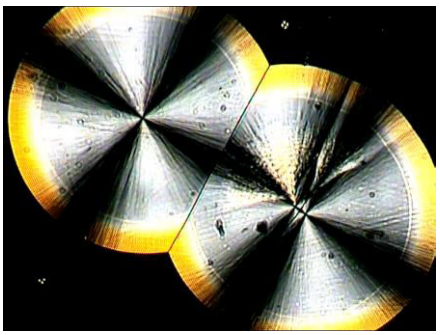

Fig. 3

In FTIR spectrum, the most proeminent vibrations observed in the synthesized stigmasteryl derivative were carbonyl group vibration, at 1728 cm^{-1} (strong) for C=O, at 1207 cm^{-1} (very strong) for C-O_{asym} and at 1070 cm^{-1} (strong) for C-O_{sym}. For methyl groups from steroid nucleus vibrations were at 2949, 2900 and 2865 cm^{-1}.

The behavior of liquid crystal can be also observed using an optical microscope with polarized light, confirming the results obtained by DSC experiments. In Fig.3 is shown the formation of spherulites, at cooling to 60 °C of the compound [1].

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Two azomonoethers isomers, dimethyl dichloro substituted: thermal and spectral behaviour

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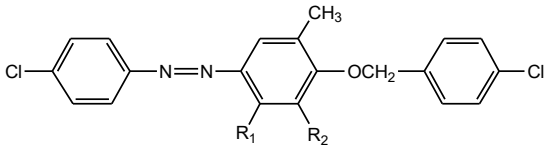
Two azomonoethers with the general formula:



where R_1 (for azomonoether 1) or R_2 (for azomonoether 2) is methyl group, were obtained by the condensation of 4-phenylazophenols with 4-chloromethyl-chlorobenzene in alkaline medium by Williamson method [1].

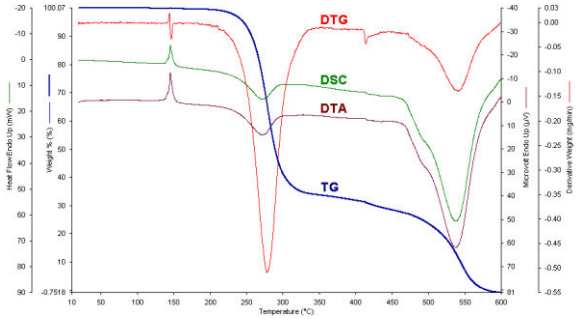


Fig. 1

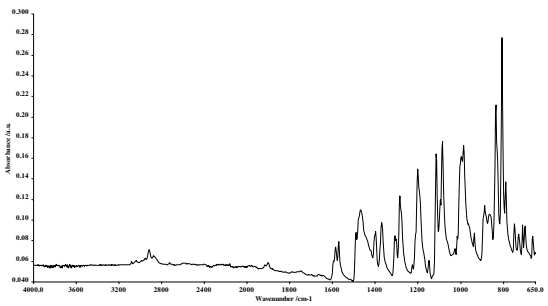


Fig. 2

Thermoanalytical curves of the azomonoether 2 (Fig.1) shows that it is stable up to 197.95 °C. Between 135.00 °C and 157.26 °C it melts. Oxidative decomposition of the azomonoether 2 occurs in two stages: first between 197.5 °C and 348 °C, and the second between 348.00 °C and 587.41 °C. In the first stage, exothermic, is lost 66.2 % by weight, and in the second stage, strongly exothermic, are losing the rest of the 33.8 % by weight [2,3].

FTIR spectrum shows absorption bands specific to azo and etheric groups (Fig. 2). The vibration frequency of N=N group appears at 1470 cm^{-1}. The band from 1285 cm^{-1} was attributed to the antisymmetrical valence vibrations and the band from 1087 cm^{-1} to the etheric symmetrical valency vibrations. The spectra also revealed absorption bands which correspond to Ar-Cl bond at their expected cm^{-1} (807 and 836).

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Thermal and kinetic analysis of some azononoetheric liquid crystals and thin films by MAPLE technique

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Azoic dyes are of large interest from the point of view of possible applications: dyes, liquid crystals as powders or thin films. Thermal analysis and kinetic studies of thermal induced changes of new compounds designed for temperature controlled applications is a real need and an advantageous pointer before trying to functionalize them.

This study aims to identify the physical and chemical transformations of several azomonoethers, related to non-isothermal increasing temperature regimes in dynamic air atmosphere and the kinetic study of the two decomposition steps occurring. Thin films were prepared by Matrix Assisted Pulsed Laser Evaporation (MAPLE) method.

The influence of different temperature regimes upon the thermal behaviour of chemical compounds can provide kinetic parameters indicating change in the reaction pathway. Because of the impossibility of evaluating the entire kinetic triplet $\{E, A, f(\alpha)\}$ that describes a physical or chemical transformation, from simple procedures like isoconversional methods, more sophisticated kinetic methods (Invariant Kinetic Parameters method, Perez-Maqueda *et al.* criterion or Master plot methods) were used. When several conversion functions may be situated on the same straight line and the correlation coefficients have high comparable values, the Perez-Maqueda *et al.* activation parameters should be compared with the invariant ones. If after using all known conversion functions there is no joint straight line to be found, then Master plot methods should be used. The kinetic analysis was performed by means of our software TKS-SP. A step by step visual fit of the normalized experimental data – $(d\alpha/dt)/(d\alpha/dt)_{max}$, by adjusting the $[f(\alpha)\cdot g(\alpha)]/[f(\alpha_{max})\cdot g(\alpha_{max})]$ master equation with the appropriate selected conversion degree and conversion function, is the main advantage in determining the true kinetic model for each constant heating rate experiment.

Thermal analysis and laser processing in organic electronics

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Organic thin film-based microdevices, such as transistors or capacitors, have tremendous potential for the design and fabrication of cost-efficient integrated circuits and/or electronic devices, or for applications where single-use devices are required. Pulsed laser deposition, matrix-assisted pulsed laser evaporation and laser-induced forward transfer are currently employed in materials science for thin film processing of soft, organic materials. Conducting, semiconducting, and dielectric compounds have been studied for use in thin film electronic and sensing devices and their properties investigated with respect to the involved laser processing techniques. Thermal analysis studies are presented and discussed, and an emphasis is put on the laser-induced thermal effects.

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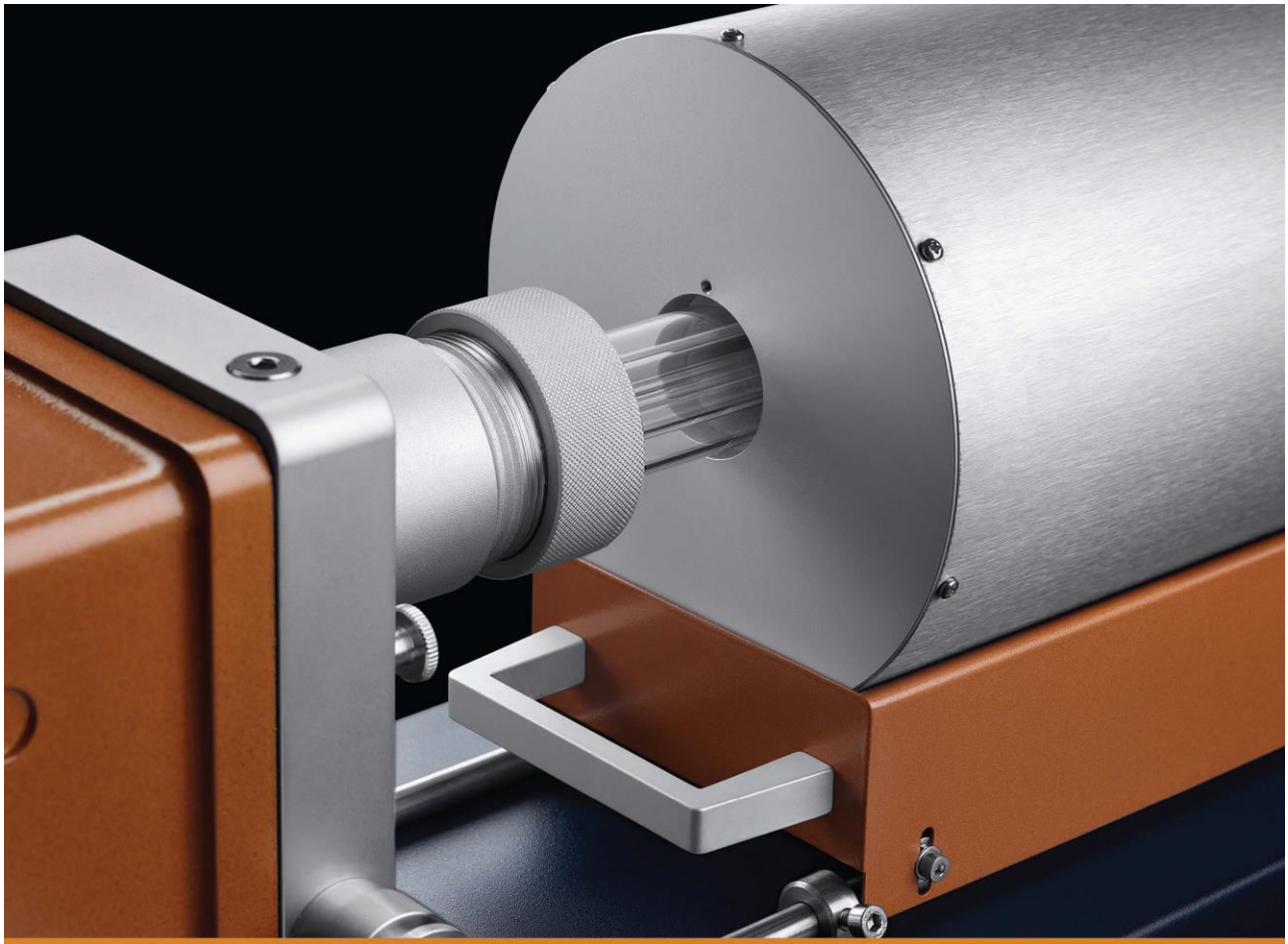

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