CEEC-TAC6 & Medicta2021

BOOK
OF
ABSTRACTS

Editors:
Andrei Rotaru
Matko Erceg

6th Central and Eastern European Conference on
Thermal Analysis and Calorimetry
&
15th Mediterranean Conference on
Calorimetry and Thermal Analysis

20-24 July 2021
Split, Croatia

Book of abstracts of the 6th Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC6) and 15th Mediterranean Conference on Calorimetry and Thermal Analysis (Medicta2021).

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The 6th Central and Eastern European Conference
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&
The 15th Mediterranean Conference on
Calorimetry and Thermal Analysis

CEEC-TAC6 & Medicta2021

20-24 July 2021 – Split, Croatia

is organized by the:

Central and Eastern European Committee for
Thermal Analysis and Calorimetry (CEEC-TAC),

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Croatian Society of Chemical Engineers (HDKIT),

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Dear Participants at CEEC-TAC6 & Medicta2021 Conference,

Let us express our great pleasure to welcome you here in Split - Croatia, for attending the joint 6th Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC6) and 15th Mediterranean Conference on Calorimetry and Thermal Analysis (Medicta2021) between 20th and 24th of July 2021; we thank very much to all 180 of you for joining us! You were invited in Split, which is the second largest city of Croatia. The city has rich history, as it was founded as the Greek colony of Aspalathos in the 3rd or 2nd century BC on the coast of the Illyrian Dalmatae, and later on was home to Diocletian's Palace, built for the Roman emperor in AD 305. Nowdays, Split is a modern city, with a vibrant cultural life.

The joint event CEEC-TAC6 & Medicta2021 gathers now 180 registered participants from 25 countries, presenting a total number of 176 scientific works. Of those, 4 are Plenary Lectures (PL), 10 are Invited Lectures (IL), 4 Parallel Sessions of Oral Presentations – 64 contributions (OP) & 3 Sessions of Poster Presentation – 112 contributions (PS). Each session of oral presentations is comprised of 16 works, while two poster presentations include 37 works and one includes 38 works.

At this edition, Awards will be offered to exceptional scientists: *i*) Prof. Herbert Danninger from Austria (Honorary Member of CEEC-TAC), *ii*), Prof. Thomas Maskow from Germany (Distinguished TA&C Researcher in Central & Eastern Europe); *iii*) Dr. Nina Obradovic from Serbia (Outstanding Young TA&C Researcher in Central & Eastern Europe); three *iv*) “Andrzej Malecki” 2021 Grants for Best Young Researcher from Central & Eastern Europe and from the Mediterranean Area in the field of Thermal Analysis and Calorimetry; two *v*) “Jaroslav Sestak” 2021 Travel Grant for Best Student from Central & Eastern Europe in the field of Thermal Analysis and Calorimetry.

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 Central and Eastern European countries and those from the Mediterranean area, Executive Organizing Committee, Central and Eastern European Committee for Thermal Analysis and Calorimetry, Committee for Thermal Analysis & Calorimetry of the Croatian Society of Chemical Engineers (HDKIT), University of Split (Sveuceliste u Splitu) and the Faculty of Chemistry and Technology (KTF) of the University of Split, University of Craiova (UCv), and Institute of Physical Chemistry “Ilie Murgulescu” of the Romanian Academy. We acknowledge the great support of our Sponsors: TA Instruments (Diamond Sponsor), NETZSCH (Gold Sponsor), Jasika d.o.o. (Bronze Sponsor) and Labtim (Exclusive Sponsor). A special acknowledgement has to be addressed to the *Journal of Thermal Analysis and Calorimetry*, *Ceramics International, Surfaces and Interfaces*, where one of their volumes will be dedicated to research papers of our conference, presented as oral or poster contributions.

The 5-day meeting is hosted at the Faculty of Chemistry and Technology of the University of Split. The official language of the conference is English.

We hope that you will enjoy the city during your stay at the CEEC-TAC6 & Medicta2021 conference, and that you will leave Split with the same good feelings and memories as those after attending the previous conferences. We expect that this conference will give you novel scientific and practical knowledge, and enrich you with a variety of new contacts.

Looking forward to seeing you at forthcoming thermal analysis and calorimetry conferences, and hopefully in 2023 for CEEC-TAC7 and Medicta2023!

Matko Erceg & Andrei Rotaru
Chairmen of CEEC-TAC6 & Medicta2021

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The joint event “6th Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC6) & 15th Mediterranean Conference on Calorimetry and Thermal Analysis (Medicta2021)” has gathered **180 registered participants** from **25 countries**, presenting a total number of **176 scientific works**. Of those, 4 are Plenary Lectures (**PL**), 10 are Invited Lectures (**IL**), 4 Parallel Sessions of Oral Presentations – 64 contributions (**OP**) & 3 Sessions of Poster Presentation – 112 contributions (**PS**). Each session of oral presentations is comprised of 16 works, while two poster presentations include 37 works and one includes 38 works.

Plenary Lectures

- ***Daniele Cangialosi*** (CSIC-Consejo Superior de Investigaciones Cientificas, Spain)
- ***Herbert Danninger*** (Vienna University of Technology, Austria)
- ***Thomas Maskow*** (Helmholtz Centre for Environmental Research, Germany)
- ***Nina Obradovic*** (Institute of Technical Sciences of SASA, Serbia)

Invited Lectures

- ***Romana Cerc Korosec*** (University of Ljubljana, Slovenia)
- ***Jordi Farjas*** (University of Girona, Spain)
- ***Loic Favergeon*** (Ecole des Mines de Saint-Etienne, France)
- ***Rodica-Mariana Ion*** (Valahia University of Targoviste, Romania)
- ***Stanislav Kurajica*** (University of Zagreb, Croatia)
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- ***Roberta Risoluti*** (Sapienza University of Rome, Italy)
- ***Ludmila N. Zelenina*** (Nikolaev Institute of Inorganic Chemistry, Russian Federation)

Tuesday, 20th of July	
8^{30}-13^{30}	***Short Summer School on TA&C***
13^{30}-14^{30}	*Lunch*
14^{30}-16^{30}	***Short Summer School on TA&C***
13^{30}-16^{30}	***Registration of participants at CEEC-TAC6 & Medicta2021***
16^{30}-18^{30}	*Afternoon break*
18^{30}-19^{20}	**Opening Ceremony**
19^{20}-20^{00}	**Herbert Danninger, PL1**
20^{00}-22^{30}	*Welcome Cocktail*

Wednesday, 21st of July				
9^{00}-9^{30}	**IL01**		**IL02**	
9^{30}-11^{20}	**Poster session 1** *Coffee break*			
11^{20}-11^{40}	OP1.01	OP2.01	OP3.01	OP4.01
11^{40}-12^{00}	OP1.02	OP2.02	OP3.02	OP4.02
12^{00}-12^{20}	OP1.03	OP2.03	OP3.03	OP4.03
12^{20}-12^{40}	OP1.04	OP2.04	OP3.04	OP4.04
12^{40}-13^{10}	**CCTAC1**			
13^{10}-14^{30}	*Lunch*			
14^{30}-14^{40}	**CEEC-TAC6 & Medicta2021**			
14^{40}-15^{20}	**Thomas Maskow, PL2**			
15^{30}-16^{00}	**IL03**		**IL04**	
16^{10}-16^{30}	OP1.05	OP2.05	OP3.05	OP4.05
16^{30}-16^{50}	OP1.06	OP2.06	OP3.06	OP4.06
16^{50}-17^{10}	OP1.07	OP2.07	OP3.07	OP4.07
17^{10}-17^{30}	OP1.08	OP2.08	OP3.08	OP4.08
17^{30}-17^{50}	*Coffee break*			
17^{50}-19^{00}	***CEEC-TAC General Assembly***			
17^{50}-19^{00}	***Medicta General Assembly***			
	Free evening			

Thursday, 22nd of July				
9^{00}-9^{30}	**IL05**		**IL06**	
9^{30}-11^{20}	**Poster session 2** *Coffee break*			
11^{20}-11^{40}	OP1.09	OP2.09	OP3.09	OP4.09
11^{40}-12^{00}	OP1.10	OP2.10	OP3.10	OP4.10
12^{00}-12^{20}	OP1.11	OP2.11	OP3.11	OP4.11
12^{20}-12^{40}	OP1.12	OP2.12	OP3.12	OP4.12
12^{40}-13^{10}	**CCTAC1**			
13^{10}-14^{30}	*Lunch*			
14^{30}-14^{40}	**CEEC-TAC6 & Medicta2021**			
14^{40}-15^{20}	**Daniele Cangialosi, PL3**			
15^{20}-20^{00}	***Afternoon break***			
20^{00}-24^{00}	*Conference Dinner*			

Friday, 23rd of July				
9^{00}-9^{30}	**IL07**		**IL08**	
9^{30}-11^{20}	**Poster session 3** *Coffee break*			
11^{20}-11^{40}	OP1.13	OP2.13	OP3.13	OP4.13
11^{40}-12^{00}	OP1.14	OP2.14	OP3.14	OP4.14
12^{00}-12^{20}	OP1.15	OP2.15	OP3.15	OP4.15
12^{20}-12^{40}	OP1.16	OP2.16	OP3.16	OP4.16
12^{50}-13^{30}	**Nina Obradovic, PL4**			
13^{30}-14^{40}	*Lunch*			
14^{40}-14^{50}	**CEEC-TAC7 / Medicta2023**			
15^{00}-15^{30}	**IL09**		**IL10**	
15^{30}-18^{00}	***Afternoon break***			
18^{00}-20^{00}	*Old-City Tour*			

Saturday, 24th of July	
9^{00}-10^{30}	*KTF Tour*
10^{30}	*Closing Ceremony*

1. Room A at KTF (A0-2, Level 0)
2. Room B at KTF (A0-1, Level 0)
3. Room C at KTF (A0-3, Level 0)
4. Room D at KTF (A1-2, Level 1)
5. Room E at FESB, next to KTF (main amphitheatre)
6. Coffee Break and Poster Session area at KTF
7. Canteen at the Student Service
1-7: Sveuciliste u Splitu, Kemijsko-Tehnoloski Fakultet, Rudera Boskovica 35, Split
8. Gusar Restaurant (Restoran Gusar)
8: Spinutska 69, Split
9. Split City Centre – *Diocletian Palace*

Program of CEEC-TAC6 & Medicta2021

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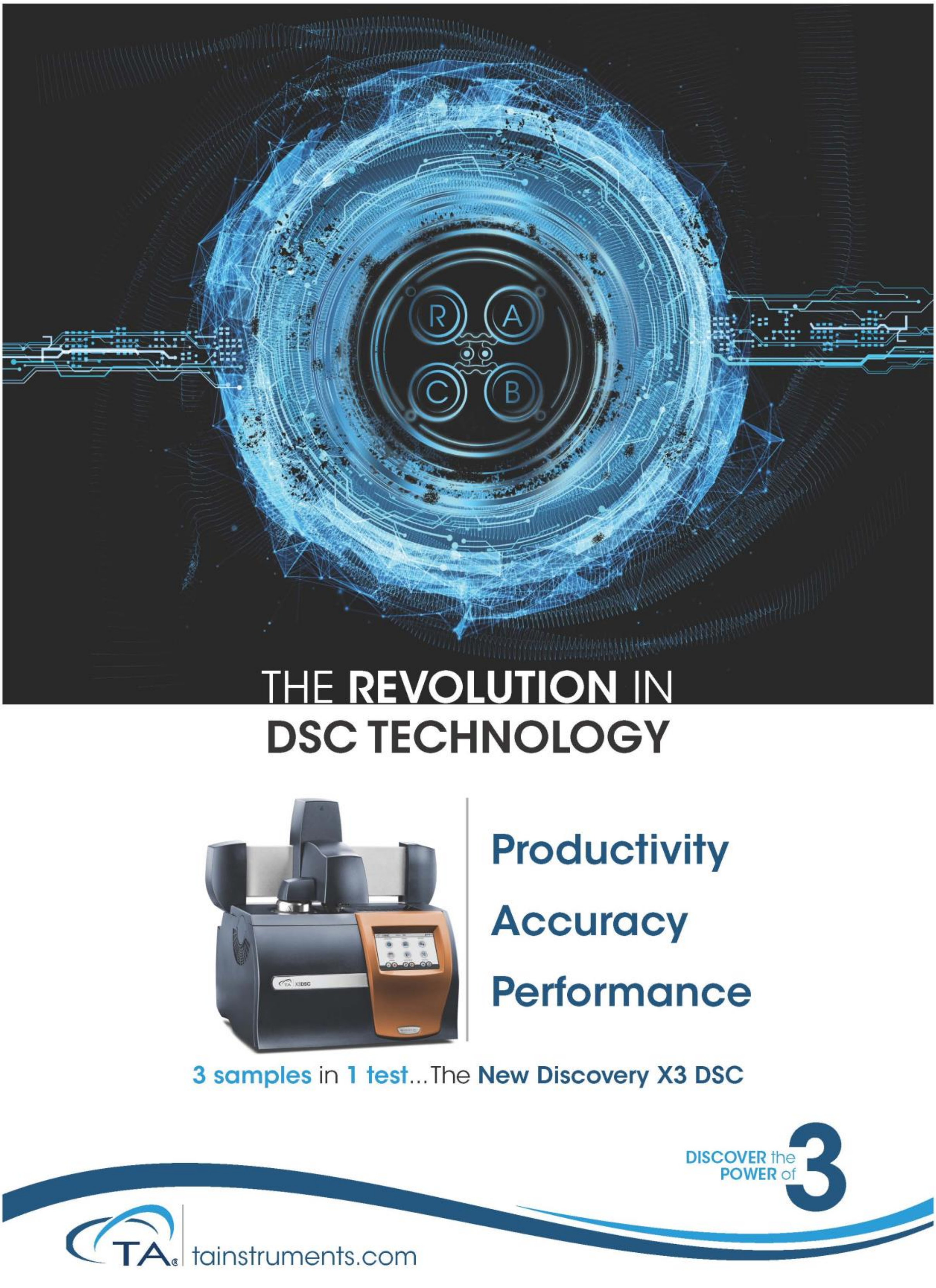

Plenary Lectures

Thermoanalytical techniques for characterizing sintering processes in ferrous powder metallurgy

Herbert DANNINGER[1], Raquel DE ORO CALDERON[1],
Stefan GEROLDINGER[1], Christian GIERL-MAYER[1]
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Abstract:

For powder metallurgy processing, the sintering stage, i.e. heat treatment of a powder compact below the melting point at least of the major component, is decisive for establishing microstructure and properties. Therefore, thorough studying of the chemical and metallurgical processes occurring during sintering is essential for attaining optimal product properties, and sintering has therefore been the focus of investigations for many decades (e.g. [1]). Here, thermoanalytical techniques, at best combined with chemical analysis, enable in-situ characterization of the sintering process from many perspectives [2]. When using these techniques in powder metallurgy, equipments such as STA or dilatometer can in fact be regarded as small-scale sintering furnaces that enable continuous recording of thermal and mass effects, in case of STA, or dimensional changes as in dilatometry [3].

Moreover, if combined with tools for chemical analysis such as mass spectrometry, also chemical reactions between substrate and atmosphere can be elucidated [4]. Here it should further be considered that the very large specific surface of a powder compact compared to a solid metallic body results in much higher reactivity with the surrounding atmosphere, this atmosphere being on one hand the “external” one, outside the body in the free space of the furnace, on the other hand the “internal” one within the pore network of the specimen.

Examples are shown for sintered alloy steels prepared through different alloying techniques, and phase transformations, liquid phase formation and deoxidation and decarburization as well as interstitial redistribution processes are described. Finally, the use of quench dilatometry for developing steel grades with sinter hardening capability is discussed.

[1] W. Schatt, Sintervorgänge, VDI-Verlag, Düsseldorf (1992)

[2] G. Leitner, W. Heinrich, K. Görting. Adv. Powder Metall & Partic. Mater. – 1995, MPIF, Princeton NJ (1995), Part 4, 259

[3] C. Gierl-Mayer, H. Danninger, Powder Metall. Progress 15 (2015) no.1, 3.

[4] R. de Oro Calderon, C. Gierl-Mayer, H. Danninger, Journal of Thermal Analysis and Calorimetry 127 (2017) No.1, 91.

The potential of biological calorimetry from the perspective of a bioengineer

Thomas MASKOW
Helmholtz Centre for Environmental Research – UFZ, Permoserstraße 15, 04318, Germany

Biotechnology promise solutions to the current challenges of the transition from a petroleum-based to a bio-based economy through the elucidation, application and utilization in technical processes of the biocatalytic mechanisms of action that have evolved over more than 4 billion years of evolution. Thermoanalytical measurement methods and thermodynamic theories with their inherent predictive power can make significant contributions here.

For instance, the metabolic heat production rate of only 100 myocardial cells or 100,000 aerobically growing bacteria or nanograms enzymatically converted material) is today measurable and reflects both kinetic and stoichiometry in real time. Metabolic heat can be monitored in reaction vessels ranging from a few nanoliters up to many cubic meters. Calorimetry does not interfere with the biological process under investigation and not require any labelling [1]. Although all these advantages make calorimetry an interesting method for many applications (e.g. in medicine, environmental sciences, ecology, biochemistry and biotechnology), the number of groups working biocalorimetrically or biothermodynamically is very small.

The rather rare applications to metabolic processes have several reasons, of which only a few will be mentioned in the following. First, it is very difficult to imagine that highly complex metabolic networks can be described well by simple thermodynamic laws [2,3]. Second, the inclusion of other, non-material forms of energy (light [4], electrical energy [5]) in biological balances is challenging. Third, additional physical processes such as surface interactions complicate thermodynamic data interpretation [5]. Fourth, calorimeter manufacturers optimize instruments for measurement sensitivity and stability or ease of use, but rarely for the special requirements of biological systems. On the basis of some selected examples, first approaches to solutions will be shown in order to be able to tap the full potential of calorimetry.

[1] O. Braissant, G. Bonkat, D. Wirz, A. Bachmann, *Thermochim. Acta*, 555 (**2013**) 64-71.
[2] V. Vojinovic , U. von Stockar, *Biotechnol. Bioeng.*, 103(4) (**2009**) 780-795.
[3] K. Vogel, T. Greinert, M. Reichard, C. Held, H. Harm, T. Maskow, *Int. J. Mol. Sci.,* 21 (**2020**) 8341.
[4] T. Maskow, A. Rothe, T. Jakob, S. Paufler, C. Wilhelm, *Sci. Rep.*, 9(**2019**) 9298.
[5] B. Korth, T. Maskow, C. Picioreanu, F. Harnisch ′, *Energy Environ. Sci.*, 9(**2016**) 2539-2544.
[6] K. Vogel, L. Pfaff, D. Breite, H. Al-Fathi, C. Ortmann, T. Estrela-Lopis, T. Venus, A. Schulze, H. Harms, U.T. Bornscheuer, T. Maskow, *Sci. Total Environ.,* 773(**2021**) 145111.

Non-equilibrium glass dynamics by advanced calorimetry

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The present contribution aims to unveil how advanced calorimetric techniques, including new generation fast scanning calorimetry, can convey information of utmost importance on the kinetics of non-equilibrium in glassy materials. I will first give a glance on well-established facets of the transformation from a liquid into a glass, the so-called vitrification or glass transition, and the evolution of the glass thermodynamic state, generally addressed as physical aging. Subsequently, I will show how recent activity on a variety of glasses revealed the presence of different molecular/atomic mechanisms triggering both vitrification and physical aging, thus questioning the common view exclusively emphasizing the role of the primary (α) relaxation [1-2].

The presence of fast mechanisms of equilibration is highlighted in view of their mild activation energy, which implies smooth increase of the time to equilibrate with decreasing temperature. This offers great potential to decrease the glass energy in time scales amenable to the experimental practice. It will be shown that – in glasses exhibiting large amount of free interface, where equilibration is accelerated with respect to bulk glasses [3] – energies down to the ideal glass, theorized long ago [4] and exhibiting entropy equal to that of the most stable crystal, can be achieved in time scales shorter than several days [5-6].

[1] D. Cangialosi, "Physical Aging of Polymer" in Encyclopedia of Polymer Science and Technology, Wiley (2018)
[2] D. Cangialosi, "Glass transition and physical aging of confined polymers investigated by calorimetric techniques" in Handbook of Thermal Analysis and Calorimetry, Elsevier 6 (2018) 301-337
[3] D. Cangialosi, A. Alegria, J. Colmenero, Prog. Pol. Sci. 54 (2018) 128-147
[4] J. H. Gibbs, E. A. Di Marzio, J. Chem. Phys. 28 (1958) 373
[5] V.M. Boucher, D. Cangialosi, A. Alegría, J. Colmenero, Phys. Chem. Chem. Phys. 19 (2017) 961-965
[6] X. Monnier, J. Colmenero, M. Wolf, D. Cangialosi, Phys. Rev. Lett. 126 (2021) 118004

Influence of $BaTiO_3/Fe_2O_3$ addition on crystallization and polymorphism of PDVF polymer matrix followed by DSC-TG

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Ceramic/polymer dielectric composites are widely used as components for electric devices, mainly because of their high chemical stability, mechanical strength, and flexibility. In order to increase dielectric permittivity, ceramic fillers with high dielectric constant have been usually incorporated in the polymer matrix in large amounts. With the aim to enhance dielectric properties of matrix, 5 wt.% of $BaTiO_3/Fe_2O_3$ core/shell composite was added into the PVDF matrix. Prior to addition, five $BaTiO_3/Fe_2O_3$ powders were prepared by different synthesis conditions. The changes in crystal structure and lattice dynamics of the obtained ceramic/polymer composite were correlated with changes in the phase composition and morphology of $BaTiO_3/Fe_2O_3$ core/shell filler. Thermal analysis such as DTA/TG/DSC are useful methods to determine various parameters in ceramic/polymer composites. We were able to corroborate that differences in phase composition and morphology of $BaTiO_3/Fe_2O_3$ core/shell filler have influence on formation of various PVDF allomorph modification, as well as a level of crystallinity.

Invited Lectures

Innovative coupled approaches in thermal analysis investigations

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Thermal analysis may be involved for the investigation of several real and complex matrices in different fields and leads to a signal resulting from a number of thermal processes.

Data collection task, whether in calorimetry, thermogravimetry or other techniques, typically involves many measurements made on many samples. Such multivariate data has traditionally been analyzed using one or two variables at a time. However, this approach fails to discover the relationships among all variables and samples efficiently. To overcome this, chemometric analysis process all of the data simultaneously for extracting information from multivariate chemical data using tools of statistics and mathematics.

A novel coupled approach based on thermogravimetry and chemometrics has been recently and effectively proposed to improve sensitivity of the measurements and to develop models of prediction to be used in analytical chemistry. In particular the improvement of the TGA/Chemometrics approach has been recently demonstrated effectiveness in clinical and forensic field. In this presentation, a multi-screening test based on the coupling of thermogravimetry and chemometrics is presented for the differential diagnosis of hereditary hemolytic anemias. In addition, application of this novel approach in the forensic field is also reported for the determination of the time since death.

[1] R. Risoluti, P. Caprari, G. Gullifa, S. Massimi, L. Maffei, F. Sorrentino, E. Carcassi, S. Materazzi. Chemical Communications 7 (2020) 141, .
[2] R. Risoluti, P. Caprari, G. Gullifa, F. Sorrentino, L. Maffei, S. Massimi, E. Carcassi, S. Materazzi, S. 56 (2020) 7557-7560.
[3] R. Risoluti, S. Canepari, P. Frati, V. Fineschi, S. Materazzi.
"2n Analytical Platform" to Update Procedures in Thanatochemistry: Estimation of Post Mortem Interval in Vitreous Humor (2019) DOI: 10.1021/acs.analchem.9b01443.

Thermal analysis of thin films – an important aspect in preparation of functional layers

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Thin films deposited as thin layers on top of a surface, change its chemical and physical properties. Today, they are used in various applications: to protect surfaces (against corrosion, abrasion, wear), as optically active layers (refractive, adsorptive) or with a specific chemical function (sensors, catalysts) [1].

Various deposition methods are available for the preparation of thin films, which can be divided into physical and chemical. Physical vapor deposition and sputtering belong to the first class, while chemical vapor deposition, spray pyrolysis and the sol-gel synthesis process where the sol is applied to the substrate by dip or spin coating, are classified as chemical ones [2].

The role of thermal analysis in the preparation of two different types of functional coatings, i.e. electrochromic nickel oxide thin films and photocatalytic titanium dioxide thin films, will be presented. In both cases thermal treatment after the deposition process is necessary to improve the adhesion of thin films to the substrate and to ensure their structural stability. For the electrochromic nickel oxide thin films, it is known that the degree of thermal treatment is the key factor affecting the magnitude of the optical modulation. Too high processing temperature significantly lowers the electrochromic effect, on the other hand, for thermally untreated films, the optical modulation also decreases soon after the beginning of the cycles. The aim of the optimization procedure was to find the temperature and duration of thermal treatment of sol-gel derived nickel oxide thin films prepared from different precursors that lead to maximum optical modulation during potential switching for a large number of cycles [3].

For the photocatalytic titania thin films, formation of the photocatalytically active crystalline phase can be followed using thermal techniques in combination with X- Ray Diffraction. At temperatures higher than the crystallization temperature, the crystallites continue to grow, resulting in a lower specific surface area and consequently a lower photocatalytic efficiency. In contrast, the band gap becomes narrower with increasing particle size, which means that a shorter wavelength is required for excitation. Therefore, the optimal temperature and duration of thermal treatment should be determined, leading to an optimal crystallite size. In this context the thermoanalytical method plays an important role [4].

[1] U. Schubert, N. Hüsing, “Synthesis of Inorganic Materials”, Wiley-VCH, (2012)
[2] L. Niinistö, J. Therm. Anal. Calorim. 56 (1999) 7
[3] R. Cerc Korošec, P. Bukovec, Acta Chim. Slov. 53 (2006) 136
[4] P. Horvat, A. Sever Škapin, U. Lavrenčič Štangar, R. Cerc Korošec, 10.1007/s10973-020-10099-x.

Non-standard kinetic analysis of polymer crystallization and liquid evaporation

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The kinetic analysis of two different physical transformations is addressed in this presentation.

First, we study the kinetics of a process that does not obey an Arrhenius temperature dependence, as it is usually the case when processes occur near the equilibrium temperature. In particular, we analyze polymer crystallization, which is usually governed by the Hoffman-Lauritzen (H-L) temperature dependence [1]. We have developed a method that allows us to obtain the H-L kinetic parameters from a set of measurements done at constant heating and at constant cooling rates. Once, the kinetics has been disclosed, we are able to predict the crystallization course for an arbitrary thermal history. This method has been applied to the crystallization of PET and PA6, that has been monitored by differential scanning calorimetry (DSC).

Second, we analyze the evaporation kinetics of a liquid placed inside the tubular furnace of a thermobalance. To this aim, we have developed a physical model that describes the evaporation kinetics under the general conditions of thermogravimetric measurements; i.e. it takes into account gas diffusion and convective gas transport [2]. This model is used to determine the equilibrium vapour pressure in a wide temperature range for triethanolamine and water. Also, the applicability of isoconversional methods to the evaporation kinetics is reviewed.

[1] J. Farjas Silva, J.P. López-Olmedo, P. Roura, Model-free isoconversional method applied to polymer crystallization governed by the Hoffman-Lauritzen kinetics, Polymer. 120 (2017) 111–118.
[2] I. Zghal, J. Farjas Silva, J. Camps, M. Dammak, P. Roura, Thermogravimetric measurement of the equilibrium vapour pressure: Application to water and triethanolamine, Thermochim. Acta. 665 (2018) 92–101.

Investigation of the influence of end-temperature on the fast pyrolysis process of oil shale and on the properties of its products

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Although the world is moving towards renewable energy, fossil fuels are still being utilized for power and oil production until cleaner technologies can be implemented. In Estonia, most power plants are still fuelled by oil shale and although the material has been extensively studied, research on the topic of valorisation and “green” technologies is still being conducted.

Using thermogravimetric analysis to study the thermal behaviour of oil shale is nothing new. Extensive research can be found on both the pyrolysis and combustion process of oil shale, also by our group [1]–[3]. The use of a high heating rate furnace (operating with a linear heating rate of up to 1000 K/min) coupled with a mass spectrometer (HHR-TGA-MS) enables investigating new areas of interest and simulating industrial conditions more accurately. In this research, HHR-TGA-MS was used to study the effect of temperature on the pyrolysis of oil shale (and imitate industrial conditions), evaporating gases and on the composition of the produced solid residue. The samples were heated to different end-temperatures with a heating rate of 500 K/min and held isothermally at the desired temperature for 15 minutes. The end-temperatures were varied from 300 to 825 °C. The evaporating gases were simultaneously analysed and specific interest was given to the change in the evolution of sulphur-containing compounds. The obtained semicoke was analysed by attenuated total reflection Fourier transformation infrared spectroscopy (ATR-FTIR) and some samples also by X-ray diffraction spectroscopy (XRD) to determine the main structural and compositional changes. SEM images were gathered to characterize the possible changes in the surfaces of the particles.

The results clearly showed the effect that the end temperature had on the process – how the mass loss from organic components can be controlled by temperature. XRD showed transformation of pyrite into pyrrhotite. The amount of K-feldspar decreased with the increase in temperature, whereas calcite followed an opposite trend. ATR-FTIR showed significant changes in the peaks corresponding to organic matter and structural changes in them – a shouldering of the main peak was observed. These results offer an overview of the complex pyrolysis process and illustrate how several analytical techniques complement each other.

[1] B. Maaten, O. Järvik, O. Pihl, A. Konist, and A. Siirde, “Oil shale pyrolysis products and the fate of sulfur,” *Oil Shale*, vol. 37, no. 1, pp. 51–69, 2020.
[2] B. Maaten, L. Loo, A. Konist, and A. Siirde, “Mineral matter effect on the decomposition of Ca-rich oil shale,” *J. Therm. Anal. Calorim.*, vol. 131, no. 3, pp. 2087–2091, 2018.
[3] L. Loo, B. Maaten, A. Siirde, T. Pihu, and A. Konist, “Experimental analysis of the combustion characteristics of Estonian oil shale in air and oxy-fuel atmospheres,” *Fuel Process. Technol.*, vol. 134, pp. 317–324, 2015.

The role of water vapor pressure during thermal decomposition of crystalline solids: its influence on both the reaction course and its kinetics

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Thermal decompositions of crystalline solids are involved in many industrial processes. Among the various features that can influence such a type of solid-state reactions, the partial pressure of the gaseous product in the reaction atmosphere is an important parameter, and its impact is probably less known than that of temperature, even if the influence of both parameters is often linked.

Indeed gaseous product partial pressure is one of the intensive parameters which allow to describe a system in a particular state: initial state, final state, balance, or for a given conversion degree. In this thermodynamic description, partial pressure gives information on the sense of evolution of a system, and so participates to the prediction whether a chemical reaction is possible or not.

From a kinetic point of view the role of the gaseous product partial pressure has been often observed. In consideration of the deviation from the thermodynamic equilibrium, an increase in the partial pressure in the reaction atmosphere often reduces the overall reaction rate of the thermal decomposition at a given temperature. However more unusual behaviours have also been observed considering the effect of the partial pressure of gaseous product on the kinetics of thermal decomposition. For example the Smith-Topley effect [1], which corresponds to an initial decrease followed by a subsequent increase then another decrease in the rate constant with increasing $p(H_2O)$ for a given temperature, was observed for several thermal dehydration of inorganic hydrates. Nevertheless the effect of the partial pressure on the reaction rate remains difficult to understand and to predict due to the complexity of the phenomena and their mutual correlations.

In this lecture, various examples of thermal decomposition reaction are presented in order to overview the role and the importance of water vapor pressure on both the thermodynamic and the kinetic descriptions of thermal decomposition of crystalline solids. The numerous difficulties linked with the effect of water vapor pressure are addressed by means of several approaches including reaction mechanism in elementary steps [2,3], surface nucleation and growth models, [2,4] universal kinetic approach [5-8] and solid solution description [9].

[1] B. Topley, M.L. Smith, Nature 128 (1931) 302
[2] J. Preturlan, L. Vieille, S. Quiligotti, L. Favergeon, J. Phys. Chem. C 124 (2020) 26352
[3] L. Favergeon, M. Pijolat, C. Helbert, J. Mater. Sci 43 (2008) 4675
[4] L. Favergeon, M. Pijolat, F. Valdivieso, C. Helbert, Phys. Chem. Chem. Phys. 7 (2005) 3723
[5] N. Koga, L. Favergeon, S. Kodani, Phys. Chem. Chem. Phys. 21 (2019) 11615
[6] M. Fukuda, L. Favergeon, N. Koga. J. Phys. Chem. C 123 (2019) 20903
[7] S. Kodani, S. Iwasaki, L. Favergeon, N. Koga. Phys. Chem. Chem. Phys. 22 (2020) 13637
[8] Y. Yamamoto, L. Favergeon, N. Koga, J. Phys. Chem. C 124 (2020) 11960
[9] L. Okhrimenko, L. Favergeon, K. Johannes, F. Kuznik, Thermochimica Acta 687 (2020) 178569.

Thermodynamic study of water evaporation processes from *α*-, *β*- and *γ*-cyclodextrin hydrates

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Cyclic macromolecules consisting of 6, 7, or 8 glucopyranose units, respectively are *α*-, *β*- and *γ*-cyclodextrins (CDs). These units form hollow truncated cone cavity with hydrophilic exterior and hydrophobic interior, which can include a wide range of guest molecules, thereby forming various host-guest inclusion complexes. These inclusions may beneficially change of CD physicochemical characteristics such as solubility, thermal stability, volatility, resistance to oxidation, visible and UV light, etc. Because of these properties CDs are widely used in analytical chemistry, catalysis and also in pharmaceutical, food and cosmetic industries. Water plays an important role in formation of the CDs inclusion complexes, since the process of complex formation is essentially a replacement reaction of water molecules located in CD cavities by hydrophobic guest molecules. Meanwhile, quantitative data on equilibria between CDs and H_2O are very scarce and contradictory, which makes it difficult to produce high-quality materials.

The purpose of this work is a comprehensive study of the *α*-, *β*- and *γ*-CD hydrates dehydration processes by static method with glass membrane-gauge manometers. The measurements have been realized in the wide intervals of temperature ($313 \leq T/\mathrm{K} \leq 506$), pressure ($1 \leq p/\mathrm{Torr} \leq 760$) and composition ($\mathrm{CD}{*}x\mathrm{H_2O}$, $2.6 \leq x \leq 15$). The accuracy of measurements for used setup was 0.5 Torr, 0.5 K and 0.01 formula units in the values of pressure, temperature and solid phase composition, accordingly [1].

As a result of this study thermal stability of investigated compounds was established, temperature dependences of pressure for dehydration processes were obtained (four types of dehydration processes were studied), enthalpies and entropies of dehydration were determined and Gibbs energy change in the process of binding water with CDs was calculated. On the base of information obtained the conclusions about the nature of the interactions between host (CDs) and guest molecules (water) were drown. The main results on *α*-cyclodextrin hydrates are published in [2-3].

The accumulation of quantitative information about the dehydration processes of *α*-, *β*-, *γ*-CDs hydrates will allow one to synthesize functional materials with desired properties in the future.

[1] L. Zelenina, T. Chusova, S. Sapchenko, E. Ukraintseva, D. Samsonenko, V. Fedin, JCT. 67 (2013) 128.
[2] A. Manakov, T. Rodionova, L. Aladko, G. Villevald, J. Lipkowski, L. Zelenina, T. Chusova, T. Karpova, JCT. 101 (2016) 251.
[3] L. Zelenina, T. Chusova, A. Isakov, T. Rodionova, G. Villevald, A. Manakov, JCT. 158 (2021) 106424.

Thermal evolution of gels prepared by modification of aluminum sec-butoxide with ethyl acetoacetate intended for use as ceria catalyst carriers

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A recent investigation of doped ceria catalyst, as well as advanced synthesis methods of ceria catalyst support will be presented. First, a brief review of the contribution in the field of nanocrystalline ceria synthesis [1] will be given, in which the synthesis and properties of ceria doped with different transition metal ions [2] will be addressed, with a particular focus on copper and manganese doped ceria [3]. Afterwards, the sol-gel synthesis of gels prepared by chelation of aluminum sec-butoxide (Asb) with ethyl acetoacetate (Eaa) in various amounts will be described [4]. Finally, special attention will be payed to thermal evolution study of the obtained gels and assessment of their suitability as ceria catalyst support. Samples were characterized by scanning electron microscopy (SEM), low angle laser light scattering (LALLS), differential thermal and thermo-gravimetric analysis (DTA/TGA), Fourier-transformed infra-red spectroscopy (FTIR) and X-ray diffraction (XRD). It was established that samples with a low Eaa/Asb ratio are mainly amorphous, whilst the samples with a greater Eaa/Asb ratio are predominantly chelate. The crystallization of γ-Al_2O_3 takes place between 600 and 1000 °C in two separate processes for all investigated samples. On the other hand, a complete transition to α-Al_2O_3 at 1200 °C occurs exclusively in samples with a high Eaa/Asb ratio, while it is only partial for samples with a low Eaa/Asb ratio. The observed mass loss is in concordance with the hypothesis that the overall gel content in the samples could be represented by a simplified formula $Al(Eaa)_xO_{(3-x)/2}$, where x is the Eaa/Asb ratio. In addition to thermal evolution, the gel-chelate duality of the samples is reflected in the morphology and particle size distribution. Proper synthesis parameters, as well as thermal treatment conditions enable the tailoring of alumina properties for ceria catalyst support.

[1] S. Kurajica, I, Minga, M. Guliš, V. Mandić, I. Simčić, J. Nanomaterials (2016) 7274949.

[2] S. Kurajica, K. Mužina, G. Dražić, G. Matijašić, M. Duplančić, V. Mandić, M. Županči, I. K. Munda, Mater. Chem. Phys. 244 (2020) 12689.

[3] S. Kurajica, I. K. Munda, G. Dražić, V. Mandić, K. Mužina, L. Bauer, G. Matijašić, Ceram. Intl. 46 (2020) 29451.

[4] S. Kurajica, G. Mali, V. Mandić, I. Simčić, G. Matijašić, K. Mužina, J. Phys. Chem. Solids 148 (2021) 109783.

When the two-state model of protein unfolding breaks?

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Lysozyme is a small globular protein with applications in the food and pharmaceutical industries. Due to its stability and availability, it is also a classic model protein. Lysozyme displays a single well-defined endothermic effect upon heating. The calorimetric and Van't Hoff enthalpies of unfolding are very close, and the unfolding process is described as a two-state conversion from native to unfolded states with no intermediates.

However, the apparent activation energy of unfolding of lysozyme in water-DMSO mixtures is lower than the enthalpy of unfolding [1], which does not fit the two-state model.

Also, the temperature dependence of the circular dichroism signal in the aromatic region diverges from the temperature dependence of the degree of unfolding determined from calorimetric data with the increasing content of the organic co-solvent.

The unfolding of lysozyme in glycerol was studied using fast scanning calorimetry in a wide range of heating rates. The apparent activation energy of the unfolding was determined using the Kissinger method [2]. The determined apparent activation energy value is again lower than the calorimetric enthalpy of unfolding and is very similar to the value determined in water-DMSO mixtures.

The approach based on Tammann's nuclei development method was applied to study the refolding of lysozyme. A folding intermediate with faster folding and refolding kinetics was found; however, this intermediate is formed only in an alternative folding pathway and does not contribute to the unfolding of the native protein.

Thus, the question arises, what kind of folding/unfolding mechanism can explain the results mentioned above?

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[1] T. Magsumov, A. Fatkhutdinova, T. Mukhametzyanov, I. Sedov, Biomolecules, 9 (2019) 547
[2] T. A. Mukhametzyanov, I. A. Sedov, B. N. Solomonov, C. Schick, Biochimica et Biophysica Acta (BBA) - General Subjects, 1862(9) (2018) 2024–2030.

Chemical and thermal analysis for architectural heritage materials

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Abstract. The characterization of historical materials is essential for investigating the chemical composition, microstructure and morphological characteristics of architectural monuments and artifacts, from which information can be deduced about their condition, environmental influence and natural aging or man-made degradation processes. Among the existing techniques, optical microscopy (OM), atomic force microscopy (AFM), which can provide real three-dimensional topographies showing the surface properties of the sample, scanning electron microscopy combined with X-ray analysis of energy dispersion (SEM-EDX), which allows acquisition of images of materials, infrared and Raman, commonly used to characterize inorganic and organic compounds, UV-visible spectroscopy (UV-vis) of great importance in architectural heritage, which can reveal various physico-chemical mechanisms that cause color. In addition, X-ray technologies are applied, such as X-ray fluorescence (XRF) and X-ray diffraction (XRD), fast and inexpensive techniques for characterizing synthetic or artificial materials. Except for these techniques, thermal analysis can quickly and accurately measure changes in crystal structure, dehydration and decomposition. These techniques are thermogravimetry (TG), derived thermogravimetry (DTG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), DSC coupled thermogravimetry (TG-DSC) [1]. The thermal analysis provides useful information about the compositions of materials that belong to our cultural heritage. In other cases, the results can be related with data obtained by other well-established techniques, confirming the relevant complementary nature of thermal analysis. An important aspect of these thermo-analytic techniques is that, although generally destructive, only a few milligrams of evidence are usually required - which is very important in the study of objects of historical or cultural value. This review describes some classic applications of individual techniques and provides scientific support to scientists and engineers to make decisions in the context of architectural heritage. The criteria for determining the preservation treatment impose compatibility as best as possible between the preserved object and the preservative and the minimally invasive intervention [2]. Some exemplifications will be done in this paper, by using the nanomaterials, as magnesium and calcium hydroxides or hydroxyapatite, tested on some architectural surfaces.

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[1] R,M,Ion, J. Therm. Anal. Calorim., 102, 1567-1572 (2010)
[2] S.M. Doncea, R.M. Ion, et al., Instrumentation Science & Technology, 38:1, 96-106 (2008)

Insight on some recent energy-structure-stability studies of organic compounds: a thermochemical approach

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Our research group is being involved for a long time in a systematic experimental and theoretical thermodynamic study over key organic compounds of different classes, since the results are important contributions to clarify the reactivity of the molecules. Our main goal is to provide reliable values for the standard molar enthalpy of formation in the gas-phase, an essential thermodynamic property on the establishment of molecular energetic and structural correlations, as well as in the assessment to the energy associated to transformations in which the compounds are involved. In this context, significant experimental work has been developed with homocyclic and heterocyclic compounds (mainly five and six membered rings) with oxygen, sulphur or nitrogen heteroatoms. Complementary, computational tools have been used to derive the values of identical parameters and the comparative analysis of the values derived by the two approaches is used to support strategies on the establishment of reliable prediction. Other thermodynamic parameters have been also determined, namely standard entropies and Gibbs functions of formation of the compounds studied [1,2].

Currently we are involved in two main projects aiming (i) the energetic characterization of compounds involved in biomass degradation processes and (ii) determination of thermodynamic properties of chemical fragrances: tools for environmental risk assessment. Indeed, the thermodynamic characterization of different chemical transformations of biomass-derived compounds still remains a challenge due to the shortage of accurate thermochemical data of the molecules involved in those processes. On the other side, accurate thermodynamic data for chemicals have major importance for the assessment of the feasibility of chemical processes, as well as for the environmental fate of chemicals.

This research addresses to fill the experimental data gaps, to validate predictive strategies, expanding them in a in a well-supported way based in reliable key data.

[1] V. L. S. Freitas, M. D. M. C. Ribeiro da Silva, J. Therm. Anal. Calorim. 121 (2015) 1059.
[2] A. L. R. Silva, A. C. M. O. Lima, M. D. M. C. Ribeiro da Silva, J. Therm. Anal. Calorim. 134 (2018) 1267.

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Oral Presentations 1

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

Model free kinetic studies of the curing behaviour of bio-based epoxy and acrylate resins

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The curing behaviour of the bio-based epoxy with anhydride hardeners (Nadic methyl anhydride-NMA and Methyl tetrahydrophthalic anhydride-MTHPA) in the presence of imidazole catalyst was studied using differential scanning calorimetry. Different model free kinetic methods (Friedman [1] and Vyazovkin [2]) were used to predict the cure kinetics and they were compared with each other. The complicated curing mechanism (due to etherification and esterification reaction) was well predicted by the model free kinetic methods and provided insight into the cure mechanism of epoxidized vegetable oil with the anhydride hardener.

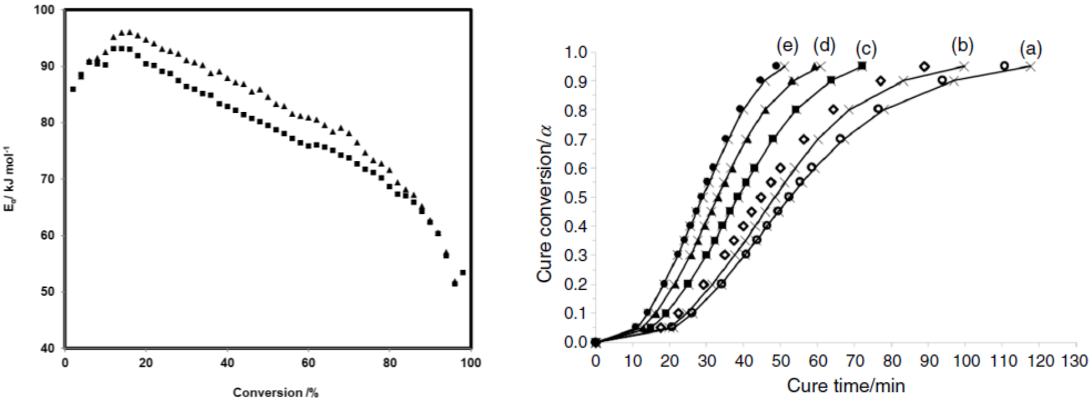

Figure 1: (A) Activation energy vs conversion for the epoxidized vegetable oil with anhydride (NMA) curing agent predicted using three isoconversional methods (▲-Friedman, ■- Vyazovkin) **(B)** α(t)-curves obtained from isothermal DSC experiments (-X-) at five isotherms (a) 40, (b) 45, (c) 50, (d) 55, and (e) 60 °C compared with α(t)-curves predicted using Ea(α) from VA method at the same isotherms (solid line – measured; dots – Predicted)

Another bio-based resin system, maleinated acrylated vegetable oil was cured in the presence of free radical peroxide catalyst and the cure mechanism was studied using Friedman and Vyazovkin method. The MAVO resin mixture reached gelation already in a very early phase of curing ($\alpha_{gel} <$ 5%). This result confirmed the assumption that gelation was responsible for the change of the reaction to diffusion-controlled process even at the very early stage of cure. The gelation was measured using the rheometer. Another effect that influenced the thermal cure at processing temperatures below 50 °C was due to vitrification. The measured α(t)-curves were compared with α(t)-curves calculated from isothermal DSC measurements (40, 45, 50, 55, and 60 °C) Fig 1 (B).

It was concluded that, model free kinetic studies helps to understand the complex curing mechanism of the bio-based resin system and in some instance these approaches proved superior to model-based predictions since quantitative knowledge on the reaction mechanism is not known. The rheological properties assist in determining quantitatively the chemorheological behaviour like gelation and vitrification.

Thermal degradation kinetics of polyurethanes and their analysis by model free kinetics and kinetic modelling

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Polyurethane (PUR) foams find their commercial use as insulating material in buildings, furniture, and in the automobile industry. As a high flammability and fast spread of flame in the course of fire are highly undesirable in these applications, there is an emphasis on studying the thermal and thermo-oxidative degradation of PUR in the absence and presence of flame retardants, also including the study of the emission of volatile gases that fuel the combustion [1].

One of the main objectives of this research is to get a thorough understanding of the thermal degradation mechanisms of PUR and PUR-derived products, like foams, and their degradation kinetics, focusing on making the relationship between the thermal degradation kinetics of PUR networks and the polyols and isocyanates they are made of. Studying degradation mechanisms and developing composition-based thermal degradation kinetic models will facilitate predicting the degradation behaviour of PUR having different compositions under a range of conditions.

The degradation kinetics of PUR and its monomer polyols and the degradation products formed, including residues or char and evolved gases, are studied in detail using TGA and spectroscopic techniques. TGA analysis on polyether and polyester-based PUR foams and their constituting monomer polyols revealed relations between their degradation paths. These findings are further supported by Hi-Res™ TGA experiments, which clearly separated the degradation steps. TGA-MS is used for simultaneous evolved gas analysis and FTIR spectroscopy is used for the analysis of residues at different instances in the degradation process.

Thermal data, obtained in TGA under different atmospheres and for different temperature programs, was kinetically analysed by using model-free kinetics (MFK), providing information for the development of a more comprehensive degradation kinetics model [2]. The relations between the chemical composition and structure of the PUR and the resulting thermal degradation behaviour can be employed to judiciously fine-tune the polymer properties.

[1] S. Duquesne, M. Le Bras, S. Bourbigot, R. Delobel, G. Camino, B. Eling, C. Lindsay, and T. Roles. Thermal degradation of polyurethane and polyurethane/expandable graphite coatings. J. Polym. Degrad. Stab., 74(3) (2001) 493–499

[2] S. Vyazovkin, A. K. Burnham, J. M. Criado, L. A. Pérez-Maqueda, C. Popescu, and N. Sbirrazzuoli. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. J. Thermochim. Acta., 520(1-2) (2011) 1–19.

Quasi-isothermal modulated DSC for characterizing sulphur vulcanization systems

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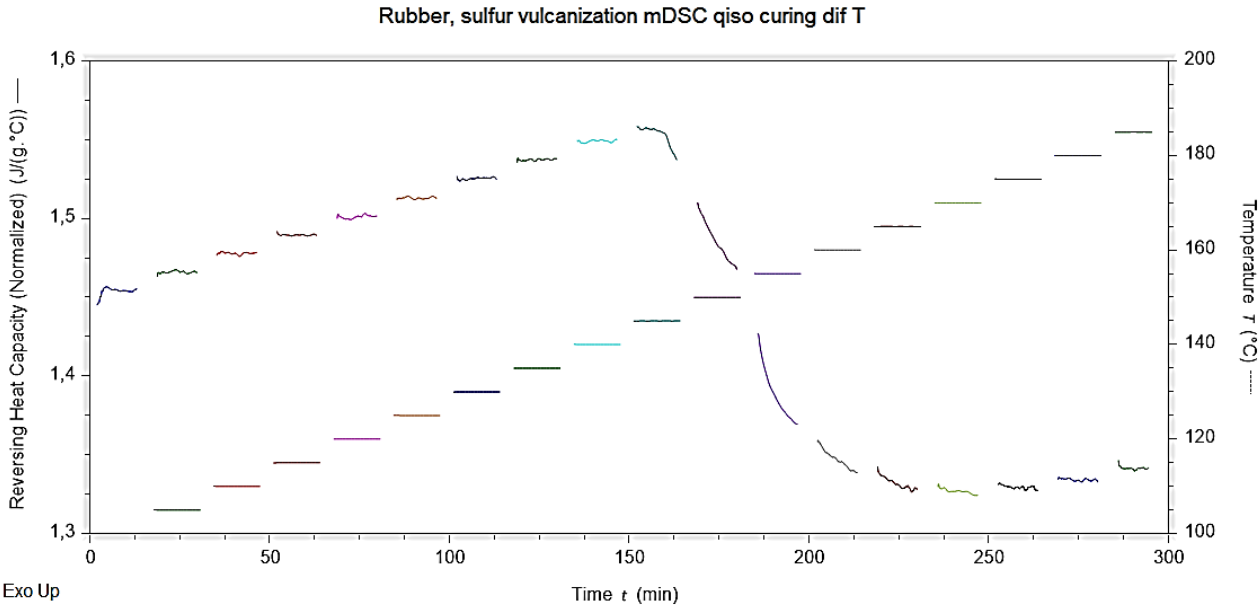
DSC is a well-accepted technique for characterizing curing processes in polymer research and corresponding branches of Industry. It plays important role during both R&D and QC stages of production. In some vulcanization systems of rubber compounds, DSC thermograms, obtained with classical approach do not reveal intense exothermal effect, enough for robust determination of the enthalpy of the process.

In such cases, the temperature modulated DSC method with constant average temperature, i.e., quasi-isothermal modulated DSC method, can be applied to follow changes in heat capacity of the vulcanized rubber. The method includes sinusoidal modulation of temperature with amplitude ± 0,5 K for each 60 seconds, while average heating rate during modulation is equal to 0 K/min. Modulation was done for 15 minutes at each single temperature in the range between 100 and 180°C with increment of 5°C.

Results clearly show start of the vulcanization at 145 °C, following with decrease of the sample's heat capacity. Noticeably, different rates of heat capacity changing at lower and at higher temperatures are very important during optimization of the rubber production.



Thermogravimetric and kinetic analysis of plastic food packaging

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Food packaging plastics are a great challenge for the waste recycling industry. The majority of food packaging consists of two or more types of polymers. Such multi-layered plastic packaging provides good mechanical properties with barriers against humidity, light and oxygen to ensure a longer shelf life of the products [1]. However, due to a variety in packaging composition, it is challenging to perform mechanical or chemical recycling of these materials, which leads to landfill or incineration plant.

Pyrolysis has been found as an alternative thermochemical energy recovery technology for mixed plastic waste and polymer materials that are challenging for material recovery [2]. Therefore, pyrolysis arises as a promising, environmentally friendly method of food packaging waste treatment. In comparison to incineration, in pyrolysis, input material is not used for direct energy generation. However, it is converted into oil, gas and char, which can be further used to produce fuels, energy and chemicals [3].

To better understand the pyrolysis process of food packaging plastics, thermogravimetric analysis was carried out to determine their thermochemical behaviour and kinetic parameters. A set of representative food packaging samples with known polymer ratios was selected in this research. Thermogravimetric measurements were conducted in a nitrogen atmosphere at heating rates of 5, 10, 15 and 20 °C/min in the temperature range 40−600 °C. Kinetic analysis was done using the isoconversional model-free Friedman method in combination with an advanced statistical approach.

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[1] Morris BA. The Science and Technology of Flexible Packaging: Multilayer Films from Resin and Process to End Use. Sci Technol Flex Packag Multilayer Film from Resin Process to End Use. 2016;1–728.
[2] Ragaert K, Delva L, Van Geem K. Mechanical and chemical recycling of solid plastic waste. Waste Manag. 2017;69:24–58.
[3] Anuar Sharuddin SD, Abnisa F, Wan Daud WMA, Aroua MK. A review on pyrolysis of plastic wastes. Energy Convers. Manag. 2016.

Kinetic Analysis of Thermal Decomposition – A comparison of Standard vs. MTGA models on Marbles

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Since its introduction in the DSC technology by Reading [1], Modulated Temperature profiles proved extremely useful in separating heating-rate-dependant phenomena from kinetic ones.

When applied to Thermo-Gravimetry this method brings to a “Model Free” equation [2] that can be applied to decomposition profiles in order to assess the value of the Activation Energy on a continuos basis. If the decomposition can be described as a first order reaction, also the pre-exponential factor can be obtained as well.

However, classically the kinetic of a decomposition process is studied by testing the same material under different Heating Rates (usually in the range 1 K/min – 10 K/min), getting the conversion plots for three or four of such rates and finally measuring the slope of the resulting curve in an Arrhenius plot. This approach has at least two main disadvantages: it is extremely time consuming, especially at low Heating Rates, and it relies on the assumption that the reaction we are observing is a first order one.

In this work we present a comparison of the two methods applied on the Calcite decomposition of Carrara Marble showing a very good agreement of MTGA data with “classic” kinetics analysis, but in a definitely shorter time.

We also compare the results with a different kind of Marble (Rosso di Verona) to prove the observed decomposition process to be exactly the same.

This assessment can be part of a wider set of analysis [3] to determine the provenance of the marble.

[1] M. Reading, B. K. Hahn and B. S. Crow, U.S. Patent 5, 224, 775 (1993)
[2] J. H. Flynn, Thermal Analysis, Vol. 2, Academic Press (1969) 1111
[3] T. Gatta *et al.*, Chemistry Central Journal, 8 (2014) 35

NETZSCH – Proven Excellence

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Before technical progress can begin, measurements, tests and analyses must be carried out. Only then can complex substances and materials be created of functional products developed.

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[1] https://www.netzsch-thermal-analysis.com/en/header/about-netzsch/

Study of material quality using thermal analysis methods

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Aluminium casting alloys are frequently used in the automotive industry (in casting applications). There are both: primary as well as secondary/recycled aluminium alloys on the market, that vary in price and quality. In this research the influence of the alloy quality on solidification, microstructure and mechanical properties was investigated.

The comparison of the mentioned properties took place in the as-cast state and the heat-treated state. The influence of alloy quality on solidification was analysed by simple thermal analysis and differential scanning calorimetry. The basic mechanical properties analysed were tensile strength, yield strength, elongation, and hardness. Preliminary research determined that recycled alloys have around 10–15% lower strength properties due to higher share of iron, which is challenging to avoid in secondary made alloys. It forms intermetallic phases that negatively affect the mechanical properties. Microstructural differences were analysed using an optical microscope.

AlSi10Mg and AlSi12 alloys made from primary and secondary/recycling aluminium (AlSi10Mg (Fe) and AlSi12 (Fe)) were compared, which contain a higher proportion of iron, which, as known, impairs mechanical properties. In the case of the AlSi10Mg alloy, the Mn:Fe ratio has been shown to have a pronounced effect on the mechanical properties, while magnesium hardens the aluminium matrix during heat treatment, which significantly increases the mechanical properties. However, the AlSi12 alloy is not a precipitation hardening alloy, so the mechanical properties do not improve significantly after heat treatment.

Key words: alloy quality, casting alloys, solidification, microstructure, mechanical properties.

Effect of NaOH on cellulose pyrolysis kinetics

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Pyrolysis/carbonization of cellulose/lignocellulose-based materials in the presence of inorganics significantly affects their transformation pathway, kinetics and carbon yield. Although of the great industrial importance of this process (for activated carbon preparation) and a long history of its utilization, the field still remains a challenge for in-deep fundamental research. Thus, the aim of this contribution is to explore the effect of NaOH on the kinetics of carbonization of two kinds of cellulose: 1) commercial microcrystalline cellulose (MCC, containing mostly cellulose I) and 2) cellulosic gel (CMG, prepared from MCC alkaline solution, formed by cellulose II and amorphous cellulose). The carbonization process was followed by TGA under inert atmosphere at different heating rates: 2, 5, 10 and 20 $\mathrm{Kmin^{-1}}$ for the mixture of cellulose with NaOH (MCC/NaOH and CMG/NaOH) and compared to the reference cellulose samples (MCC, CMG) behaviours. Dependence of the apparent activation energy (E_a) of the carbonization step on conversion degree was calculated by Starink method. Detailed calculations were performed by non-linear regression with 2 – 4 parallel reaction steps.

Thermal degradation of samples with NaOH (CMG/NaOH and MCC/NaOH) starts at lower temperature compared with MCC and CMG indicating the catalytic effect of NaOH. This feature was confirmed by the decrease of calculated E_a values (Fig. 1) in the presence of NaOH, especially in the case of CMG. Calculations, according to Starink equation, led to fluctuated E_a values at high conversion factor (above 0.7 and even above 0.4 in the case of MCC/NaOH sample). Non-linear regression calculations showed that carbonization of studied samples could be kinetically described by 2 – 3 parallel reaction steps, except of MCC/NaOH for which using 4 steps led to better results.

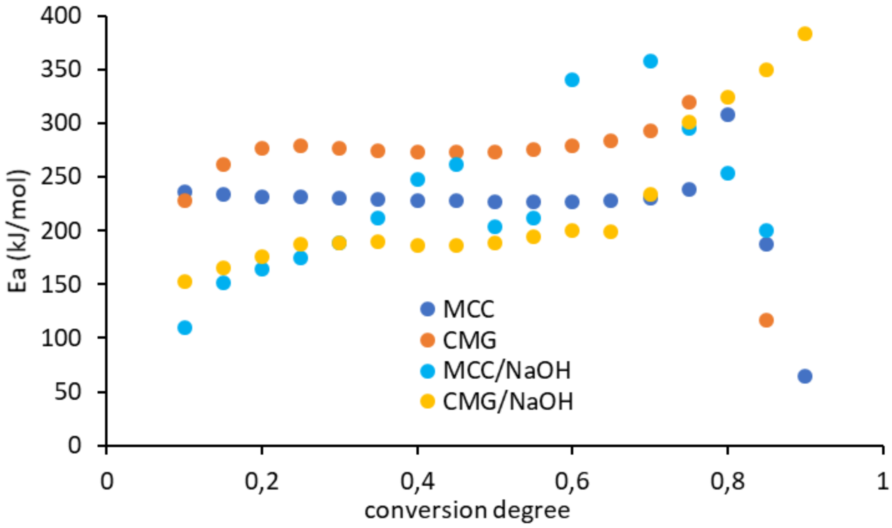

Figure 1. Dependence of activation energy (Starink method) on conversion for cellulosic samples and their mixtures with NaOH.

Kinetics from one TG measurement with combined temperature program

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In addition to common methods for determining the kinetic parameters of thermal reactions from thermoanalytical data based mostly on the linearization of the basic kinetic equation or isoconversional approach, it is possible to solve the kinetics of thermal reactions using numerical solution of the kinetic equation by nonlinear regression. This approach has some disadvantages, especially of a numerical nature, on the other hand, it allows to use the same methodology to process isothermal and non-isothermal data including their combination. The aim of this contribution is to show the possibilities (and problems) of nonlinear regression solution of the kinetics of thermal reactions on the example of simple oxidation of graphite.

The graphite sample was heated in an oxidizing atmosphere at rates of 2, 10 and 20 K / min up to 1000 ° C, and further by a temperature program combined from heating (20 and 10 K / min) and isothermal steps at 650, 700 and 750 °C. Kinetic parameters were calculated from the obtained TG curves by the integral isoconversional Starink method or by non-linear regression (from individual measurements and from their combination).

The obtained results show that nonlinear regression generally leads to different results than Starink's method, but provides a better agreement of the experimental data with the calculated theoretical curves. In addition, non-linear regression processing of one TG curve with a combined temperature program (containing different heating rates and isothermal steps, Fig. 1) seems to allow to obtain kinetic data comparable to the results obtained from several measurements with different heating rates.

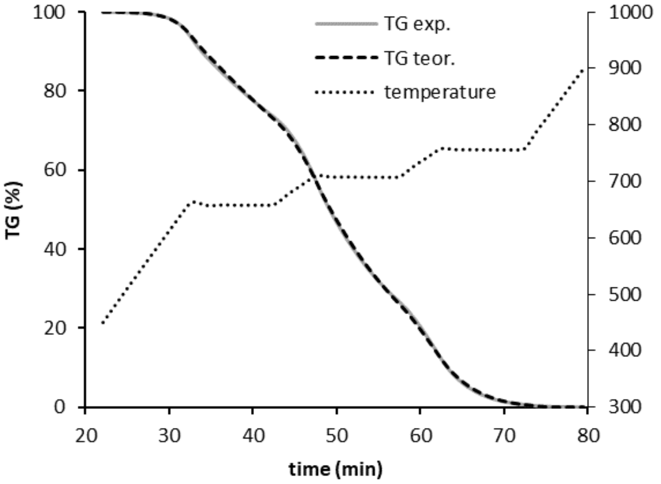

Fig. 1 Comparison of theoretical and experimental curves of graphite oxidation during combined heating

Jasika company - Laboratory solution

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Effect of Mn on the chemical driving force and bainite transformation kinetics in medium-manganese alloys

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Growing requirements for high strength alloys in the automotive industry increase a need for developing new improved steel grades. The steels should compromise very good mechanical properties with the cost of their production [1-2]. It is of primary importance to know the phase transformation behaviour during heat treatment. This knowledge allows us to control cooling conditions of steel products, which leads to formation of desirable microstructures. For the development of the heat treatment for new steel grades, the theoretical knowledge of the influence of selected alloying elements on chemical driving force of phase transitions is crucial. The theoretical approach helps in the understanding of the importance of chemical composition strategy, and its effect on the phase transformation behavior [3]. Manganese is a very important element in advanced high strength steels. This element affects the chemical driving force and subsequent phase transformation kinetics [4].

The present work shows the use of advanced thermodynamic calculations for determination of bainite transformation kinetics in advanced steels with different manganese contents (a range from 3 to 5wt.%). The analysis of the chemical driving force changes for different manganese contents is conducted. According to it, manganese slows down the bainite transformation kinetics because it lowers the chemical driving force of gamma to alpha transformation. The dilatometric analysis was carried out to determine the real kinetics of bainite transformation in alloys containing 3.1, 3.6 and 4.7% of manganese. The isothermal holding was carried out at 400°C for each steel. The isothermal holding time was 15 min. For the steel with the highest Mn content additional holding for 180 min was also needed. Light and scanning electron microscopy were used for detailed microstructural studies.

[1] M. Haupt, A. Dutta, D. Pong, S. Sandlobes, M. Nellessen, G. Hirt, Procedia Engineering, 207, (2017), 1803-1808
[2] H. Misra, A.K. Chandan, S. Kundu, Mat. Sci. Eng. A, 701, (2017), 319-327
[3] M. Morawiec, V. Ruiz-Jimenez, C. Garcia-Mateo, A. Grajcar, J Therm. Anal. Calorim., 142, (2020), 1709-1719
[4] M. Morawiec, A. Grajcar, W. Zalecki, C. Garcia-Mateo, M. Opiela, Materials, 13, 2020, 1-15

Bainitic transformation kinetics in single and double isothermal treatments of medium-Mn steels

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At an isothermal holding temperature, as the bainite transformation progresses, the remaining austenite decreases in size and at the same time is enriched with carbon [1]. Carbon enrichment of austenite under isothermal bainite transformation conditions is explained by Bhadeshia [2]. According to this theory, the bainite transformation takes place below the temperature T0, at which austenite and ferrite with the same chemical composition have the same free energy value. If the temperature T0 is presented in the temperature - carbon concentration system, the line T0 is formed.

During isothermal holding of steel in the bainite transformation range, initially the free energy of the α phase is lower than the free energy of austenite, which is the driving force of diffusionless bainite transformation. As the bainite transformation progresses, the carbon is removed from the supersaturated bainitic ferrite and enriches the remaining austenite fraction. Due to the inhibitory effect of silicon on the precipitation of cementite – for sufficiently long time of isothermal holding - the bainite transformation will be stopped when the carbon concentration in the austenite reaches the T0 line, allowing to obtain retained austenite [3].

The present research concerns dilatometric studies of bainitic transformation kinetics of medium-Mn steel in single and double isothermal treatments. The newly implemented heat treatment route consists of holding the steel slightly above a critical temperature (martensitic start) to create a bainite fraction needed for partial stabilization of austenite (decrease of M_S). Subsequently, the isothermal temperature is reduced to the new critical temperature. The second step is implemented to refine the matrix and austenite grain size and thus increase the retained austenite stability. The aim of the research is to analyze and compare the double-step heat treatment kinetics with the conventionally used one-step treatment. The kinetics modeling was performed using JMatPro software. One- and two-step physical simulations of heat treatment were performed using a dilatometer. The size and morphology of the phases in the microstructure were revealed using light and scanning electron microscopy. The research showed significantly increased kinetics of the bainitic transformation with decreasing temperature from 400 to 300°C. The second transformation step is slower due to a smaller remaining phase of austenite.

[1] B. Ehrhardt, T. Gerber. Steel Grips, 4 (2004) 247-255
[2] H.K.D.H. Bhadeshia. The Institute of Materials, The University Press, Cambridge (1992)
[3] A.K. Srivastava, G. Jha, N. Gope, S.B. Singh. Mater. Charact., 57 (2006) 127-135

Initial stage of gas and ionic clathrate hydrates formation: Primary and secondary nucleation, formation of metastable phases and their recrystallization

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A detailed study of the processes of nucleation and growth of gas and ionic clathrate hydrates in water–hydrate former and water–hydrocarbon–hydrate former systems was carried out. Both model substances and real oils were used as hydrocarbons. The problem addressed by this study is to identify the mechanism of the initial stage of hydrate phase formation at temperatures below 0°C, which is crucial for the development of hydrate-based technologies. In our recent works, it has been shown that the possibility of secondary nucleation of ice and methane hydrate via the relay mechanism strongly depends on the composition of oil used as well as on the temperature and pressure conditions.

A curious feature of hydrate nucleation in such systems is the formation of a metastable hydrate phases [1-3]. The formation of the metastable phases was observed at high cooling rates, which suggests the possible quenching of the products of the initial crystallization stage. Data on the effect of the cooling rate and the type of dispersion medium on the phase composition of hydrate being formed allows the mechanism/staging of the hydrate crystallization process to be established (an amorphous phase–a metastable hydrate–a stable hydrate). In addition, the effect of gas phase on the mechanism of relay crystallization of ice in water-in-oil emulsions was studied. In the absence of gas pressure, the secondary nucleation of ice in such systems is hindered, but the formation of the crystalline phase proceeds independently in each drop.

It should be noted that at present there are almost no established ideas about the stages of formation of the crystalline phase in water–oil–gas flows as well as in pure water–gas systems. Meanwhile, this information is crucial for understanding the processes of gas hydrate inhibition and promotion.

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[1] J.M. Schicks, M. Luzi-Helbing, J. Chem. Eng. Data, 60 (2015) 269.
[2] A.S. Stoporev, A.G. Ogienko, A.A. Sizikov, A.P. Semenov, D.S. Kopitsyn, V.A. Vinokurov, L.I. Svarovskaya, L.K. Altunina, A.Y. Manakov, J. Nat. Gas Sci. Eng., 60 (2018) 284.
[3] A.S. Stoporev, A.G. Kiiamov, M.A. Varfolomeev, T.V. Rodionova, A.Y. Manakov, Mendeleev Commun., 31 (2021) 17.

Kinetic parameters in the general rate equation

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Condensed 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. To describe their kinetics, the single-step approximation mathematically expressed in the form of general rate equation are mostly applied [1]:

$$\mathrm{d}t \quad = k(T)f(\alpha) \qquad (1)$$

Eq.(1) is called the general rate equation. Among the methods based on Eq.(1), the isoconversional (or model-free) ones are most popular, mainly in evaluation of the experimental results obtained from measurements carried out under linear heating rate.

In papers published, it can be very often encountered that the experimental results are evaluated by several methods and the results are mutually compared. Flynn-Wall-Ozawa [2,3] (FWO), Kissinger-Akahira-Sunose [4] (KAS) and Starink [5] methods belong to this group. All the methods reside in the treatment of kinetic results by the relationship

$$\ln\left(\frac{\beta}{T^{a}}\right) = -b\frac{E}{RT} + c \Rightarrow \ln\beta = -b\frac{E}{RT} + a\ln T + c \qquad (2)$$

where β is the heating rate, T is the isoconversional temperature, E is the activation energy and a, b, c are constants. The values of constants a, b, c depend on the approximation applied for the calculation of temperature integral [1]. The activation energy is obtained from the slope of the dependence $\ln(\beta/T^{a}) = \mathrm{f}(1/T)$. If one takes into account the a and b values for individual methods, by differentiation of $\mathrm{d}(\ln\beta)/\mathrm{d}T$ can be obtained:

$$1.058E_{\mathrm{FWO}} = E_{\mathrm{KAS}} + 2RT = 1.0037E_{\mathrm{Starink}} + 1.8RT \qquad (3)$$

From Eq.(3) it is seen that the activation energies from FWO, KAS and Starink methods are interrelated and it makes no sense to make far-reaching conclusions from their comparison. Moreover, it is to bear in mind that all the three methods are integral and they can be mathematically incorrect in the case of variable activation energy [6].

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1. Šimon P.: J.Therm.Anal.Calorim. **82** (2005) 651-7.
2. Ozawa T.: Bull.Chem.Soc.Jpn., **38** (1965) 1881-6.
3. Flynn J.H., Wall L.A.: Polym.Lett. **4** (1966) 323-8.
4. Akahira T., Sunose T.: Trans. Joint Convention of Four Electrical Institutes **1969**, paper No. 246.
5. Starink M.J.: Thermichim.Acta **288** (1996) 97-104.
6. Šimon P., Thomas P., Dubaj T., Cibulková Z., Peller A., Veverka M: J. Therm. Anal. Calorim. **115** (2014) 853-9

High temperature thermochemical energy storage (TES) for concentrated solar power plants (CSP)

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Concentrated solar power plants (CSP) concentrate the solar irradiation using mirrors to drive an engine that produces electricity. Thus, in principle, electricity can be produced only when there is solar irradiation. Modern CSP plants have an energy storage system that allows producing energy even at night. The state-of-the-art technology for energy storage in commercial CSP plants is based on molten salts. This technology has several limitations, namely limited power cycle efficiency because of the maximum working temperature of the salt, a relevant energy consumption to maintain the salt in the molten state to avoid solidification and corrosion and high price issues. A new alternative to such molten salts is the use of thermochemical energy storage. It is of the most interest the system based on the calcination-carbonation reaction of $CaCO_3/CaO$, known as Calcium Looping (CaL process) [1]. This CaL uses limestone, which is an abundant and cheap mineral, as raw material. Concentrated solar energy is used to promote the endothermic calcination of the limestone, producing CO_2 and CaO that are stored in different containers. When energy is required, the stored reactants are mixed to perform the exothermic carbonation reaction that produces $CaCO_3$ and releases the stored energy.

In the frame of the SOCRATCES project, funded by the European Union's Horizon 2020 research and innovation programme under grant agreement No 727348 this technology is being demonstrated in a pilot plant scale.

[1] C.Ortiz, J.M.Valverde, R.Chacartegui, L.A.Perez-Maqueda, P.Giménez. Renewable and Sustainable Energy Reviews., 113 (2019) 109252

Characterization, thermal and ceramic properties of clays from Alhabia (Almería – Spain)

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In the present investigation, a clay deposit from Alhabia (Almería, southwest Spain) has been studied. A characterization of several selected samples has been performed using a set of techniques applied in previous studies. Mineralogical, by X-ray diffraction (XRD), and chemical, by X-ray fluorescence (XRF), characterization of these samples is presented. Textural analysis, by particle size determination (clay, lime and sand contents by sieving and sedimentation), liquid and plastic limits (Atterberg), and nitrogen adsorption-desorption isotherms (BET and Langmuir models) with determination of pore sizes, has been also carried out. Thermal analysis methods, mainly thermogravimetry (TG) and differential thermal analysis (DTA), have been applied to achieve a more complete characterization of these samples. In a next step of this investigation, a selected sample has been considered for a ceramic study by firing pressed bodies up to 1300 °C under laboratory conditions.

According to XRD semiquantitative results, all the studied samples were constituted by quartz (30-35 wt.%), layer silicates such as chlorite-serpentine (15-20 wt. %) and illite/muscovite (15-20 wt. %), calcite (10-15 wt. %) and minor amounts of iron oxides and posible gypsum. Carbonate content, assumed as calcite, was determined by calcimetry and an average value of 13 wt. % was found. This value agrees with the above result. The raw clay presented a content of organic matter of 2.48 %. The average clay (< 2 μm) content was found higher than 70 %, with liquid and plastic limits of 45.20 % and 30.90 %, respectively. The plasticity index was 14. 30 %. The specific surface area (according to the BET model) of the raw clay samples were ~ 19 m^2/g, although this value diminished after grinding, reaching values < 6 m^2/g. Possibly the grinding conditions influenced this behaviour.

Thermal analysis (TG-DTA) up to 1100 °C confirmed the mineralogy of these clay samples, with thermal decomposition of the layer silicates by thermal dehydroxylation and calcite decarbonation, with total mass losses in the range 12-15 wt. %. The main ceramic properties of a ground sample have been determined by firing at several temperatures, showing the evolution of linear shrinkage, water absorption capacity, bulk density, apparent porosity and sintering features.

Porous ceramic bodies (20-30 %) have been obtained at temperatures lower than 1100 °C due to the thermal decomposition of the layer silicates and mainly to the presence of calcite in the raw samples. Calcite ($CaCO_3$) decomposed with evolved carbon dioxide and forming calcium oxide (CaO). This oxide reacted with the amorphous Al-Si products originated by fired clay minerals and quartz, forming high-temperature silicates. They were identified by XRD, such as anortite ($Ca_2Al_2SiO_8$) and gehlenite ($Ca_2Al_2Si_2O_7$), besides hematite and unreacted quartz. The phase composition provided by the phase equilibrium diagram SiO_2-Al_2O_3-CaO in the presence of Fe_2O_3 was compared with these experimental results. The ceramic behaviour, vitrification and sintering of this sample were discussed taking into account the formation and evolution of crystalline phases in the fired clay and posible applications.

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Oral Presentations 2

Thermodynamics, Thermochemistry & Calorimetry and Thin Films & Nanomaterials

Mechanochemical synthesis of manganese doped ceria nanoparticles

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Ceria, CeO_2, is an important rare earth oxide material with cubic fluorite type structure. Pure ceria is an n-type semiconductor with two stabile oxidation states, Ce^{3+} and Ce^{4+}, making it suitable for various applications. [1] Energy and catalyst applications are mostly based on great oxygen storage capacity, redox properties and ionic conductivity of ceria. Ceria is frequently used in solid oxide fuel cells, catalysis, sensors and high temperature ceramics. [2]

Good catalytic properties and ionic conductivity depend on thermal stability which nanomaterials lack. Doping with various metals, including transition metals such as manganese helps to overcome pure ceria shortcomings. Manganese is known to have many oxidation states and because of the synergistic effect between MnO_x and CeO_2 can modify oxygen storage capacity and mobility.

Mechanochemical synthesis is a method that can yield fine homogenous powders. Intensive mechanical milling causes chemical reactions between precursors and results with products that usually form at much higher than room temperatures. Negative features of ball milling can be agglomeration or heat generated while milling.

Nanoparticles of pure and Mn doped ceria were attained by mechanochemical synthesis from chlorides. After synthesis, x-ray diffraction (XRD) and differential thermal analysis (DTA) were performed giving insight into acquired phases and their thermal decomposition. Scherrer equation was used on 500°C for 2h annealed samples to calculate ceria crystallite size. Morphology of the prepared samples was investigated on a scanning electron microscope (SEM), while N_2 adsorption-desorption isotherms gave insight into surface and pore features. Catalytic character of doped and pure ceria samples was measured via toluene conversion in a 150°C – 450°C temperature interval. All of the prepared samples show pure ceria phase after thermal treatment. DTA and XRD results show that the incorporation of manganese in ceria enables easier ceria formation as well as generates smaller crystallites.

[1] S.Kurajica, I.K. Munda, F. Brleković, K. Mužina, G. Dražić, J. Šipušić, M. Mihaljević, Manganese-doped ceria nanoparticles grain growth kinetics, J Solid State Chem (2020) 291, 121600, 9p
[2] S.Kurajica, K. Mužina, G. Dražić, G. Matijašić, M. Duplančić, V. Mandić, M. Župančić, I.K. Munda, A comparative study of hydrothermally derived Mn, Fe, Co, Ni, Cu and Zn doped ceria nanocatalysts, Mater Chem Phys (2020) 224, 122689, 9p.

Thermal stability study of hydrothermally-derived copper-doped cerium (IV) oxide nanoparticles

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Cerium (IV) oxide (CeO_2) is known for its high oxygen storage capacity, low cost, good mechanical properties and poisoning resistance. On that account, ceria-based nanocatalysts are widely applied in various fields such as industry, environmental protection and energy generation. Most of the chemical processes in question require elevated temperatures, where the problem of grain growth of nanoparticles occurs. The increase in the particle size causes the reduction of specific surface area and, consequently, the decrease of catalytic activity. Doping of ceria with different transition metals is one way of slowing down the growth process. [1, 2] Our previous research showed that the addition of 10 mol. % of copper increases the thermal stability [2], as well as the catalytic activity [3] of CeO_2, which is why Cu was chosen as a dopant for further research.

In this work, pure and copper doped cerium (IV) oxide nanoparticles ($Cu_xCe_{1-x}O_2$, where x = 0, 0.1, 0.2, 0.3 and 0.4) were prepared by hydrothermal synthesis and characterized using X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). The crystallite sizes determined from XRD patterns by using the Scherrer's equation were between 3.7 and 3.1 nm, while TEM analysis showed spherical particles with sizes matching the calculated crystallite sizes. As-prepared samples were thermally treated at different temperatures and processing times, after which an isothermal model was applied in the study of grain growth kinetics. It was established that the grain growth process can be divided into two regions, low-temperature (300-450 °C) and high-temperature (500-700°C) region, each with its own growth regime. While the grain growth is sluggish at lower temperatures, it accelerates at higher temperatures in all of the samples. However, the results show that the addition of copper has a positive effect on the thermal stability of cerium (IV) oxide, and the grain growth decreases with the increasing copper amount.

[1] S. Kurajica, I.K. Munda, F. Brleković, K. Mužina, G. Dražić, J. Šipušić, M. Mihaljević, J. Solid State Chem., 291 (2020) 121600
[2] K. Mužina, A. Bajrović, M. Župančić, S. Kurajica, Technologica Acta, 13 (2020) 15-19
[3] S. Kurajica, K. Mužina, G. Dražić, G. Matijašić, M. Duplančić, V. Mandić, M. Župančić, I.K. Munda, Mater. Chem. Phys., 244 (2020) 122689.

N/TiO_2 nanocomposites: nitrogen effect on the material properties

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TiO_2 heterogeneous photocatalysis is actively studied as an alternative technology for the degradation and/or removal of organic micropollutants (OMPs) present in water [1-2]. However, photoactivation of TiO_2 occurs only under UV light and the photogenerated charges that start oxidation processes recombine quite fast, affecting the photocatalytic activity [3]. Therefore, this study focuses on the synthesis of nitrogen-doped TiO_2 for enhancing its photocatalytic activity under visible light, using the non-conventional microwave-assisted method, and evaluating the amount of nitrogen on the photocatalytic activity under different sources of radiation for the degradation of a model pollutant – antibiotic drug ciprofloxacin in aqueous solution. Nitrogen-doped TiO_2 (N/TiO_2) photocatalyst was synthesized by the microwave-assisted method, using urea as a nitrogen source. To evaluate the effect of nitrogen in the photocatalytic and morphological properties, N/TiO_2 were prepared varying the amount of urea. The obtained materials were characterized by XRD, FTIR, Raman spectroscopy and N_2 adsorption isotherms. The only crystalline phase present in the N/TiO_2 materials was anatase. The incorporation of urea as a nitrogen source does not affect the crystallinity either the crystal phase of TiO_2. Although the urea incorporation reduces the specific surface area, the obtained materials have three times bigger surface area than commercial catalyst Degussa P25. N/TiO_2 materials show photoactivity under UV, Solar light simulator and visible light, while commercial photocatalyst Degussa P25 TiO_2 shows activity only under UV light and Solar light simulator. Increasing the amount of urea increases the photocatalytic activity of the materials under the different radiation sources for the degradation of ciprofloxacin. However, beyond a specific concentration, there is no further improvement of the materials' photoactivity.

[1] R. Fagan, D.E. McCormack, D.D. Dionysiou, S.C. Pillai, Mater. Sci. Semicond. Process. 42 (2016) 2–14.
[2] M. Čizmić, D. Ljubas, L. Ćurković, I. Škorić, S. Babić, J. Hazard. Mater. 323 (2017) 500–512.
[3] A. Truppi, F. Petronella, T. Placido, M. Striccoli, A. Agostiano, M.L. Curri, R. Comparelli, Catalysts. 7 (2017) 100.

Comparison of amine and sulphide layer-by-layer synthetic route for preparing of the photovoltaic CdSe quantum dots thin-films

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Quantum dots (QDs) are semiconducting nanoparticles interesting due to their size-dependent optoelectronic properties. Cadmium selenide QDs are generally used in photovoltaic applications due to their tuneable bandgap. Various physical and chemical methods can be used for QDs preparation but chemical routes are more advantageous due to facile QDs shape and size control. However, when preparing thin-films from colloidal QDs, obtaining satisfactory geometry arises as the main obstacle due to particle aggregation. The former can can be prevented by applying surface modification agent during the course of the synthesis.

Here we compare two methods for surface modification of colloidal CdSe QDs in the course of the layer-by-layer (LbL) deposition of thin-films; (i) by ligand exchange and (ii) by silanization. Also, the impact of the solution temperature was also considered.

Firstly, the prepared precursor solutions were injected into the growth solution. Longer reaction time resulted in bigger CdSe QD with narrower bandgaps. Surface was modified by: (i) ligand exchange of trioctylphosphine (i) silanization with tetraethoxy silane. Then the thin-films of CdSe QDs were created by LbL with varying several solution temperatures and number of layers. The linking layers for silanized and exchanged ligands QDs were (3-aminopropyl)triethoxysilane and poly(diallyldimethylammonium chloride). Layers were connected via electrostatic assembly or through hydrogen bonding and condensation reactions. Colloidal QDs solutions and derived thin-films were examined using dedicated structural analysis and combination of spectroscopic, morphologic and microscopic techniques. The analyses confirmed successful silanization, i.e. interconnecting of the QDs into thin-films. Testing confirms that morphology, surface roughness, thin-film thickness and appropriate distribution of the QD domains remain due to careful ligand exchange in solution stage, pointing out in thermally stable films without aggregation-based defunctionalisation.

[1] J. Li, J. Chen, Y. Shen, X. Peng, Nano Res., 11 (2018) 3991-4004
[2] K. Surana, P.K. Singh, H.W. Rhee, B. Bhattacharya, J. Ind. Eng. Chem., 6 (2014) 1-6
[3] B.K. Pong, B.L. Trout, J.Y. Lee, Langmuir, 24 (2008) 5270-5276
[4] X. Liu, J. Han, W. Wu, Q. Shi, W. Li, C. Li, Chem. Lett., 45 (2016) 10-12

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Tailoring TiO_2 properties by synthesis conditions and annealing

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Photocatalytic activity of TiO_2 depends on its properties significantly, among the most important factors allotropic modification and particle size can be included. While there is ample literature on these attributes and their impact on photocatalysis, very few papers describe direct approaches for preparation of titania with precisely defined features. The aim of this study was to describe, how TiO_2 properties (ratio between anatase and rutile phase and their crystallite size) can be influenced by using of various precipitation agents (amines), annealing temperature and peroxide treatment. Peroxoamino-titanates and their precursors were characterized by *in situ* high temperature XRD, simultaneous TG-DTA with EGA, microscopy techniques and elemental CHNS analysis.

Thermal degradation of amorphous materials progressed in two steps corresponding to evolution of moisture and desorption or evaporation of organics in amino-titanates. In the case of peroxide treated samples organic part was oxidized by evolved oxygen to H_2O, CO_2 and NO_x, in case of higher quantity of present organics even during additional third step. Although the anatase crystallization was observable only in few samples by DTA, crystallization temperature agreed with *in situ* HT-XRD results. While anatase crystallization temperature (325 – 425 °C) was influenced mainly by used amine, H_2O_2 treatment affected its initial particle size (5 - 40 nm). Higher formation temperature of anatase increased initial anatase crystallite size in peroxoamino-titanates, while in amino-titanates (without H_2O_2 treatment) decreased.

Extended thermal stability of anatase up to 800-900 °C (at the point of transformation to rutile) together with appropriate low (tens of nanometers) crystallite size predetermine thus prepared TiO_2 to be a highly efficient photocatalysts [1]. Results achieved in this work offer a procedure how to gain titania with required properties by set up of synthesis conditions and annealing.

[1] J. Šubrt, P. Pulišová, J. Boháček, P. Bezdička, E. Pližingrová, L. Volfová, J. Kupčík, Materials Research Bulletin, 49 (2014) 405-412

The effect of porosity and particle size on the kinetics of carbon surface oxidation

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The effect of porosity and particle size on the kinetics of carbon surface oxidation was investigated. Three carbon xerogels differing in porosity (micro-, micro-meso-, and micro-meso-macroporous materials) were prepared by method proposed by Bulavova [1]. Four different particle size fractions obtained by crushing and sieving (0-0.15, 0.15-0.75, 0.75-1.25, 1.25-200 mm) and cubes with side length ± 2.2 mm from each carbon xerogel were used as samples. Scanning and transmission electron microscopy and N_2 sorption at -196°C were performed to check their pore characteristics.

The kinetics of carbon surface oxidation was explored by thermogravimetry in oxidizing atmosphere (50% O_2 + 50% Ar). Isothermal experiments were conducted at 240, 270 and 290°C (temperatures were chosen based on preliminary non-isothermal experiments).

From the isothermal thermogravimetry records, significant dependence of oxidation kinetics on particle size was observed in the case of purely microporous sample. Its oxidation is controlled by diffusion due to only microporous character in combination with larger particle size. In the case of micro-mesoporous sample, the dependence of oxidation kinetics on particle size was observed too but in considerably smaller extent due to presence of mesopores (and thus easier diffusion) in sample structure. In the case of micro-meso-macroporous sample, no effect of particle size on the kinetics of surface oxidation was detected due to macroporosity of sample.

On the basis of the isothermal thermogravimetry data, apparent kinetic parameters for oxidation of each sample were determined with assumption of three reactions (carbon burn off, creation of oxygen surface groups and their decomposition) by calculation method suggested by Hotova [2].

Analysis of obtained parameters proved that porosity and particle size of carbon have no influence on the apparent kinetic parameters (including kinetic model) of its surface oxidation. The good agreement between theoretical and experimental data showed that applied kinetic model describes oxidation of carbon xerogels very well (despite the fact that the oxidation of micro and micro-mesoporous samples with larger particle sizes is controlled by diffusion).

[1] P. Bulavova, J. Parmentier, V. Slovak, “Facile synthesis of soft-templated carbon monoliths with hierarchical porosity for fast adsorption from liquid media”, Microporous and Mesoporous Materials, (2018) 272 155-165

[2] G. Hotova, V. Slovak, “Optimization of oxygen chemisorption on the carbon surface based on kinetic analysis of isothermal thermogravimetry”, Thermochimica Acta, (2018) 666 82-90

Thermoporometry: the effect of the carbon surface chemistry on the amount of non-freezable water

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Thermoporometry method (TPM) is one of the promising alternatives to commonly used techniques for the porosity characterization. The TPM method is based on the depression of melting/freezing temperature of a liquid entrapped in pores [1-2]. Despite of its simplicity, it is not very popular and is rarely used because of the problems connected with the conversion of DSC signal to pore size distribution which is based on Gibbs-Thomson equation together with the concept of non-freezable pore water (δ). The δ value could affect the final PSD information from TPM measurement, thus, its correct value is requested. Nowadays, it is known that the δ depend on the temperature [3], but the effect on the surface chemistry was not studied yet. It is believed that the surface chemistry (e.g. oxygen functional groups) will affect the amount of non-frozen water and also the δ.

Five carbonaceous materials with different surface oxidation degree were prepared to study the effect of surface chemistry on the amount of non-freezable water. Each sample was tested on the DSC instrument with different sample:water ratio. DSC experiments were performed in nitrogen atmosphere (50 ml min^{-1}) from -90 °C to 25 °C with prefreezing step (heating rate 1 °C min^{-1}).

Based on the performed experiments it was found out, that the studied carbonaceous materials contain different amount of oxygen (determined by elemental analysis), concretely 15, 18, 21, 23 and 25%. Thus, it can be also concluded that with the higher amount of total oxygen, the higher quantity of oxygen groups will be present on carbon surface. From the obtained DSC signals, it was obvious that all the studied samples contain 2 endothermic peaks of melting corresponding to bulk (□0 °C) and pore (lower temperature) water. To quantify the non-freezable water in individual samples, the linear relationship between total mass of water and the total heat of water melting was plotted and the absolute quantity of unfrozen water was given by the intercept of the line equation. It was confirmed, that the higher the amount of oxygen is (15 - 25%), the higher the amount of unfrozen water was detected (0.18 – 0.33 g g^{-1}). This finding also implies that also the δ layer values will not be constant for all carbonaceous materials, like it is used to up now (δ=0.8 nm for carbon) but it will vary and will also depend on the carbon surface chemistry. The recommendation, which could be stated, is that it is not appropriate to use the "constant δ value", but to obtain the reliable results from TPM, it is necessary to determine the δ value for the studied samples and count the effect of surface chemistry.

[1] M.J. van Bommel, C.W. den Engelsen, J.C. van Miltenburg, J. Porous Mater., 4 (1997) 143-150.
[2] P. Veselá, J. Riikonen, T. Nissinen, V.-P. Lehto, V. Slovák, Thermochim. Acta, 621 (2015) 81-89.
[3] H.R.N.B. Enninful, D. Schneider, R. Kohns, D. Enke, R. Vaiullin, Microporous Mesoporous Mater., 309 (2020) 110534.

Thermoporometry of carbons: Is a delta layer really constant?

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Thermoporometry is considered to be an alternative technique for the assessment of mesopores (pore diameter = 2 – 50 nm) and smaller macropores (pore diameter > 50 nm). The thermoporometry is based on a DSC measurement of the depression of the melting/freezing temperature of a liquid entrapped in pores (pore liquid) compared to the bulk liquid. Water is commonly used as a probe liquid due to its high heat of fusion enhancing the sensitivity of DSC measurement [1]. To obtain the pore size distribution (PSD) of the measured sample, the so-called Gibbs-Thomson equation is applied to the measured DSC record. The equation contains parameters describing the given experimental system, one of them is called delta (δ). The δ can be understood as a thickness of a so-called non-freezable layer and is considered to be a constant for a given system (probe liquid/measured solid); $\delta = 0.8$ nm is usually adopted for carbon [2]. However, it has been recently found that its value can change depending on the *surface chemistry* of the sample [3]. Following this finding, the aim of this contribution is to point out (i) the "non-constancy" of the delta layer and (ii) to show how it affects the calculated textural properties of the samples.

To fulfill the aims, five carbons differing in the quantity of the surface oxygen has been prepared [4] and DSC signal with the different sample:water ratio was recorded in nitrogen atmosphere (50 ml min^{-1}), heating from -90 °C to 25 °C with pre-freezing step (heating rate 1 °C min^{-1}). Surface oxygen was determined by elemental analysis and their porosity was obtained by the independent N_2/77K physisorption.

Performed experiments proved that the studied carbons contain different amounts of oxygen ranging from 15 to 25%, which we assume to be mostly a surface one. Based on our findings (see the contribution of Zelenková et al. Thermoporometry: the effect of the carbon surface chemistry on the amount of non-freezable water) it was found that carbon surface chemistry considerably influences the quantity of non-freezable pore water. Using simple calculations (to be presented) that take into account textural parameters from the gas physisorption (like BET or mesopores surface area, micropore volume), we found that that the δ layer may vary for our samples from 0.46 to 2.72 nm with increasing carbon surface oxidation degree. This brings us to the conclusion that the delta layer is not constant. It is important to emphasize that especially small mesopores are strongly influenced by the chosen value of the delta layer, so care should be taken to choose it correctly. It was also found that thermoporometry and gas physisorption give similar mesopore volume (0.701, resp. 0.715 cm^3 g^{-1}) for less oxidized samples. For highly oxidized samples, the results may vary significantly.

[1] P. Veselá, J. Riikonen, T. Nissinen, V.-P. Lehto, V. Slovák, Thermochim. Acta, 621 (2015) 81-89.
[2] T. Yamamoto, S.R. Mukai, K. Nitta, H. Tamon, A. Endo, T. Ohmori, M. Nakaiwa, Thermochim. Acta, 439 (2005) 74–79.
[3] D. Majda, M. Zimowska, K. Tarach, K. Góra-Marek, B.D. Napruszewska, A. Michalik-Zym, J. Therm. Anal. Calorim., 127 (2017) 207–220.
[4] G. Hotová, V. Slovák, Anal. Chem., 89 (2017) 1710–1715.

Thermoanalytic characterization of binder burnout and sintering of lead-free piezoelectric KNNLT multilayer laminates with Ni electrodes

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Piezoelectric multilayer actuators (MLA) are electronic devices which allow for transformation of electric signals into displacements and are used for many applications, including automotive injection or precision positioning systems. Since classic piezoelectric lead zirconate titanate (PZT) materials are environmentally problematic and are subject to regular reviews of exemptions to RoHS regulations, there is an urgent need for lead-free materials for MLAs. Sodium-potassium niobate (KNN)-based ceramics have been identified as potential lead-free alternative to PZT and KNN-based multilayer actuators have been investigated. For competitive actuator systems it is required to include base metal electrodes (BMEs). However, thermal processing of such KNN-based multilayers with Ni- or Cu electrodes necessitates precise control of the oven atmosphere in order to control the phase composition and functional properties of the lead-free piezoceramics and the base metal electrodes as well. Sintering of KNN-based MLAs with BMEs is performed at low oxygen partial pressure followed by a reoxidation treatment at lower temperature and intermediate p_{O2} in order to reduce the concentration of oxygen vacancies and provide a sufficient resistivity in the KNN ceramics and, simultaneously, the BME must not be oxidized.

Ceramic KNN green tapes are starting materials for the multilayer process to assemble MLAs. Green tapes are made by tape casting using a slurry consisting of a solvent, binders, plasticizers and dispersion aids. After printing of electrodes and stacking, the thermal process of debindering is carried out in order to remove all organic materials from the green tapes as prerequisite for subsequent sintering steps. Standard green tapes contain poly vinyl butyral (PVB) binders which are typically burned out at 450°C in air. Use of BMEs, however, does not allow for binder burnout in air atmosphere at high temperatures to avoid potential oxidation of the BME. Instead, green tapes with printed BME electrodes require individual debindering schedules and smart sintering and reoxidation protocols.

We report here on thermoanalytic investigations of the debindering behaviour of PVB-based KNNLT green tapes with Ni electrodes. The thermal decomposition of the binder was studied for different oxygen partial pressures. Complementary studies of the debindering process in different atmospheres were performed in a tube furnace equipped with p_{O2} sensors which allows in-situ observations of oxygen uptake or release. We also report on phase composition, microstructure and functional properties of the KNNLT-based components which were sintered and reoxidized under reduced p_{O2}.

Are the heat capacities of liquids calculated from *pVT* equations of state and speeds of sound reliable?

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Precision calorimeters commonly used for the determination of heat capacities are expensive instruments, and the measurement itself is a rather difficult and time-consuming task. Alternatively, the heat capacity of a liquid can be calculated from its volume or density expressed as a function of temperature and pressure, and from the speed of sound in the medium. The following thermodynamic relationship applies to the specific heat capacity at constant pressure C_p:

$$C_p = T \cdot \alpha_p{}^2 \cdot \rho^{-1} (\kappa_T - \kappa_S)^{-1},$$

where T is the temperature, ρ is the density, α_p is the isobaric thermal expansibility, and κ_T and κ_S are the isothermal and isentropic compressibilities, respectively. The latter is related to the speed of sound u and density ρ by the Laplace's formula:

$$\kappa_S = \rho^{-1} \cdot u^{-2}.$$

The reported study was aimed at a comparison of the heat capacities obtained calorimetrically with those calculated in the described manner. All necessary data were taken from the literature. The heat capacities of fifteen liquids at various temperatures were compared. In the majority of cases, the agreement was very good, especially if all the experiments were performed in one laboratory. For example, the relative differences between the heat capacities of 1-chlorohexane, based on the data reported in [1], and obtained in the two ways were (0.21, –0.30, and 0.04) % for the temperatures (25, 35, and 40) °C, respectively.

It seems justified to conclude that the suggested indirect method of heat capacity determination leads to reasonable results. The modern density and speed of sound meters are sufficiently accurate for this application. The only caveat is that the method cannot be used for the liquids with very low α_p, such as *e.g.* water at 4 °C.

[1] M.F. Bolotnikov, Y.A. Neruchev, J. Chem. Eng. Data 49 (2004) 202

Metal-organic sources of functional film materials: thermodynamics and structure-property relationships

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Platinum group element-based coatings are widely applied in various fields including catalysis, aerospace and optical industries. Moreover, an excellent biocompatibility of these materials combined with the high corrosion resistance and good electrochemical characteristics is provoking constantly rising interest from medicine [1]. Metal-Organic Chemical Vapor Deposition (MOCVD) is the main method to obtain such materials. Volatile metal compounds with organic ligands are used as metal-containing sources (precursors) to obtain the functional coatings and films by the gas-phase methods. To optimize the deposition conditions for film materials, knowledge of the vapor pressure and volatilization thermodynamics of the precursor used is required. Obviously, the experimental conditions for the volatilization of complexes with various ligands differ significantly, leading to the fact that, in most cases, the technological conditions are selected intuitively. The report will describe in detail an approach to a comprehensive study of the thermal and structural features of precursors using a combination of various experimental methods and a quality control methodology for the obtained and existing thermodynamic data, which make it possible to trace changes in the thermal properties of complexes during changes in the organic component and establish reasonable structure-property relationship

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[1] K. I. Karakovskaya, S. I. Dorovskikh, E. S. Vikulova, I. Y. Ilyin, K. V. Zherikova, T. V. Basova and N. B. Morozova, Coatings, 11 (2021) 78.

Thermochemical properties of Sulfur-containing Compounds with Influence on Atmospheric Chemistry

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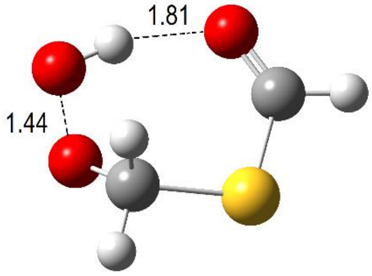

We have computationally studied the thermochemical properties of a variety of sulphur-containing organic compounds (including radicals) with relevance on atmospheric chemical processes, such as the oxidation of dimethyl-sulfide, the most abundant biological source of sulfur to the marine atmosphere [1]. A reliable estimation of the standard molar enthalpies of formation, $\Delta_f H_m^0$ (g), and the bond dissociation enthalpies, *BDE*, in the gas phase at 298.15 K has been performed, by means of atomization [2] and isodesmic reactions methods using G*n* (*n* = 3, 4) [3,4] and M05-2X (DFT) levels of theory. G*n* methodologies, particularly G4 have been shown be an accurate theoretical method to provide reliable $\Delta_f H_m^0$(g) and *BDE* values for a wide variety of organic compounds [5,6].

[1] P.R. Veres *et al*. PNAS 117 (2020) 4505 - 4510
[2] A. Nicolaides, A. Rauk, MN Glukhovtsev, L. Radom. J. Chem. Phys. 100 (1996) 17460.
[3] L.A. Curtiss, K. Raghavachari, P.C. Redfern, V. Rassolov, J.A. Pople. J. Chem. Phys. 109 (1998) 7764.
[4] L.A. Curtiss, P.C. Redfern, K. Raghavachari. *J. Chem. Phys.* 2007, 126, 084108.
[5] J.Z. Dávalos, R. Notario, C.A. Cuevas, J.M. Oliva, A. Saiz-Lopez. *Comp. Theor. Chem.* 1099 (2017) 36.
[6] G. Perdomo, H. Flores, F. Ramos, R. Notario, V.L.S. Freitas, M.D.M.C. Ribeiro da Silva, E.A. Camarillo, J.Z. Dávalos. J. Chem. Thermodyn. 122 (2018) 65-72.

Optical and DSC methods for phase behaviour study of petroleum paraffins. Features and advantages

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Developing the previously proposed optical method for determining the temperatures of phase transitions of n-alkanes (melting, crystallization, rotator phases) [1, 2], this work compares the capabilities of the optical method and the method of differential scanning calorimetry (DSC) for studying the phase behaviour of petroleum paraffins. Melting and crystallization temperatures were determined for six samples of petroleum paraffins by DSC and optical methods. To carry out studies by the optical method, using ultrasonic dispersion and without the addition of surfactants, aqueous dispersions of petroleum paraffins were prepared. The particle sizes in dispersion samples are characterized by dynamic light scattering (DLS), nanoparticle tracking analysis (NTA) and scanning electron microscopy (SEM). The characteristic particle size of the dispersed phase in all samples is of the order of 100-200 nm. By measuring the temperature dependence of the scattered light intensity on such dispersions, it is possible to determine the phase transition temperatures of the dispersed phase (paraffin particles). The phase transition of paraffin particles will be accompanied by a change in their refractive index and lead to bright features in the temperature dependence of the scattered light intensity. The temperatures of the phase transitions of all studied petroleum paraffins determined by two experimental methods are in good agreement with each other. It is important to note that the optical method makes it possible to determine the temperatures of phase transitions of the dispersed phase at such low particle concentrations (~ 10E-5 mass%), at which the DSC sensitivity is no longer sufficient.

[1] V.N. Kuryakov, Yu. Zaripova, M.A. Varfolomeev, P.G. De Sanctis Lucentini, A.A. Novikov, A.P. Semenov, A. Stoporev, P.A. Gushchin, E.V. Ivanov, J. Therm. Anal. Calorim., 142 (2020) 2035
[2] V.N. Kuryakov, D.D. Ivanova, A.P. Semenov, P.A. Gushchin, E.V. Ivanov, A.A. Novikov, T.N. Yusupova, D. Shchukin, Energy & Fuels 34 (2020) 5168

Roman Danube limes mortars - thermal characteristics and identification of production technology

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Modern conservation science requires a holistic multidisciplinary research approach to reveal traditional technologies used for production of historical building materials which are a prerequisite for a practical sustainable conservation of the structures. Our research contributes to understanding of building materials and technology used in Roman times on the territory that is today Serbia.

The main research task was to design compatible mortars for future conservation works. In order to achieve that first, the mortar samples were collected from different sites located on the Roman Danube limes (period 1st-4th century). Then the comprehensive laboratory investigation followed and physical properties, thermal characterization, raw material compositions, mineralogical and microstructural properties were determined. Several different methods were used: chemical analysis, XRF and XRD for identification of the major crystalline phases and binder/aggregate ratio; FTIR analysis for detailed evaluation of the organic and inorganic components and TGA/DSC for identification of CO2/H2O ratio and index of hydraulicity.

The results obtained indicate vast diversity among the examined mortar samples and their properties considering density, binder/aggregate ratio, usage of pozzolans and consequently index of hydraulicity. These results assisted the research team to identify the traditional production technologies of the examined Roman mortar samples and enable responsible conservation approach to the selected objects. Moreover, the information about mortar samples and production technologies enhances scientific understanding of the local communities who lived on the Danube limes in nowadays Serbia centuries ago, as well as their everyday lives and technological progress.

Key words: Roman mortars, production technology, index of hydraulicity, conservation approach

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The effect of hollow glass microspheres on oxidative degradation of Poly(ε-caprolactone)

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A large number of thermoplastics are available with fillers that are added mainly to optimize material properties such as stiffness, fire resistance, thermooxidation stability, etc. Fillers in thermooxidation may act either as pro-degradants or stabilizers. Its effect is determined by the extent of interaction of filler and polymer and by the filler load. Morphology of the polymer can influence the sample mechanical response and also the resistance against the oxidation stress [1]. Poly(ε-caprolactone) (PCL) is a biodegradable polymer that may be potentially used as a replacement for synthetic polymers in biomedical applications and environmentally acceptable packaging and the glass beads are preferred as fillers, especially when composite properties such as isotropy or low melt viscosity are essential [2].

The aim of this work was to study the effect of hollow glass beads as a filler on the oxidative degradation of PCL. The effect of glass beads on PCL has been studied by the thermogravimetry (TG) and chemiluminescence (CL). To analyse the non-isothermal TG records we assumed that the records are composed of three independent processes of first-order kinetics [3]. CL and TG records confirm the superposition of both prodegradation and stabilization effects of hollow glass beads. Thermogravimetry measurements on PCL with loads 5 and 10 wt.% of hollow glass microspheres confirm the stabilising effect while higher loads give a pronounced prodegradation effect. It is also seen on the non-isothermal chemiluminescence temperature ramps.

Acknowledgements
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[1] H. Zou, S. Wu, J. Shen, Chem. Rev. 108 (2008) 3893
[2] M. Sánchez-Soto, A. Gordillo, M. LL. Maspoch, J.I. Velasco, O.O Santana,A.B. Martí, Polym. Bull. 47 (2002) 587-594
[3] J. Rychlý, L. Matisová-Rychlá, K. Csomorová, I. Janigová, M. Schilling, T. Learner, Polym. Degrad. Stab., 96 (2011) 1573-1581

The advanced study of thermal degradation of intumescent coatings with TGA-IST16-GC/MS technique

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Intumescent systems are used to protect combustible materials (wood, polymers, metals) from the attack of heat and fire.

Intumescent coatings are mineral or organic-resin based products that expand many times their original thickness when exposed to flame, produce foams and forming a protective carbonaceous char that acts as an insulating barrier between the fire and the substrate.

However, this barrier is temperature labile; above a certain temperature it breaks down and burns as a result of combustion. In this way, intumescent materials are considered as materials that mainly prolong an early stage of fire development and thus are an important part of fire protection.

In previous studies and reports, we have used TGA-MS and DSC techniques in combination with microscopy observations to explain the mechanism of action of the intumescent material, efficiency and compatibility with our substrate, wood. A very important part of the MS analysis remained unanswered and relates to the toxicity of the smoke during combustion in terms of the formation of gases with mass peak $m/z = 78$, which could be benzene.

Our Mettler Toledo TGA-IST16-GC/MS instrument provided insight into our sample with its combination of a gas chromatograph (GC) and a MS. The GC separates the collected gases, so that simultaneously collected substances can be better identified by the MS detector. A novel system includes a heated storage interface (IST). This interface can store up to 16 gas fractions collected over the course of a TG experiment at different temperatures. It allows the emission profile of selected evolved compounds as a function of thermogravimetric decomposition temperature [1].

In the lecture, we will extend the GC-MS insight into the temperature-dependent evolution of the intumescence barrier and explain the true chemical nature of the problematic mass peak $m/z = 78$.

[1] N. Fedelich, J. Therm. Anal. Calorim., 127 (2017) 947

Oral Presentations 3

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

Development and characterization of lignin-based self-healing bio-aromatic networks

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Driven by the need to develop more sustainable materials, the biopolymer industry has been growing rapidly in recent years. This can be mainly attributed to the increasing production capacity of a variety of aliphatic bio-based thermoplastic polymers, such as polylactic acid [1]. In contrast, the development of bio-aromatic thermoplastics, rubbers, and thermosets from sustainable resources is lagging behind. As a biogenic by-product of the paper and pulp industry, lignin is a promising aromatic resource that could provide for interesting properties when integrated into polymers, resins, or composites [2,3]. However, these materials are often limited in their recycling possibilities, which restricts the development of highly sustainable materials.

This work aims at developing lignin-based self-healing networks using the thermo-reversible Diels-Alder reaction between furan and maleimide groups. To create highly crosslinked thermoreversible networks, furan-modified lignin and a furan-bearing Jeffamine (F5000) were reacted with a bismaleimide (DPBM). To gain insight in their structure-property relations, the obtained networks were analysed using a broad range of thermal analysis and other characterization techniques: modulated temperature differential scanning calorimetry, thermogravimetric analysis, dynamic mechanical analysis, dynamic rheometry, and tensile testing. The networks showed a substantial increase in mechanical properties by introducing furan-functionalized lignin: going from a Young's modulus of 13 MPa for the reference network up to 425 MPa for a 29 wt% lignin-containing network. Moreover, their healing capacity and processing opportunities were repeatedly tested, showing reproducibly promising results.

[1] P. Skoczinski, R. Chinthapalli, M. Carus, W. Baltus, D. de Guzman, H. Käb, A. Raschka, J. Ravenstijn, “Bio-based Building Blocks and Polymers – Global Capacities, Production and Trends 2019 – 2024”, nova-Institut GmbH, (2020)
[2] P. Ortiz, R. Vendamme, W. Eevers, Molecules, 25 (2020) 1158, 11 p.
[3] R. Vendamme, J.B. de Bueren, J. Gracia-Vitoria, F. Isnard, M.M. Mulunda, P. Ortiz, M. Wadekar, K. Vanbroekhoven, C. Wegmann, R. Buser, F. Heroguel, J.S. Luterbacher, W. Eevers, Biomacromolecules, 21(10) 4135-4148

Modelling cheomorheology of reacting polyurethanes

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In resin transfer moulding (RTM) a composite material is made by injecting a reactive resin through a fibre bed. To make a polyurethane based composite, a reactive resin starts as a mixture of two liquids, a polyisocyanate and a polyol and due to polymerization ends up as a polyurethane network. As a result, rheological behaviour changes from viscous to visco-elastic to elastic. To control and predict this rheological behaviour, the kinetics of this reaction must be known and predicted. [1]

Using thermal analysis techniques, like differential scanning calorimetry (DSC) and micro-calorimetry, the heat flow generated during polymerization reaction can be measured as a function of time and temperature. As the heat flow stands in direct correlation with reaction rate, the kinetics of the polymerization can be measured. Here a combination of isothermal and non-isothermal measurements is used in combination with different mixing rations of the initial compounds, to have a broad range of condition during which the reaction can take place. These calorimetric measurements are then used to construct and evaluate a mechanistic model. With this approach the global polyurethane reaction is subdivided in a set of (elementary) reaction and a heat flow can be simulated. Using a least squares curve fitting algorithm on the experimental and the simulated heat flows, the reaction rate parameters of the kinetic model can be determent. An advantage of this mechanistic modelling approach is that the concentrations of the different functional groups, like primary and secondary alcohols, presence of ether groups, catalysts, … are explicitly calculated and can be used to study different compositions.[2]

When the all different conditions can be predicted at reasonable accuracy a robust model is obtained. In a next step the mean molecular weight can be estimated using a statistical method, the so-called “in-out recursive analysis” developed by Macosko and Miller [3,4]. The growth of the molecules is calculated based on the conversion of the materials, leading to molecular weight, gelation, crosslink density and elasticity modulus calculations.

With the use of dynamic rheometry, first the viscoelastic behaviour of fully reacted polyurethane with different molar masses were measured, combined into a single curve using a timer-temperature superposition method. With a Cross-model the viscoelastic behaviour as function of the molar mass could be modelled. In a second step the evolution of the viscous behaviour of the reacting polyurethane was measured. The obtained evolution could then be compared to predicted molar mass evolution. A good correlation between the increasing molar mass and the viscosity could be observed. This allows for the prediction of the viscous properties purely based on the kinetics, reaction conditions and the selection of the monomers.

[1] Shojaei A., Ghaffarian S. R., Karimian S. M. H., Polym. Composite, 2003, 24 (4), 525-544.
[2] Ghoseishi R., Zhao Y., Suppes G. J., J. Appl. Polym Sci, 2014, 131 (12), 40388,
[3] Miller D. R., Enrigue Valles C. M., Polym. Eng. Sci. 1979, 19 (4), 272–284.
[4] Miller D. R., Sarmoria C., Polym. Eng. Sci. 1998, 38 (4), 535–557.

Characterization and thermoanalytical study of novel valsartan coamorphous systems

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Valsartan, an antagonist of angiotensin II receptor, is a class 2 API according to the Biopharmaceutical Classification System (BCS) [1]. The synthesis of coamorphous systems was selected to improve the physicochemical properties of valsartan. Coamorphous are defined as a single phase amorphous solid system composed of low molecular weight binary or multi-components [2]. Three coformers were selected to synthesize (1:1) coamorphous systems with valsartan: *L*-proline, 4,4'-bipyridyne, and trimethoprim. The systems were synthesized by neat grinding. A halo in the PXR diffractograms showed that the amorphization was efficient. The FTIR of the pure components and the coamorphous systems were compared showing that: *L*-proline interacts weakly with valsartan, a slight shift is observed in the valsartan carboxylic acid stretching band (ν C=O); 4,4'-bipyridyne forms hydrogen bonds with valsartan, giving rise to weak broad bands at 1930 and 2470 cm^{-1} [3]; and trimethoprim forms an ionic bond with valsartan, observed as the replacement of the valsartan carboxylic acid stretching band (ν C=O) by the corresponding carboxylate ones. Finally, the glass transition temperatures of pure valsartan and coamorphous systems were determined by DSC. Pure valsartan has a glass transition at 77.9 ºC. For the binary systems the glass transition was observed at 48.4 °C (val:4,4-bipyridine), 73.2 °C (val:*L*-proline), and 101.2 °C (val:trimethoprim). Therefore, the preliminary study of coamorphous systems showed that the highest glass transition is observed in the salt coamorphous system (val:trimethoprim). Further research is being made to identify how stoichiometry, molecular mobility, and intermolecular interactions affect the glass transition of the coamorphous systems.

[1] D.J. Shin, B.R. Chae et al, Pharmaceutics. 11 (2019).
[2] Q. Shi, S.M. Moinuddin, T. Cai, Acta Pharm. Sin. B. 9 (2019) 19–35.
[3] A. Mukherjee, S. Tothadi et al, CrystEngComm. 15 (2013) 4640–4654.

Thermal and Mg – ion conductivity properties of PEO/PVP-I blended polymer electrolyte membranes

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In the present study, authors report about experimental investigations on thermal and magnesium (Mg^{+2}) – ion conductivity properties of polyethylene oxide (PEO) and polyvinyl pyrrolidone – iodine complex (PVP-I) polymers based blended electrolyte systems doped with magnesium sulfate ($MgSO_4$) salt.

Towards the development of better rechargeable electrochemical energy storage systems complementing to the lithium – ion batteries, research on alternative active Mg^{+2} - ions conducting systems has gained significant interest. Magnesium is one of the lightest multivalent metals identified for battery applications and magnesium is the most abundant element in earth's crust, sea water and geographically prevalent than lithium [1].

Since the breakthrough in the discovery of the Na^+ and K^+ - ions conductivity through the matrix of the polymer membranes, solid polymer electrolytes (SPEs) came into the light and they have been gaining substantial interest in both scientific and industrial sectors [2]. In SPEs, the polymer acts as a host for the salt ions and at above the glass transition temperature, polymer facilitates the 'free three dimensional space in the matrix' for the benefit of augmentation in the mobility ions.

PEO/PVP-I/$MgSO_4$ based polymer blend electrolyte membranes were fabricated by solution cast technique and as prepared free-standing membranes were directionally stable provided with an average thickness of 170 micros. The miscibility of the two polymer and variation of thermal properties as a function of salt doping concentration such as melting (T_m) and glass transition (T_g) temperatures were investigated by means of differential scanning calorimetry (DSC). The shift in position of optical absorption edge towards higher wavelength as a result of increase in salt doping concentration evidenced for the enhanced interaction between salt ion and polymer chains. Electrochemical impedance spectroscopy (EIS) measurements were performed in the temperatures range 30°C – 70°C and investigated the variation in room temperature Mg – ion conductivity and dielectric properties as a function of salt doping concentration and temperature.

[1] B. Park and J. L. Schaefer, J. Electrochem. Soc. 167 (2020) 070545.
[2] A. Du, H. Zhang, Z. Zhang, Adv. Mater.31 (2019) 1805930.

Alkali-metal cation coordination to calix[4]arenes containing triazole functionalities

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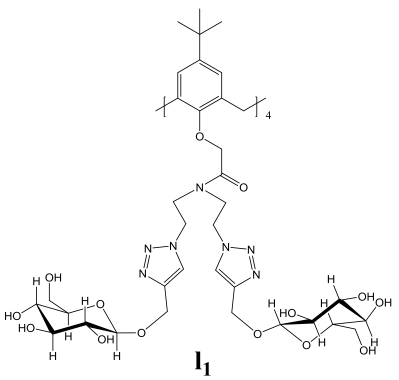
The medium effects on the complexation of alkali-metal cations with calix[4]arene derivatives containing triazole subunits (compunds **L** and **l**) was systematically explored by means of microcalorimetric and UV-Vis spectrophotometric titrations in dimethylformamide, methanol water and acetonitrile. First two solvents were chosen for the purpose of comparison of receptors binding abilities as both ligands exhibit sufficient solubility required for complexation investigations in these media. The cation hosting in MeCN was studied to compare the ligand **L** with other tertiary amide calixarene derivatives. On the basis of ligand dissolution enthalpies, and the literature data, the enthalpies of reactants and the product transfer among solvents were obtained. The studied compounds binded alkali-metal cation rather efficiently and similarly in methanol and in dimethylformamide, whereas the acetonitrile was the most favourable reaction medium for alkali-metal cation reactions with receptor **L**. Compound **l** proved to be a remarkable host for Na^+ in water. The cation binding was enthalpically controlled. The complexation of Li^+ with ligand **L** in acetonitrile was the only entropically favourable reaction. The peak-affinity of both compounds for Na^+ was noticed for all studied reactions. The ^{1}H NMR investigations revealed relatively low affinity of the calixarene sodium complex for the inclusion of solvent molecule in the calixarene hydrophobic cavity, with the exception of acetonitrile. In many examined cases, the considerable solvent effect on the complexation equilibria was proven to be an interesting interplay between the transfer enthalpies and entropies of the reactants and the products.



L **l_1**

Structures of compound **L** and gylcocalixarene **l**

Addressing of different synthetic and shaping approaches for preparing β-TCP-based substrates for biomineralisation of HAP

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Nowadays, calcium phosphate (CaP) ceramics are a leading standard for bone grafting materials in bone tissue engineering due to the structural similarity with the mineral part of the bone **[1]**. CaP ceramics show bioactivity, osteoinductivity and osteoconductivity, all of which are processes that highly depend on macro-microporosity of the ceramic material **[2]**. α- and β-tricalcium phosphate ($Ca_3(PO4)_2$), hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) and biphasic calcium phosphates (BCP) which are a mixture of HAP and β-TCP, stand out among CaP synthetic ceramic materials **[3]**. In this study, we elucidated what we believe is the most convenient synthetic route for preparing β-TCP. We precipitated calcium deficient hydroxyapatite (CDHA) from aqueous solutions of $CaNO_3{\times}4H_2O$ and $(NH_4)_2HPO_4$ under carefully controlled pH. We evaluated the benefits of slow vs. rapid CDHA precipitation. Either way, a subsequent calcination was necessary to obtain the β-TCP.

The goal was to establish solid β-TCP bodies with substantially different macro and microstructures, for the purpose of evaluating the course of the HAP biomineralisation. The as-derived β-TCP powders were used for the preparing of the porous bodies using freeze casting, 3D printing and sponge replication templating. The X-ray diffraction confirmed monophasic β-TCP for the slow precipitation after calcination, while traces of β-CPP were observed for the fast precipitation after calcination. Critically, no presence of HAP was observed. Microstructural differences were described in detail and compared using compressive strength, total porosity, adsorption-desorption tests and electron microscopy. The described β-TCP synthetic and open-pore body-forming route are fundamental for bone engineering application.

[1] A. El-Ghannam, Bone reconstruction: from bioceramics to tissue engineering, Expert Rev. Med. Dev. (2005) 87-101
[2] P. Habibovic, H. Yuan, C.M. van der Valk, G. Meijer, C.A. van Blitterswijk, K. de Groot, 3D microenvironment as essential element for osteoinduction by biomaterials, Biomaterials 26 (2005) 3565-3575
[3] J.M. Bouler, P. Pilet, O. Gauthier, E. Verron, Biphasic calcium phosphate ceramics for bone reconstruction: A review of biological response, Acta Biomaterialia 53 (2017) 1-12

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Comparison of the effects of biodegradable and conventional polyester-based microplastics on soil abiotic processes

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The properties, occurrence, and adverse effects of conventional microplastics are examined worldwide. However only few studies have focused on biodegradable microplastics (micro-bioplastics), whose abundance in environment is expected to grow continuously [1]. After the entrance to soil, the micro-bioplastics may interact with parts of soil organic matter (SOM) via weak interactions and induce the structural changes in SOM. This affects primarily the properties of SOM and secondarily also the properties of SOM water, which alters soil ecosystem functions [2].

In this study, selected abiotic soil indicators were determined for soil contaminated with polyhydroxybutyrate (PHB) microbioplastics and PET microplastics to evaluate their effect on soil. Peat was used as a model of soil organic matter. Water holding capacity of SOM, strength of water binding (evaporation enthalpy of soil water), water molecule bridges stability (demonstrated as a steep increase in heat capacity, WaMB) and content of soil aliphatic crystallites (via melting enthalpy) were determined using Differential Scanning Calorimetry (DSC) in soils dried under three different relative humidities.

We have found that both kinds of microplastics decreased the strength of water binding in soil as well as the content of aliphatic crystallites. In addition, WaMB stability and water holding capacity of SOM were different for each microplastics and humidity. These results implicate that both conventional microplastics and micro-bioplastics negatively affect soil water and structure, which may consequently have an adverse effect on soil functions. This observation applies mainly for initial stages of introduction of microplastics into soil, when the microplastics interact with SOM parts and changes its supramolecular structure. In the case of micro-bioplastics, in a relative short period, the soil microorganisms start to biodegradation which assumingly leads to different effect comparing to conventional microplastics. Bioplastics are considered as a promising alternative for conventional plastics in agriculture, however more research in this area is required before any worldwide application on agricultural soil.

Acknowledgement:

The financial support of projects FCH-S-21-7398 and Kvalitní interní granty VUT EF19_073/0016948 of Ministry of Education, Youth and Sports are acknowledged.

Reference:

[1] Fojt J, David J, Přikryl R, Řezáčová V, Kučerík J. 2020. A critical review of the overlooked challenge of determining micro-bioplastics in soil. Science of The Total Environment 745.
[2] de Souza Machado AA, Kloas W, Zarfl C, Hempel S, Rillig MC. 2018. Microplastics as an emerging threat to terrestrial ecosystems. Global Change Biology 24:1405-1416.

Resorcinol-formaldehyde condensation – DSC study

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Resorcinol-formaldehyde (RF) gels are important precursors of nanostructured carbons. Porosity can be partly controlled in the course of RF sol-gel polycondensation reaction. The aim of this contribution is to demonstrate the possibility of DSC as a tool for characterisation of RF gels during their synthesis.

RF condensation is two-step exothermic process (formation of hydroxymethyl derivatives of resorcinol and formation of crosslinked three-dimensional network - gel). Its conversion degree can be followed by heat evolution measurement under various heating rates which enables isoconversional kinetics analysis. Non-linear model-fitting analysis was based on the Sestak-Berggren [1] reaction model $f(\alpha) = \alpha^m (1-\alpha)^n$. Obtained kinetic equation allows to determine the temperature program (heating from 10 °C to 40 °C at 3 K min^{-1}, isothermal step for 40 min, heating to 100 °C at 3 K min^{-1}) leading to separation of both step which can be useful for influencing the final properties of gels - mainly porosity.

Products prepared at different time at 40 °C show very similar properties, confirmed especially by FTIR analysis and thermal decomposition, but they significantly differ in low temperature transformations investigated using DSC. The melting peaks were shifted to higher temperature with progressive reaction time and consequently deformed by a new phase transition during melting (possibly glass transition of formed polymer, Fig. 1).

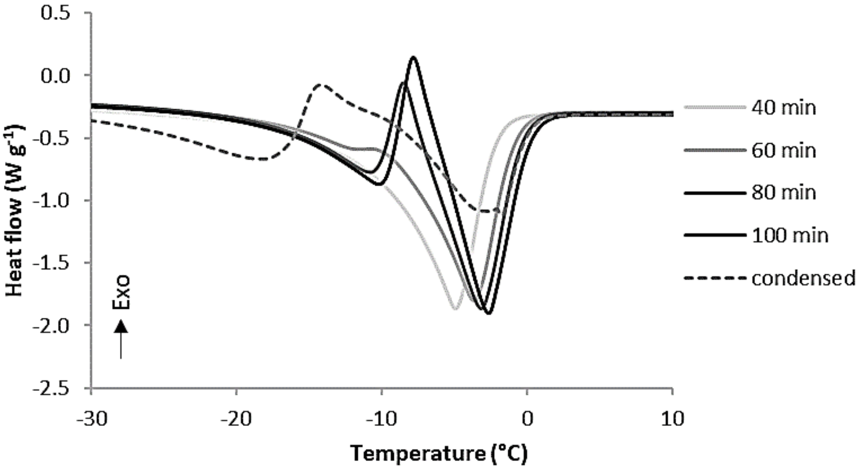

Fig. 1 DSC curves of melting of RF mixtures with different times of condensation (at 40 °C)

[1] S. Vyazovkin, A.K. Burnham, J.M. Criado, L.A. Pérez-Maqueda, C. Popescu, N. Sbirrazzuoli, Thermochim. Acta. 520 (2011) 1-19

Using of DSC for identification of polyethylene terephthalate (PET) waste of various origin and composition for physical recycling

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Physical recycling of polymers is among the important strategies of circular economy. It is also implemented into EU legislation, which aims to dictate the content of recycled polymers in new products.

PET (polyethylene terephthalate) is one the mostly used polymers in packing industry. The methods of its physical recycling are relatively simple, they include separation of waste plastics, shredding (mostly bottles to flakes) and washing. The resulting PET pieces are then extruded and re-granulated. The key problem for successful recycling and re-granulation is various types of PET including already recycled PETs, bottles with additives, preforms, regranulates or virgin PET. Each of these types may have different properties that affect their suitability for recycling process.

In this study, we present DSC as a method for the identification of these different types of PET. In principles, the method uses the simple parameters obtained from a DSC run such as temperatures and enthalpies of melting, crystallization and glass transitions of the first and second heating and cooling cycles. We collected 79 samples of different types of PET, which included virgin PET, preforms, regranulates, bottles with varying content of rPET (recycled PET) and so called bioPET, bottles with additives, recycled products, PET-G and controllably degraded samples at high temperatures.

The method is based on the assumption that thermal history, composition and degree of recycling would affect the DSC parameters of the PET. Glass transition, crystallization and melting behavior of PET were used as primary parameters for advanced statistical analysis, which allowed to distinguish the samples into groups according to their history and properties. In particular, principal component analysis (PCA) showed the possibility to distinguish several groups i) virgin PET (before, but also after controlled degradation); ii) PET affected by high temperature or the addition of other substances (degraded samples, bottles with additives and products from rPET); iii) rPET, bioPET and PET-G; iv) preforms, bottles and PET flakes.

To sum it up, simple DSC run can be used to distinguish PET materials of different origins and recycling degree based on the interrelationship between thermophysical properties.

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Micro(bio-)calorimetry - An early warning tool for the detection of microbial contaminations in drinking water

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Access to safe and clean drinking water is a human right. Unfortunately, poor maintenance and hygiene can compromise the quality and safety of drinking water. The types of contamination can be diverse and pathogenic microorganisms pose an immediate threat to humans, as a single pathogen can cause life-threatening disease within a few days [1]. Consequently, microbiological laboratories are looking for rapid and reliable techniques to detect pathogens in water. At the moment, conventional bacteriological detection methods are predominant. Briefly, a defined sample volume is applied directly to the solid culture medium (agar; 0.5 to 1 mL) or a pre-enrichment step is performed via membrane filtration (50 to 100 mL) and the grown colonies are counted after a defined period of time. However, despite the simplicity of the method, the main limiting factor is the speed of detection for this analysis [2]. However, time is of essence if countermeasures are to be taken.

In 2012, we were able to demonstrate that bacterial contamination in tap water can be detected very quickly by [3]. Recently, Fricke et al. introduced this method to the detection of *Legionella pneumophila* [4], a pathogen found in drinking water that regularly causes major outbreaks worldwide. What is still missing, is a specially designed calorimeter that meets the criteria for detecting bacterial contaminations in drinking water.

In our study, we constructed an isothermal microcalorimetric test system that was special designed for the microbiological analysis of drinking water and cooling tower samples. Our results demonstrate that microcalorimetry can contribute as an early warning system in the context of conventional, culture-based detection of waterborne pathogens in drinking water. Depending on the degree of contamination, detection can be recognized within 24 h (compared to 5 to 10 days in the case of conventional detection of *L. pneumophila*). The greatest advantage of this microcalorimetric approach is its compatibility with existing standards. Sample preparation and processing can be performed according to existing standards. Even a quantitative evaluation in the form of CFU/mL is possible thanks to the sample vessels selected by us.

[1] U. Szewzyk, R. Szewzyk, W. Manz, K-H. Schleifer, *Annu. Rev. Microbiol.*, 54 (**2020**) 81-127.
[2] FY. Ramírez-Castillo, A. Loera-Muro, M. Jacques, P. Garneau, et al., *Pathogens*, 4 (**2015**) 307-34.
[3] T. Maskow, K. Wolf, W. Kunze, S. Enders, H. Harms, *Thermochim.Acta*, 543 (**2012**) 273-280.
[4] C. Fricke, J. Xu, F-L. Jiang, Y. Liu, H. Harms, T. Maskow, *Microb. Biotechnol.*, 13(**2020**) 1262-72.

Thermal methods for estimating the stabilization effect of heterocycles in biopolymer matrix

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In recent years, there has been particular interest in the development of biodegradable and biocompatible natural polymers that could act as solid polymer electrolytes [1]. The advantages they offer are high abundance, biocompatibility, biodegradability, and cost-effectiveness. However, the conductivity of biopolymers is very low and technically they are not electric conductors. Therefore, different approaches have been proposed that have improved their ambient conductivity: for example the blending of two polymers, using a variety of salts or the nitrogen-containing heterocycles.

Membrane technology requirements at present focus on three main aspects such as high proton conductivity, long lifetime, and good thermal stability. All these aspects relate to the strength of the bond between the cellulose matrix and the functionalizing molecule. On the one hand, a stronger hydrogen bond improve the thermal resistance, on the other hand, it reduces the mobility of molecules, which leads to a low value of electrical conductivity [2]. Thermal methods of analysis, including DSC and TGA, are significant for estimating the stabilization effect of heterocycles in biopolymer matrix. Moreover, the lifetime was determined using the Kissinger-Akahira-Sunose model and to verify the of theoretical calculations, measurements as a function of time were carried out. [3]

The research focuses on the thermal stability of the obtained composites based on cellulose and heterocyclic dopant. The influence of stoichiometry of compounds and different types of dopant (Imidazole, 1,2,3-Triazole) were investigated. The research was carried out in various synthesis conditions: under vacuum and normal atmosphere. The obtained results were confirmed by NMR and FTIR method.

Acknowledgments

This work was supported by the National Science Centre, Poland [grant number 2017/25/B/ST8/00973]

[1] O. Selyanchyn, R. Selyanchyn, S.M. Lyth, Frontiers in Energy Research, 8 (2020)596164
[2] J. Tritt-Goc, Ł. Lindner, M. Bielejewski, E. Markiewicz, R. Pankiewicz, Carbohydrate Polymers 225 (2019), 115196
[3] J. Tritt-Goc, Ł. Lindner, M. Bielejewski, E. Markiewicz, R. Pankiewicz International Journal of Hydrogen Energy, 45 (2020) 13365

Modified cereal straw - a novel, functional additives for elastomer biocomposites

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Strategies for implementing sustainable development principles for the preparation and modification of polymer composites require the search for new and environmentally friendly solutions. The aim of the scientific activity is in line with the global trend in the production of materials based on the use of renewable raw materials of biological origin and concerns the knowledge, research and explanation of the effectiveness of different lignocellulosic biomass as a source of active functional compounds for modification of polymer composites.

Cereal straw represents interesting alternative for commercial fillers and could be successfully applied as a low-cost filler, which improved several properties of natural rubber composites. The work carried out included both the characteristics of pure and modified bio-fillers as well as elastomer composites. The analysis of the chemical composition of the additives, depending on their type, was performed using analytic methods. Moreover, the particle size of the fillers used as well as the oil absorption number (DBPA) were measured. The structural, morphological and dispersion properties of both biomodifiers and new composite systems have been determined by spectroscopic (FTIR) and scanning electron microscopy (SEM) analysis. The effectiveness of the modifications carried out through the characteristics of intermolecular interactions at the filler-elastomer interface have been examined using dynamic mechanical analysis (DMA). Moreover, tests of spatial structure, mechanical (hardness, tensile and tear strength), thermal (TGA, DSC) and rheometric properties of composites have been performed. In addition, the resistance of materials to aging (temperature, oxygen, UV radiation) has also been determined.

Application of lignocellulosic biomass in the form of cereal straw for natural rubber composites, indicated high application level of those type of materials. Moreover significant multifunctional properties of the materials can be reached by application different modification techniques. Additional ecological and economic benefits can be achieved while solving typical agricultural problems with the usage and management of such plants.

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Modified biomass as a filler for rubber biocomposites

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The interest in using an agricultural waste as a raw material for the production of polymer composite materials has been steadily increasing in recent decades [1]. Agricultural residues, such as straw and weed are inexpensive, renewable and easily accessible lignocellulose fiber sources almost worldwide. An important aspect of the use of natural fillers for polymer composites is their thermal stability [2]. The research aims to gain new knowledge on the effectiveness of various methods of plant waste modification to obtain active components for the production of elastomer composites. Presented work includes an in-depth characterization of the plant-based additives as well as its effect on the properties of elastomer mixtures and vulcanizates. In the research, bio-fillers are analyzed in detail in terms of their chemical structure, thermal stability and surface morphology. Besides, their compatibility and characteristics of interactions in the elastomeric medium are determined.

The detailed characteristic of the cereal straw containing thermal gravimetric analysis (TGA) and the analysis of their surface including measurements of contact angle (CA) and scanning electron microscopy (SEM) was studied. The properties of biocomposites have been examined in terms of the kinetics characteristics by differential scanning calorimetry (DSC) and rheometric properties of elastomer mixtures. Analysis of the new composites included static mechanical and thermal properties were carried out. Examinations of flammability using by conical calorimetry were performed. This work is the innovative technological solution, which is designed to recognize the opportunity to create composites with high application level, associated with a significant change in multifunctional properties. Moreover, addition of the cheap filler into elastomer allows to reduce the manufacturing costs.

[1] S. N. Monteiro, V. Calado, R. J.S. Rodriguez, F. M. Margem, Journal of Materials Research and Technology, 1 (2012) 117-126,
[2] K. Sathasivam, M.R.H.M. Haris, J Therm Anal Calorim., 108 (2012) 9–17

Acknowledgement: This research was supported by the National Science Centre, Poland (PRELUDIUM no. 2018/31/N/ST8/00802). Participation in the conference was supported by Project "PROM - International scholarship exchange of PhD candidates and academic staff" is financed by the European Social Fund, Operational Programme Knowledge Education Development for 2014-2020, non-competition project entitled "International scholarship exchange of PhD candidates and academic staff", no POWR.03.03.00-00-PN13/18.

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Alizarin/vermiculite hybrid pigment as promising multifunctional colorant for elastomer composites with improved performance

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Owing to its excellent thermal stability, chemical resistance as well as environmental benignity, hybrid pigments based on mineral fillers attracts great interest of many researchers. These organic-inorganic systems exhibiting the advantages of both an organic dye and an inorganic host are increasingly displacing dyes and pigments traditionally used in polymer technology [1]. To date, although much attention has been paid to develop and apply new hybrid pigments in different thermoplastic materials, the effect of these materials on the elastomer composites is not well-described in the literature.

The objective of this study was to prepare and characterize the novel organic-inorganic pigment based on alizarin dye (1,2-dihydroxyanthraquinone) and vermiculite mineral as well as to explore its potential as multifunctional additive for acrylonitrile-butadiene rubber (NBR) composite. The interactions between alizarin and vermiculite were inspected by secondary ion mass spectrometry (ToF-SIMS) and Fourier transform infrared spectroscopy (FTIR). The morphology, color characteristic and stability of the hybrid pigment were characterized by X-ray diffraction analysis (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and UV-Vis spectroscopy. Afterwards, the fabricated organic-inorganic pigment was incorporated into NBR matrix cured with sulphur-based crosslinking system via blending method. The curing behaviour, mechanical and thermal combustion properties of the novel, colourful NBR composites were studied respectively through rheometric measurements, crosslink density analysis, dynamic mechanical analysis (DMA) and microscale combustion calorimeter (MCC).

The obtained results suggested that the as-prepared alizarin/vermiculite hybrid pigment with improved physico-chemical properties could be simultaneously served as a promising colorant and functional additive to be applied in polymer composites. The prepared NBR composites colored with studied hybrid pigment exhibited pH-sensing activity and reduced flammability.

[1] Pardo, R. et al. *Chemical Society Reviews* **2011**, 40, 627-687.

Epoxy–based S–IPNs as eco–friendly flame retardants

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Epoxy resins are versatile reactive compounds possessing excellent properties, such as: good addition to different substrates, great resistance to corrosion, chemicals and abrasion, flexibility, moderate toughness, etc. [1]. Due to their properties, epoxy resins are widely used in different domains: engineering and construction, in circuit boards, aeronautics, construction etc. However, epoxy resins show increased flammability and possess low thermal stability [2]. Hence, enhancing their flame resistance together with maintaining their properties and with recycling and minimizing environmental impact is to this day an important challenge.

Three semi–interpenetrating polymer networks (S–IPNs) were obtained from an epoxy resin (DGEBA) cured with aromatic, cycloaliphatic and aliphatic hardeners and having as linear component an aromatic oligophosphonate. The miscibility of the components in the S–IPNs was studied via DSC and morphological studies (SEM–EDX). The thermal stability of the S–IPNs was assessed by TGA in both inert and air atmospheres. The evolved gases analysis was studied through TGA–FTIR and Py–GC–MS coupled techniques. The flame retardant capacity of the S–IPNs was demonstrated via pyrolysis combustion flow calorimetry (PCFC). The residual char yields resulted from TGA were analyzed by SEM–EDX. The obtained results demonstrated the eco–friendly character of the S–IPNs through the absence of halogens and the low phosphorus content and volatiles evolvement.

[1] R. Thomas, P. Vijayan, S. Thomas, "Recycling of thermosetting polymers", Transworld Research Network, (2011) 122-129
[2] A. Toldy, A. Szabó, Cs. Novák, J. Madarász, A. Tóth, Gy. Marosi, Polym. Degrad. Stab., 93 (2008) 2007

Acknowledgment

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Effect of thermal treatments on the performance of carbon xerogels in an electrochemical capacitor

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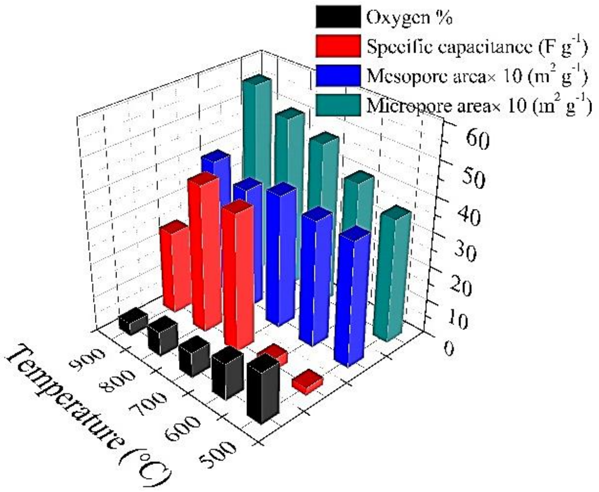
Carbons with well-designed porous structure and surface chemistry is a key for enhancing the performance of electrochemical capacitor (EC). This contribution addresses the effect of carbonization temperature and activation method on properties of carbon xerogels (CX) and their performance for use in EC electrodes. The sol-gel polycondensation reaction between resorcinol and formaldehyde was used to obtain a cross-linked gel network, followed by ambient drying and carbonization at temperatures from 500 °C to 900 °C. Further, the access to meso and micropores was improved through either physical (CO_2) or chemical (KOH) activation of CXs [1]. The physicochemical aspects of prepared CXs were characterized using nitrogen adsorption-desorption experiments, elemental CHNS analyses, Fourier-transform infra-red spectroscopy, X-ray diffraction, Raman spectroscopy, and scanning electron microscope images. The cyclic voltammetry, chronopotentiometry, and impedance spectroscopy were performed on xerogel electrodes, using KOH as electrolyte.

Depending on the temperature of carbonization and activation, the obtained CX materials significantly differ in porosity (micropore area in the range 361-1331 m^2g^{-1}, mesopore area in the range 358-576 m^2g^{-1}), total oxygen content (4-20 %) and surface chemistry (C-O, C=O, C-OH, etc.). The increase in surface area or volume of micro-mesopores and the changes in oxygen content follow expected trends with carbonization temperature and varied extent of both types of activation. The results of electrochemical performance measurements show that the hierarchical porous structure obtained within CX enables better access for the electrolyte ions to form an electric double layer as well as the oxygen functionalities introduce pseudo-capacitance. However, the electrochemical performances do not exactly follow this trend, which is reviewed critically in this contribution.



[1] M. P. Chavhan, S. Ganguly, J. Solgel Sci. Technol., 88 (2018) 395

Oral Presentations 4

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

Breakdown of the anodized nanostructured anatase for photovoltaic devices: the effect of electrolyte composition on preparation of large surfaces of nanotubes

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The insight in recent investigations of titanium dioxide show this material is maybe the most extensively studied semiconducting material with application in the area of photovoltaics (PV), sensors, water splitting, etc. PV titania is active in generation, transport and recombination of photo-induced electron-hole pairs under illumination, thereof, it is worth considering upgrades of its key parameters. It is already well known that recombination consequences may be reduced by texturization of the surfaces, where the discovery of 1D materials was shown as beneficial. TiO_2 nanotubes (TNT) were first time successfully electro-chemically prepared by Zwilling [1]. Here we focus on the electrochemical field assisted growth and etching over intermediate phase to yield ordered hollow 1D nanostructures [2].

Having previously optimised the electrical conditions and cell geometry, here we focus on the electrolyte contribution, specifically water content which can influence the equilibrium of the several competing process responsible for the nanotubes formation: titania formation, TNT formation over intermediate titanium hexafluoride and etching of the mentioned phases. Higher water content increases electrolyte conductivity, consequently allowing faster oxidation of Ti and subsequently faster etching. Higher water content also contributes to the dissolution of the only water-soluble phase in the system; the titanium hexafluoride. At moderate water content increase, these processes facilitate the initial titania protective layer formation (titania prevents short circuits) and TNT growth (better charge transfer) as well as diminish the scram of residual titanium oxide or hydroxide phases (better charge transfer, better transparency, post-treatment not necessary). Highest water content promotes excessive oxidation/etching where first TNTs with expanded tip (crown-like TNTs), and then wormholes arise. Similarly, disproportioning in dissolution/oxidation/etching occurs at the lowest water contents resulting in less perfect NT. (Micro) Structural, electrical and spectroscopic characterisation of NTs and electrolytes enabled identification of mechanisms and bottlenecks in the course of the anodization. Thereof we can prepare larger homogeneous crack-free TNT surfaces.

[1] V. Zwilling, M.Aucouturier, E.Darque-Ceretti, Electrochim. Acta, 45 (1999) 921-929
[2] G.K. Mor, O.K. Varghese, M. Paulose, et. al., J. Mater. Res., 18 (2003) 2588-2593

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Surface mobility in chalcogenide glass-forming materials

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Surface mobility, such as surface diffusion and near-surface viscosity, is important for a broad range of chemical and physical processes that take place at the surfaces of solids, including surface crystallization. Comparison of surface crystal growth with surface diffusion has a significant impact on the understanding of the crystal growth process, which is important for the preparation, processing, and utilization of amorphous materials. In the standard crystal growth models, the mobility of the reorganizing structural units is described by a diffusion coefficient which is usually substituted by bulk viscosity.

In this contribution, the surface mobility in amorphous chalcogenide glass-formers is studied by following the temporal evolution of periodic structures embossed into the surface. The measurements provide information about the near-surface viscosity, as well as, the surface diffusion coefficients. The data are compared with nanoindentation measurements. The relation of surface mobility are discussed concerning the surface crystal growth in different chalcogenide glass-formers.

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Development of nanostructured transparent electrodes for solar cells based on aluminium doped zincite

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Modern solid-state solar cells are multi-layered composites; such configuration allows immense area for upgrades but not without struggle. As the main problem of all modern photovoltaic devices we find the mutual dependence of layers, i.e. the difficulty to predict the exact behaviour due to complex transport mechanisms at the boundaries between thin-film interfaced to other layers. Among such constituents, we find transparent electrodes or transparent conducting oxide layers (TCO), primarily aluminium doped zincite (AZO). AZO is a system thought to be well known, yet synthesis and deposition, chemical modifications, nano-morphological and nano-structural organisation parameters are still not unambiguously related to final functionality. For example, it is not clear how nanostructurisation of AZO would affect light trapping and vertical conductivity, while retaining of lateral conductivity for same thickness of films. The questions regarding general compatibility in interfacing of adjacent layers in SC also remain unclear.

The benefits of AZO are thermal stability and mild deposition conditions. We follow these benefits and here we show evaluation of various softer chemical deposition methods for preparing AZO in planar configuration, as well as nanostructured, vertically aligned AZNR films that will retain conductivity, transparency and layer interconnectivity.

The successfulness of the synthesis method was checked by means of GIXRD, FTIR-ATR and SEM/EDS. PL/DRS-UV-VIS and DLTS monitored compositional parameters behind transparency as well as lateral and perpendicular conductivity. In addition, parameters from profilometry, contact angle and TEM/EELS analysis shed more light on what synthesis seem to be more favourable for specific property. The utilisation of the observed parameters and behaviour was discussed from the point of view of TCO and CTO performing solar cell layers. The concept of developed material may shift the strategies of the solar cell design.

This investigation of AZNR may cause the reconsideration of the paradigm of solar cell assembly since the AZNR additionally show conceptual similarities with charge transfer oxide (CTO) layers.

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The effects of thiocyanates on hydration and properties of zinc containing Portland cement

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Contamination of cement binders with zinc represents a significant problem due to the negative effects on cement hydration. Zinc compounds cause a drastic increase in setting time due to prolonging the induction period. The currently accepted mechanism behind this effect is the formation of $Ca(Zn(OH)_3)_2 \cdot 2\ H_2O$ hydrates on the surface of cement grains that deplete Ca^{2+} ions from the pore solution and creates a diffusion barrier.

Hydration accelerators are commonly employed in the concrete industry to counter long setting time caused by low temperature and contamination by heavy metals. These compounds influence both hydration kinetics and composition of hydration products. The influence of various compounds on the mechanism of cement hydration can be studied using calorimetric methods such as isoperibolic and isothermal calorimetry while properties of hydrated cement pastes are commonly studied using differential thermal analysis (DTA), X-ray diffraction (XRD), porosimetry and scanning electron microscopy (SEM). Some setting accelerators have been found to significantly decrease setting time of zinc contaminated cement. Out of the most used compounds in commercial accelerators, the efficacy of thiocyanates is yet to be determined.

The result show that thiocyanates have induce visible change in hydration mechanism of cement to various degrees depending on concentration and on the presence of the specific cation.

Application of isothermal and isoperibolic calorimetry to assess the effect of zinc on hydration of cement blended with fluidized bed combustion ash

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In recent years, the amount of zinc in cement has increased. Zinc enters the cement mainly from solid waste or tires, which are widely used as fuel for combustion in a rotary kiln. Zinc can enter cement also as a part of secondary raw materials. Fluidized bed combustion ash is one of the secondary raw materials that can be used in combination with cement. Zinc in cement mainly causes a delay in hydration. In this work, zinc was added to cement in a mixture with fluidized bed combustion ash in the form of two soluble salts of $Zn(NO_3)_2$, $ZnCl_2$ and poorly soluble compound ZnO. The concentration of added zinc was chosen as 0.05, 0.1, 0.5 and 1 wt. percent. Isoperibolic calorimetry was used to monitor the hydration process under real conditions, while isothermal calorimetry performs it at a defined selected temperature. The results show that the combination of zinc and fluid ash accelerates hydration. Newly formed compounds during hydration were identified by X-ray diffraction (XRD).

Ionic conductivity and dielectric relaxation of NASICON superionic conductors at the cryogenic threshold

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NASICON sodium-based superionic conductors have recently found renewed interest as solid electrolytes in sodium-ion batteries due to their exceptional ionic conductivity being on the same scale as liquid electrolytes. Since sodium ions in the crystal lattice move among interstitial positions through site-specific bottlenecks, the overall conductivity is strongly dependent on the NASICON composition. We report on the synthesis protocols and processing parameters of $Na_3Zr_2Si_2PO_{12}$ prepared by the conventional solid-state reaction (SSR) route. We critically evaluate important observations made in the extended literature on the topic, focusing on the thermally-induced 2nd order transition from monoclinic to rhombohedral lattice structure and the onset of zirconia contamination – both phenomena investigated in detail by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in an inert atmosphere at temperatures corresponding to the SSR synthesis parameters, i.e. above 1100°C. We expand the dataset availability concerning measurements of ionic conductivity and dielectric permittivity for NASICON by focusing on the transition threshold at 160°C, where the crystal lattice fully converts into its rhombohedral form and exhibits its inherent superionic properties, and then extending the scanning range down to the cryogenic threshold at -160°C.

The influence of copper ions on the formation, thermal stability and porosity of dibasic calcium silicate hydrates

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The pollution of the environment is one of the major concerns humanity is facing, while volatile organic compounds (VOCs) are one of the major contributors to global air pollution [1]. In the past decades, many methods have been applied for the neutralization of VOCs (ozonation, adsorption, etc.) [2]; however, the conversion of VOCs to CO_2 and H_2O is one of the most common attractive ways. Unfortunately, the conversion requires catalysts with expensive precious metals, thus the creation of a new generation and cheaper catalyst is in great demand [3]. It is known that synthetic calcium silicate hydrates have a large surface area and during calcination recrystallize to thermal stable compounds – calcium silicates [4]. Also, calcium silicate hydrates have good adsorption properties for transitional metal ions, which can be used in the production of catalyst [5]. However, there is little data about the influence of transitional metal ions on the formation and properties of dibasic calcium silicate hydrates.

This work aims to determine the influence of copper ions on the formation, thermal stability, and porosity of dibasic calcium silicate hydrates. For the synthesis the mixture of CaO, SiO_2 ($CaO/SiO_2 = 1.5$) and $Cu(NO_3)_2\cdot 3H_2O$ solution ($c = 10$ g Cu^{2+}/dm^3) was used. The solution to solid ratio of the suspension was equal to 10:1. The synthesis was carried out under hydrothermal conditions at 175 °C temperature for 16 h. The thermal stability of products was determined by using *in-situ* XRD in a modular temperature chamber from RT to 1000 °C temperature. The shape of particles was evaluated with SEM and TEM, while the porosity of the sample by using N_2 adsorption-desorption isotherms as well as BET and Kelvin equations.

It was obtained, that during hydrothermal synthesis, semicrystalline type calcium silicate hydrates with CuO were formed. SEM and TEM results showed, that CuO particles are nanosized with clews-like or rod-like shapes. It was calculated, that sample is mesoporous material with pores of 7–15 nm diameter. According to BET equation calculation, the specific surface area of the synthesis product was equal to 80.24 m^2/g. It was determined, that during calcination the products, which can be used for VOCs conversion to CO_2 and H_2O, were formed.

[1] M.Z. Jacobson, et. al. 100% Clean and Renewable Wind, Water, and Sunlight All-Sector Energy Roadmaps for 139 Countries of the World," Joule, vol. 1, no. 1, 6 September 2017, pp. 108-121.
[2] C. Yang, et. al. Chem. Eng. J., vol. 370, pp. 1128-1153.
[3] H. Wang, et. al. Ind. Eng. Chem. Res., vol. 59, no. 7, pp. 2908-2920.
[4] F. Tang, L. Li and D. Chen. Adv. Mater., vol. 24, no. 12, pp. 1504-1534.
[5] X. Xia, et. al. Catalysis Communications, vol. 118, pp. 15-18.

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The thermal stability of synthetic dibasic CSH with substituted Cr^{3+} ions

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Recently, the research of inorganic material of binding materials filed is dedicated that can help to reduce atmosphere pollution. Therefore, the European Green Deal Commission goal for Europe's economy and society is to become climate-neutral by 2050 [1] and take advantages of industry 4.0 for developing environmentally friendly materials [2].

In this case, "green" cementitious materials with reduced carbon emissions (up to 30-70 %) can be produced by using hydrothermal treatment and require lower calcination temperature, also less pure starting materials [3]. Moreover, during hydrothermal synthesis another problem can be solved and water contaminated with heavy metals, purified. One of the heavy metals is chromium, which salt contamination is worldwide problem [4] and is dangerous to biological systems [5].

However, one of the greatest challenges is to understand the mechanism of metal ions intercalation into CSH (calcium silicate hydrates) structure and to investigate formed compounds properties. Thus, the aim of this work is to synthesize CSH substituted with Cr^{3+} ions via hydrothermal treatment and to investigate compounds thermal stability.

The synthesis of CSH with additive of Cr^{3+} samples were performed on the hydrothermal method. The dry primary mixture with the molar ratio CaO/SiO_2 (C/S) = 1.5 were homogenized and then the nitrate solution of Cr^{3+} ions (5 or 15 g/l) have been prepared by dissolving nitrate salt in the distilled water. The hydrothermal synthesis was carried out in autoclave (200 °C, 1 h). The thermal stability of synthesized samples was investigated in a furnace in 280, 500 and 1000 °C temperature.

It was investigated, that after hydrothermal treatment all Cr^{3+} ions were intercalated into crystalline or amorphous structure compounds. However, data obtained after calcination showed that by increasing process temperature until 1000 °C chromium containing compounds (calcium chromate, calcium chromium silicon oxide and/or calcium chromium oxide, uvarovite) crystallized. Moreover, Cr^{3+} ions additive had positive influence on surface area of formed compounds. All chemical-physical properties were characterized by XRD, DSC, SEM, EDX, BET methods.

[1] European climate Law, "Proposal for a REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL establishing the framework for achieving climate neutrality and amending Regulation (EU) 2018/1999" (2020)
[2] V. M. John, Quattrone M., Abrão P.C.R.A., Cardoso F.A. Cem. Concr. Res., 124 (2019) 105832
[3] E. Gartner, Sui T. Cem. Concr. Res., 114 (2018) 27-39
[4] M. Shahid. Chemosphere, 178 (2017) 513-533
[5] H. Peng, Guo J. Environ. Chem. Lett., 18 (2020) 2055-2068

Thermal stability of hydrothermally synthetic covellite in 0-650 °C temperature range

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Even though the investigation of copper sulfides synthesis approaches covers several decades, among the diverse developed methodology, researchers still face the issues of fabrication such as long synthesis duration, high energetic consumption, relatively low quantity of obtained product, the use of organic reagents in order to control the morphology of the products [1–4]. Hence, the synthesis covers high implementation costs. In order to adapt covellite synthesis for enlarged production and to avoid possible toxicity of organic reagents, the aim of this work was to synthesize covellite hydrothermally in the aqueous solution by using mixtures copper oxide and elemental sulfur and to investigate the changes of products properties caused by thermal conditioning.

Both reagents were mixed by molar S and CuO ratio at 1:1.15. Hydrothermal treatment has been carried out in stirred suspensions in 150 ml stainless steel autoclave by mixing 5 g of a sample with 50 ml of water and maintaining at 145–180 °C for 0.5–4 h. Thermal properties of products were determined by annealing the synthesized product in 100-650 °C temperature. The methods of XRD, STA, FTIR, UV-vis absorption analysis were used to characterize the used materials and the products.

[1] Auyoong YL, Yap PL, Huang X, Abd Hamid SB. Optimization of reaction parameters in hydrothermal synthesis: a strategy towards the formation of CuS hexagonal plates. Chem Cent J. 2013;7:67.

[2] Saranya M, Santhosh C, Ramachandran R, Kollu P, Saravanan P, Vinoba M, et al. Hydrothermal growth of CuS nanostructures and its photocatalytic properties. Powder Technol. 2014;252:25–32.

[3] Hong J, Kim B-S, Yang S, Jang A-R, Lee Y-W, Pak S, et al. Chalcogenide solution-mediated activation protocol for scalable and ultrafast synthesis of single-crystalline 1-D copper sulfide for supercapacitors. J Mater Chem A. Royal Society of Chemistry; 2019;7:2529–35.

[4] Mulla R, Jones DR, Dunnill CW. Economical and Facile Route to Produce Gram-Scale and Phase-Selective Copper Sulfides for Thermoelectric Applications. ACS Sustain Chem Eng. American Chemical Society; 2020;8:14234–42.

Parameter influence on kilchoanite synthesis and its application for CO_2 hardening concrete

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The measures used to reduce CO_2 emissions in the cement industry – clinker additives, alternative fuels, energy cost optimization, engineering solutions [1] are insufficient and new binding materials have to be found. One promising method is the production of low-base calcium silicate cements [2], as fewer carbonate raw materials are required and the synthesis temperature is lower. They harden in a CO_2 environment, thus binding these gases to stable carbonates. We have found [3] that α-C_2SH can be used instead of anhydrous calcium silicates for the production of CO_2 curing concrete. Consumption of even more carbonate rocks can be reduced by using kilchoanite instead of α-C_2SH, as the molar ratio of CaO/SiO_2 decreases from 2.0 to 1.5. The carbonation processes of this compound have not yet been studied.

Mixture of α-C_2SH and kilchoanite was hydrothermally synthesized in unstirring suspensions ($CaO/SiO_2 = 1.5$, w/s = 10.0) at 200 °C from lime ($CaO_{free} = 99.18$ %) and trepel ($SiO_2 = 77.03$ %). The optimal duration of the hydrothermal treatment – 8 h. For the carbonation curing, synthesis products were mixed with standard sand (1:3) and pressed (pressure 1.5 MPa) to form ø36x36 mm cylinders. Hardening of the samples was carried out in a CO_2 environment at 1.5 MPa and 25–65 °C for 4–72 hrs. Products were analysed by DSC, TG, XRD, FT-IR and SEM analysis.

It has been shown for the first time that a mixture of α-C_2SH and kilchoanite can be used instead of anhydrous calcium silicates to produce in CO_2 atmosphere hardening concrete. By increasing the curing duration at 25 °C, the compressive strength of the samples gradually increases and reaches 16.85 MPa in 24 h. Increasing the temperature to 45 °C has a positive effect on the mechanical properties of concrete, because after hardening for 24 h, the value of compressive strength was 20.23 MPa. Instrumental analysis methods revealed that amorphous SiO_2 predominates in the central part of the newly formed particles, and it is surrounded by calcite shells.

Products made of α-C_2SH and kilchoanite binder meet the requirements of Standard EN 206:2013+A1:2016 and can be used to produce C20/25 compressive strength class (medium strength) concrete. The results showed that α-C_2SH and kilchoanite are a suitable alternative binders that could be used for concrete production, thus reducing the amount of carbonate rocks and greenhouse gas emissions.

[1] E. Benhelal, et al., J. Clean. Prod. 51 (2013)
[2] Bao Lu, et. al., Construction and Building Materials, 417-423, (2018)
[3] R. Siauciunas, et al., Ceramics International, (2020) Volume 46, Issue 18, 29436-29442

Formation of ice within cement-based materials during the first 28 days of hydration

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The cement-based materials gain their strength through the hydration reaction. According to the European Standards [1], the nominal compressive strength of cementitious samples should be measured after 28 days since mixing. Nevertheless, on building sites there frequently is a strong tendency towards conducting the process of construction completion as quickly as possible, which is mainly caused by the economic aspects. Hence, sometimes there appears a need for conducting concrete works during winter conditions. Freezing is the one of the most severely affecting factors with regard to the stability of cementitious materials [2].

The main purpose of the presented research was to monitor the amount of ice formed within pore system of cement matrix during the first 28 days of hydration process. Water freezing in cement paste proceeds at depressed temperature, which can be calculated using Gibbs-Thomson equation [3]. The experimental analysis was performed using differential scanning calorimetry. Cement paste samples were frozen after 1, 2, 3, 7, 14, 21, and 28 days of maturing. The change of the in-pore ice content profile in temperature domain along with hydration was calculated based on determined thermograms. The two dominant mechanisms inducing water freezing can be recognized in cement paste: gradual ice penetration and ice nucleation. The change of microstructure along with hydration was additionally monitored using mercury porosimetry. The obtained results allowed to determine the threshold properties, which have to be met in order to provide the resistance of cementitious materials to the single freezing at early age.

[1] EN 196-1 Test Methods for Cement, CEN TC 51.

[2] T. C. Powers and T. L. Brownyard, "Studies of the Physical Properties of Hardened Portland Cement Paste," *Journal of American Concete Institute*, no. 43, 1947.

[3] M. R. Landry, "Thermoporometry by differential scanning calorimetry: experimental considerations and applications," *Thermochimica acta*, vol. 433, no. 1-2, pp. 27-50, 2005.

Monitoring the phase transitions in intercritically annealed multiphase 5Mn alloy using in situ high-temperature X-ray diffraction

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Intercritically annealed multiphase medium Mn steels have received much research attention due to their potential application as modern automotive sheets. The enhanced interest in these steels is related to the combination of excellent mechanical properties and formability which is attributed to transformation of metastable retained austenite into martensite during deformation [1]. Retained austenite can be stabilized to room temperature through partitioning of austenite stabilizing elements such as carbon and manganese during intercritical annealing. With sufficient chemical stabilization of austenite, it is possible to obtain the microstructure consisting of ferrite and austenite after cooling to room temperature [2, 3]. Mechanical properties of intercritically annealed steels are related to volume fraction and the stability of retained austenite which depends on the temperature and time of isothermal holding step [4].

The present study was performed to characterize the influence of intercritical temperature and holding time on the phase transitions in a multiphase 5Mn steel using in situ high-temperature X-ray diffraction. The steel was subjected to isothermal holding treatments at 650-700°C for different holding times, from 15 min to 5 hours. Diffraction data were collected to determine the changes of phase composition and lattice parameters during intercritical annealing. The obtained results showed that temperature and holding time directly affect the amount and thermal stability of retained austenite. The microstructure analysis was performed by means of scanning electron microscopy.

[1] B.G. Zhang, X.M. Zhang, H.T. Liu, Mater. Sci. Eng. A, 793 (2020) 139289.
[2] J.J. Mueller, X. Hu, X. Sun, Y. Ren, K. Choi, E. Barker, J.G. Speer, D.K. Matlock, E. De Moor, Mater. Des., 203 (2021) 109598.
[3] D. Han, Y. Xu, R. Liu, F. Peng, Y. Zou, W. Sun, Scr. Mater. 187 (2020) 274-279.
[4] X. Hu, J.J. Mueller, X. Sun, E. De Moor, J.G. Speer, D.K. Matlock, Y. Ren, Front. Mater. 8 (2021) 621784.

Thermal analysis of intermetallic phases formed in Co-Al and Ni-Al based superalloys doped with Y

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Yttrium has been regarded as a promising alloying element for superalloys [1]. Y improves many properties of materials such as resistance to creep or oxidation [1, 2]. Although papers concerning effect of Y on properties of Fe and Ni-based alloys are available, there is little work on effects of this element on microstructure and oxidation of cobalt-based superalloys, especially in the case of γ–γ' cobalt superalloys.

In this work, the effect of Y-doping on as-cast microstructure of the γ'-forming Co-Al-W alloys is investigated. The microstructural analysis and differential scanning calorimetry was performed for alloys in Co-Al-W-Y, Co-Ni-Al-Y, Co-W-Y, Co-Al-Y, and Ni-Al-Y systems. The alloys were prepared via vacuum induction melting (VIM) technique. The differential scanning calorimetry (DSC) was used in order to investigate thermal effects connected with melting and crystallization of Y-containing intermetallic phases. The microstructure was analyzed by means of scanning electron microscopy (SEM), energy dispersion spectrometry (EDS), and electron backscatter diffraction (EBSD).

The measurements in the temperature range of 40–1400 °C were performed using multi-HTC high-temperature calorimeter from Setaram. The measurements were performed under the Ar protection; the heating rate was 5 $°C\ min^{-1}$. In the case of SEM/EDS analysis, the scanning electron microscope (SEM, Hitachi S-3400 N) equipped with the energy dispersion spectrometer (EDS, Thermo Noran System Seven) was used. For qualitative analysis of interdendritic precipitates, the energy backscattered diffraction (EBSD, Inca HKL, INCA HKL Nordlys. II (Channel 5)) was performed.

Taking into account structure, chemical composition in micro areas, and thermal effects, intermetallic phases formed in Co-W-Y alloys were similar to those of crystallized in binary Co-Y. However, crystallization of Y-doped alloys based on Co-Al and Co-(Ni)-Al-W systems results in formation of stable ternary Y-Co-Al and quaternary Y-Co-Ni-Al precipitates. Al-containing Y-Co precipitates exhibit lower melting temperature compared to those of phases in Co-Y and Co-W-Y alloys.

This work was supported by National Science Centre (Project 2018/29/N/ST8/02062).

[1] X.L. Li et al., Mater. Charact., 95 (2014) 171-179
[2] S. Zhenxue et al., J. Rare Earths 31 (2013) 795

Synthesis and thermal study of hybrid organic-inorganic ceramics based on layered perovskite-like niobate $KSr_2Nb_3O_{10}$

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The crystal structure of layered perovskite-like oxides can be represented as layers with a perovskite structure, separated by an interlayer space having a different structure. The structural features of such oxides open up nontrivial ways of modifying their structure and, as a consequence, changing their properties as well as ferroelectric properties, their ionic conductivity, and catalytic and photocatalytic activity. In the context of varying properties of particular interest are reactions of grafting and intercalation of organic molecules into the interlayer space of the oxide. However, the use of materials based on such compounds can be limited by their thermal stability.

In the present work, we report the results on the synthesis and thermal stability of organic-inorganic hybrids with n-alkyl amines and n-alkyl alcohols based on the protonated forms of layered perovskite-like strontium niobate $HSr_2Nb_3O_{10}\cdot yH_2O$ which belongs to the Dion-Jacobson phases.

The protonated form of oxide $HSr_2Nb_3O_{10}\cdot yH_2O$ (obtained by ion exchange of interlayer cations of the initial alkaline form $KSr_2Nb_3O_{10}$) was used as a precursor for organic modification. The intercalation and grafting reactions were carried out under standard laboratory or hydrothermal reaction conditions depending on the alkyl chain length. In some cases, graft derivatives were obtained at transesterification conditions using as the precursor compounds with a shorter carbon chain. The phase composition of the obtained products, as well as the change in the interlayer distance due to the introduction of organic molecules, was confirmed by the data of XRD analysis, the surface morphology of the modified oxides was observed using SEM, and the presence of an organic modifier in the sample was confirmed by the data of NMR and IR spectroscopy.

The thermal stability and quantitative composition (in respect to water and organic molecules) have been analyzed using TG, STA-MS, and thermal X-ray diffraction analysis data. It was found that the thermal stability of intercalates is similar to analogs of calcium niobate [1]. The major amount of intercalated amines are released at temperatures slightly above room temperature. The graft derivatives are more stable than intercalated samples and show only insignificant mass loss up to 280 °C. The increase in mass in an oxidizing atmosphere above 400 °C and subsequent weight loss above 600 °C are characteristic of each kind of hybrids and especially will be discussed.

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[1] V. V. Voytovich, S. A. Kurnosenko, O. I. Silyukov, I. A. Rodionov, I. A. Minich and I. A. Zvereva., Front. Chem., 8 (2020) Art. 300.

A critical assessment of the fire properties of different wood species and bark from small and bench scale fire experiments

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Abstract

Wood and bark are ubiquitous and obviously the most abundant raw material for various applications including construction. While wood is relatively flammable, the bark is known to have high fire resistance and insulation capabilities due to its high lignin content. This study therefore assesses the flammability of different wood species with their bark to ascertain the unique insulation properties. Material characterisation methods such as microscale combustion calorimetry (MCC) method A and B tests, oxygen bomb calorimetry and thermogravity (TG) analysis tests were employed to acquire the fire properties of beech, fir, oak, pine and spruce with bark and without bark. From the TG test, oak with bark recorded a significantly lower mass loss rate and had the highest char residue. The MCC experiments showed that beech, oak and spruce without bark had higher peak heat release rates and heat release capacities compared to the samples with bark. However, the results for fir and pine with bark showed higher heat release properties. In addition, the calorific and heating values were higher at 0% moisture content compared to 8%.

Keywords: Wood, Bark, Microscale Combustion Calorimetry, Thermogravity Analysis, Oxygen Bomb Calorimetry.

Thermal durability of γ-Fe_2O_3 nanoparticles produced by laser pyrolysis

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Iron oxide nanoparticles (NPs) are used in a wide variety of applications, ranging from energy storage to biomedicine, due to their unique properties, especially their capacity to be controlled by means of an external magnetic field. However, one crucial aspect when it comes to their final structural or magnetic properties is the synthesis method, with different results coming from chemical, mechano-chemical, hydrothermal, and sol-gel methods. Laser pyrolysis presents an alternative option, where the synthesis is conducted on the intersection between a focused continuous wave of high-power CO_2 laser radiation and a streaming flow consisting of reactant, sensitizer, and inert sheath gases. The main advantages of using laser pyrolysis for iron oxide NP synthesis include the low degree of contamination, as well as the control over size distribution and morphology – the latter extending to the selection between different iron oxide allotropes, from α-Fe_2O_3 hematite to γ-Fe_2O_3 maghemite and Fe_3O_4 magnetite. Herein we report on the laser pyrolytic synthesis of γ-Fe_2O_3 NPs with controllable size distribution, using iron pentacarbonyl as the iron precursor and ethylene as the energy transfer agent. Synthesized NPs are then investigated as to their thermal durability using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), assisted by X-ray diffractometry (XRD) for detecting thermally induced alterations of the crystal lattice. The aim is to gauge possible applications that exceed the non-demanding temperature range of biomedicine, as well as the feasibility of thermal decontamination methods for biomedical γ-Fe_2O_3 NPs.

Poster session 1

Dynamic Mechanical Analysis for Polymer Characterization: from Thin Films to Stiff Composites

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DMA is by far one of the most sensitive techniques to measure the glass transition (Tg). For example in highly crosslinked thermosets or composites with high amount of fibres it can be difficult to measure Tg with a DSC, while DMA easily allows this. Moreover DMA is one of the few techniques sensitive to measure secondary relaxations (b, g, etc). These are very important as they affect impact resistance and other end-use properties.

In this work we present practical examples of different DMA applications (Nylon 6, ABS) under different conditions of frequency, temperature and relative humidity.

Characterization of Bitumen by MDSC® and Hi-ResTM TGA

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Bitumen is used in numerous building applications, e.g. paving roads, waterproof sealing of roofs.

It is important to characterize the glass transition Tg of the bitumen, as the mechanical properties of the material undergo a big change at this temperature. In general DSC is very suitable to detect even weak glass transitions, however in case that other thermal events occur in the same temperature range Modulated DSC [1] will be necessary for detection of the Tg. TZero Technology [2] proves to be particularly effective for that purpose.

A constant chemical composition of the bitumen might be required for the application. TGA allows quick fingerprinting/determination of the composition of materials if the different constituents decompose in a different temperature range. In case there is overlap high-resolution TGA techniques might be necessary for accurate fingerprinting of the material.

[1] M. Reading, Trends Polym. Sci., 1, pp. 248-253 (1993).
[2] R.L. Danley, Thermochimica Acta, 395, pp. 201-208 (2003).

Thermoanalytical study of Norfloxacin and Pyrazinoic Acid cocrystal

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Pharmaceutical cocrystals are multicomponent crystalline forms formed from the intermolecular interaction of a drug and one or more coformers [1]. The interaction does not interfere in the therapeutic activity of the drug but may positively affect the physicochemical properties, i.e., solubility and dissolution rate [1,2]. Norfloxacin (NOR) is a broad-spectrum antibiotic classified as class IV of the Biopharmaceutical Classification System (BCS) [3]. Therefore, a cocrystal of NOR was synthesized with Pyrazinoic acid (PZCA), a generally recognized as safe (GRAS) coformer. The NOR-PZCA cocrystal was synthesized using liquid assisted grinding (LAG). The formation of the NOR-PZCA cocrystal can be substantiated by: (1). an intermediate thermal stability (235.2 °C) and a higher melting point (254.8 °C) (*Figure 1-a,b*); new diffractions peaks at 5.88°; 13.55°; 23.54°; 27.04°, and 28.44° (*Figure 1-c*); (3) the ν C-N band of PZCA shifted from 1311 cm^{-1} to lower frequencies (1363 cm^{-1}), and the reduction in intensity of the NOR band at 1250 cm^{-1}, assigned to the aliphatic amine stretching (ν C-N). Altogether the analyses substantiated the formation of the cocrystal through the changes in the thermal properties, diffraction pattern, and vibrational spectra compared to the pure components.

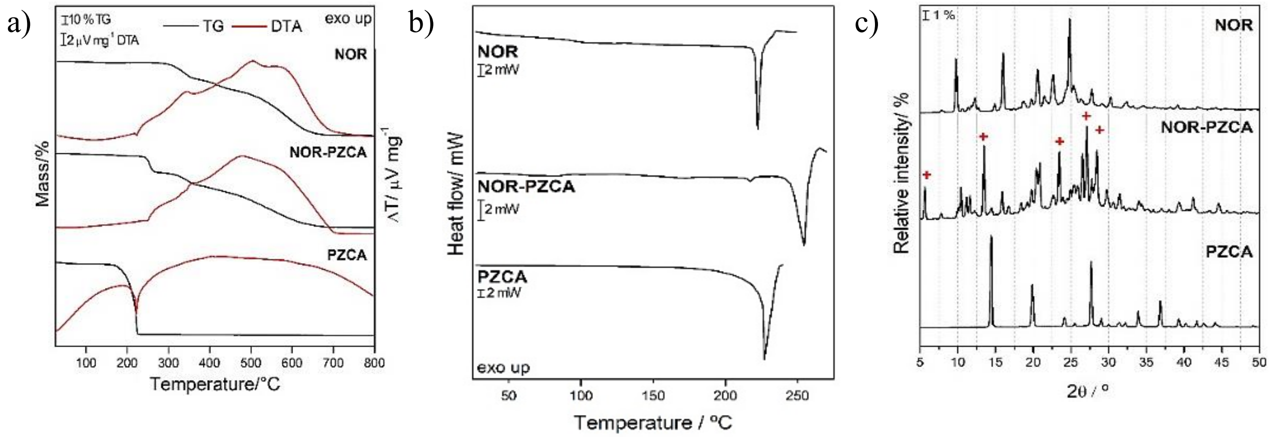

Figure 1 - (a) TG-DTA, (b) DSC, (c) DRXP of NOR, PZCA, and NOR-PZCA.

[1] P. Jayram, P. Sudheer, International Journal of Pharmaceutics, (2020) 246–252
[2] B. Bhattacharya, A. Mondal, S.R. Soni, et al., Cryst. Eng. Comm., (2018) 6420–6429
[3] S. Basavoju, D. Bostrom, S.P. Velaga, Crystal Growth & Design, (2006) 2699-2708

Thermal decomposition of Cd ion exchanged clinoptilolite

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The spectrum of applications of clinoptilolite and zeolitic porous minerals covers several branches of modern industry namely ecology, water purification etc. The Cd clinoptilolite has been obtained by ion exchange of initial purified Bulgarian natural clinoptilolite with cadmium salts. The ion exchange was conducted at room temperature and 90 ^{o}C with 0.5 M cadmium salts for 24-96 hours. The conservation of the clinoptilolite structure during the exchange was monitored by X-ray powder diffraction while the subsequent stability was investigated by thermal methods. A comparison of the dehydration of the exchanged and natural clinoptilolite forms was investigated. After the water release the next effect is the combination of the Cd release and collapse of the clinoptilolite framework. The loss of longue range order e.g. crystal structure, results in the availability of the originally trapped in the clinoptilolite framework Cd ions.

***Key words*:** Clinoptilolite, ion exchange, X-ray, thermal decomposition, DSC, DTA-TG

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Thermal characteristics of clinoptilolite from Bulgarian deposits

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The Bulgarian deposits of the zeolitized clinoptilolite tuffs are related to the products of the Plinian activity (ignimbrites and fall-out tuffs) namely to volcanic activity in the Eastern Rhodopes. Nowadays most of the "glassy" clasts of the pyroclastic rocks are converted into clinoptilolite tuffs with slightly variable chemical composition. The differences in chemistry are associated with manmade system activities and/or alternatively are due to the impurities associated with the clinoptilolite (e.g. opal, cristobalite, etc.). The average clinoptilolite content (wt%) in the different samples from the different deposits varies from 50% (Svatba) to 90% (selected areas of Beli plast). The quantity of the impurities has been determined by X-ray analyses in combination with EDS or XRF analyses. Granting that the main clinoptilolite characteristic is the ion exchange – the thermal properties are also interesting in vue of the potential applications. Those are directly linked to the water content, the chemistry and the principle ions present in the clinoptilolite extra-framework. Here we report and compare the DTA-TG characteristics of several samples from different Bulgarian deposits. The hydration/dehydration stages and the decomposition are studied in detail using a combination of diffraction and DTA/DSC-TG techniques.

Key words**:** Clinoptilolite, X-ray, thermal comportment, DSC, DTA-TG

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Thermal properties of nanocomposite of liquid crystalline SB(3R)-11 molecules and carbon nanotubes

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In the present work, we demonstrate the thermal properties and the phase transitions of a nanocompostite, prepared from SB(3R)-11 and single wall carbon nanotubes, SWCNT. SWCNT were purchased from Meijo company, Japan. Thermotropic liquid crystalline molecule ((*R,E*)-4-(4-((3,7-dimethyloctyl) oxy) styryl) phenyl 4-(undecyloxy) benzoate), SB(3R)-11 was synthesized in Centre for nano and soft matter sciences [1]:

The nanocomposite was prepared from solution of SB(3R)-11 in 1-Methyl-2-pyrrolidinone, NMP (Alfa Aesar, CAS: 872-50-4) and suspension of SWCNT in the same solvent. The mixture of both was stirred for about 4 hours and then the solvent was left to evaporate at 60°C. The final nanocomposite consisted of 10 weight percent of the nanotubes.

The thermal behaviour was investigated by means of DSC. On cooling, SB(3R)-11 displays sequence of transitions: I (isothropic melt) - N (nematic) – Sm (smectic) - Cr (crystalline). On heating, the sequence is Cr – Sm – N – I but there are some differences in the positions and enthalpies of the DSC peaks. The DCS thermograms of the nanocomposites differ drastically – they do not represent well-defined separate DSC peaks but rather the heat flow, HF curve has a considerable slope. There is an exothermal peak, appearing at about 12°C on cooling, which not represented in the neat SB(3R)-11.

In order to understand the results, investigations with POM were performed. SB(3R)-11 and the nanocomposite were subjected to quenching and slow cooling from isotropic melt. The results clearly prove that there is still some ordered state in the nanocomposite but it differs from that observed in the neat SB(3R)-11. Hence, the slope of the nanocomposite DSC should be explained by slow continuous change in the structure, leading the some ordered (either liquid crystalline or crystalline) final state.

[1] B. N. Veerabhadraswamy, D. S. Shankar Rao, S. Krishna Prasad, C. V. Yelamaggad, New J. Chem., 39 (2015) 2011

Investigation on the variation of the surface and structure properties of polished GaN and AlN single crystals after femtosecond laser irradiation

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GaN and AlN substrates are considered as a hard-to-process materials due to their extreme hardness and strong stability against chemicals. Femtosecond laser sources can be used to treat GaN and AlN surfaces under ambient conditions, pressure and temperature with and without the destruction of their crystal structures and damaging the surface properties. However, the combination of exposure time and power must be adjusted for the desired treatment. In the present study GaN and AlN polished single crystal surfaces were exposed to femtosecond laser irradiation under ambient conditions. The laser irradiation was carried out by a laser pulses having 350fs time duration on 1.03nm wavelength and pulse power up to 2.1 μW. Repetition rate of the laser operation was 200kHz. The GaN and AlN irradiated substrates were characterized by X-ray single crystal, X-ray micro-diffraction and SEM in order to assess the presence of structural and surface effects: phase changes or conversion, oxidation, passivation etc. In parallel DSC/DTA thermal investigations were carried out to assess the maximal temperature that can be attained under the irradiation. The single crystal micro-focus and powder micro-diffraction studies were concentrated on different points (50 x 50 μm) of the GaN or AlN original and irradiated surfaces. With increasing irradiations exposure times and power, the surface of the GaN or AlN samples started to erode almost immediately. Nevertheless, the surface and bulk crystal structure was maintained up to certain time and powder. In general, increasing the irradiations exposure times and power e.g. depth, led to the formation of pits and appearance of particles along the step edges, resulting in drastic roughening of the surface. The investigation of repeated irradiation treatment of the same surface area of the samples is under investigation.

***Key words*:** GaN, AlN, femtosecond, X-ray, thermal stability, DSC

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Effects of natural zeolite additive on the thermal and crystal-chemical properties of white cement mortars

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The decorative cement mortars and concretes are an artificial imitation of the natural rocks. Their main advantage is better workability, but durability and stability are the key use objectives. To achieve good aesthetic surface and multilateral application of decorative cement (as decorative stamp concrete, pots, balustrade, ornamental stones, restoration of architectural monuments, decoration of facades, fences, terraces, etc.), the use of white Portland cement mixed with white or color fine and coarse aggregates are necessary. The mentioned above requirements, together with the disparate surface properties of used aggregates, and the necessity of a greater quantity of water during cement composites preparation, suggest the differences in the newly-formed structures compared to the conventional ones.

Clinoptilolite is a zeolite mineral with excellent pozzolanic activity. Clinoptilolite, a zeolite mineral, has excellent pozzolanic activity, defined by its ability to react with calcium hydroxide and create a cementitious phase (insoluble calcium silicates). Its incorporation to the cement mortars behaves economic, engineering, and durable effects, typical for natural pozzolans. Unlike light in color pozzolans (as silica fume, metakaolin, etc.), clinoptilolite is soft and ductile. Moreover, it modifies the rheological behavior of fresh mixes and takes an active part during cement hydration. These specific features predetermine the possibility of incorporation of clinoptilolite in white cement mortars and concrete to produce architectural elements and details. Free of any additional pigments, the hardened white in color mortars behave an ancient view due to the characteristic color of clinoptilolite.

This study has investigated the effect of white Portland cement replacement by clinoptilolite up to 10 wt% in different cement composites. The density of composites structures at 28 and 120 days of water curing was evaluate by measurements of physical-mechanical properties - density, compressive strength, and porosity. Crystal structures and sample morphology have been investigating by X-ray powder diffraction analysis, FTIR spectroscopy, scanning electron microscopy, and Thermal analysis (TG-DTG-DSC). The applied complex of analytical techniques allows identifying the newly-formed solid phases in the hydrated cement composites, defining their structural characteristics, and analyzing the properties of cement.

It has been determining: the sulfate/carbonate-containing solid phases; the dehydration, decarbonation, and dehydroxylation steps; sample reaction mechanism of thermal decomposition, which are the parameters revealing the influence of clinoptilolite additive and water-to-cement ratio on the physical-chemical properties of cement composites.

***Key words*:** White Portland cement, decorative mortar, cement hydration, natural zeolite, thermal decomposition, X-ray, SEM

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Stability of waste oil in water emulsions in dependence on temperature

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Environmental protection issues and rational use of natural resources are becoming the focus of attention nowadays. It has been found that the construction of road infrastructure is one of the most polluting activities. [1]

Road construction is accompanied by a number of processes that directly or indirectly affect the environment. Dust, noise and vibrations are the three most damaging effects of road construction and management. [2,3] However, good condition of pavement could have a significant influence on noise and vibration reduction, fuel consumption, reduction of CO_2 emissions, and even on road accidents. Optimizing industrial processes, creating a quality infrastructure and making it as sustainable as possible is a step towards the environment protection during road construction. [1]

Circular economy is an approach to sustainable development which creates value and prosperity through extending product lifespan and relocating waste from the end of the supply chain to the beginning. In a circular economy, materials for new products come from old products by reusing, re-manufacturing or recycling. It is said that the circular economy could save European businesses up to $630 billion a year. [4]

Waste oil from oil refinery plants mixed with water and a biopolymer creates a water emulsion suitable for using in construction of road infrastructure. The aim of this work is to determine the thermal stability of waste oil/water emulsion. Emulsion stability was investigated by conducting rheology measurements at 30 °C and 60 °C, microscopy analysis of droplet size distribution and subjecting emulsion to laboratory centrifuge at elevated temperatures.

[1] Terrones-saeta, J. M., Suárez-macías, J., Iglesias-godino, F. J. & Corpas-iglesias, F. A. Development of porous asphalt with bitumen emulsion, electric arc furnace slag and cellulose fibers for medium traffic roads. *Minerals* **10**, 1–21 (2020).
[2] Barikayeva, N. et al, About Forecasting Air Pollution in the Construction of Highways, IOP Conf. Ser.: *Mater. Sci. Eng.* **463**, 1-3 (2018)
[3] https://www.roadex.org/e-learning/lessons/environmental-considerations-for-low-volume-roads/environmental-issues-related-to-road-management/ (30.5.2021.)
[4] https://www.nationalgeographic.com/magazine/article/how-a-circular-economy-could-save-the-world-feature (30.5.2021.)

Thermal characterization of waste oil in water emulsions

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The main aim of circular economy is to eliminate waste by continual use of resources. Circular systems employ reuse, sharing, repair, refurbishment, remanufacturing and recycling to create a closed-loop system, minimizing the use of resource inputs and the creation of waste and pollution, including the carbon emissions. Waste materials and energy become an integral part or resource for another industrial process or natural cycles such as compost production. Thus, petroleum waste can be used for the production of insulating materials or water in oil emulsions with specific use in road construction. In this study the general thermal and calorimetric behavior of water in oil emulsions of various compositions were analyzed by the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Further, the same techniques were used for the precise determination of water content. thermal and oxidative stability.

Glass transition temperature of cellulose acetate mixture and poly(dimethylaminoethyl methacrylate-co-methyl methacrylate)

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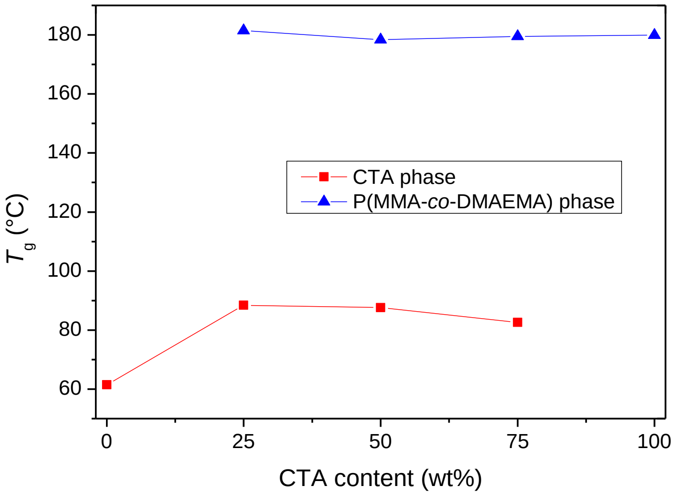
Cellulose acetate (CA), a bio-based polymer, is widely used to make membranes for water treatment and gas separation. The CA has good hydrophilicity, good separation properties in desalination processes, high water fluxes. However, CA membranes are susceptible to biofouling and microbial attack. Modification of CA membranes with amphiphilic polymers such as poly (dimethylaminoethyl (PDMAEMA) copolymer can affect the antifouling properties. The miscibility of the components in the polymer blend can affect the morphology of the prepared membrane and hence the membrane properties such as pure water flux and separation. Herein, polymer blends of cellulose acetate (acetylation degree 39.8% and 43.4%) and P(methyl- methacrylate-co-dimethylaminoethyl-methacrylate) were prepared by solution blending in a wide range of compositions (25-75 wt%). The three- component solvent acetone/dioxane/water was used to prepare the samples of cellulose diacetate (CDA) (acetylation degree 39.8 %) based polymer blends, while acetone/dioxane/methanol was used to prepare the samples of cellulose triacetate (CTA) (acetylation degree 43.4 %). These solvents are commonly used for the preparation of cellulose acetate membranes. The miscibility of CA and P(MMA-*co*-DMAEMA) in polymer blends was investigated by differential scanning calorimetry. Miscible polymer blends exhibit glass transition temperature, while partially miscible and immiscible blends exhibit glass transitions of each component. Contact angle measurements were also performed with water and diiodomethane to calculate the free energy of CA and P(MMA-*co*-DMAEMA). The wetting coefficient (S), parameter that indicates wetting of one component with the other, was calculated based on the surface free energy of CA and P(MMA-*co*-DMAEMA). Both blends, CDA and CTA based, exhibited glass transition (T_g) for both components, indicating the presence of two phases in the polymer film. The T_g of P(MMA-co-DMAEMA) increased towards higher temperatures (21-27 °C), while the T_g of cellulose acetate changed slightly (decrease up to 2 °C). Such increase in the T_g of P(MMA-*co*-DMAEMA) indicates partial mixing of the components in the P(MMA-*co*-DMAEMA)-rich phase.



Influence of sialylation on the thermodynamic parameters for the binding of ferric ion to human serum transferrin

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Human transferrin is the main ferric transport glycoprotein in the blood plasma. Its polypeptide chain is folded into two structurally similar but functionally different lobes, referred to as N- and C-lobe. Each lobe can be further divided into two domains enclosing a deep hydrophilic cleft bearing an iron binding site. Transferrin structure consists of 679 amino acids with two *N*-glycan structures covalently attached to residues ANS 413 and ASN 611 on the C-lobe. The *N*-glycan structures terminate with sialic acid. This study investigated the influence of transferrin sialylation on the thermodynamic parameters for the binding of ferric ion to human serum transferrin using isothermal titration calorimetry (ITC).

Isothermal titrations were performed using two different types of human serum transferrin: native apotransferrin (Tf+s) and desialylated apotransferrin (Tf-s). The desialylated apotransferrin was prepared by incubating native apotransferrin with immobilized neuraminidase enzyme in the buffered solution for 48 h and later washed using working buffer (0.1 M HEPES, 25 mM $NaHCO_3$, pH 7.4) [1]. The *N*-glycan analysis by UPLC-MS confirmed the difference in the sialylation patterns of Tf+s and Tf-s [2]. Ferric ion was introduced in the titration solution as nitrilotriacetate complex with molar ratio of Fe:NTA = 1:2. The concentrations of the working solutions (apotransferrin and FeNTA) were determined spectrophotometrically before measurement.

Resulting ITC curves displayed two inflection points typical for a model of two binding sites. The first injections showed the binding of ferric ion to the C-site which saturates first, whereas the N-site saturates after the C-site [3]. Data analysis was based on the model of two sets of independent sites and best-fit parameters were calculated using Marquardt algorithm [4]. The calculated parameters suggested that the degree of sialylation affects the thermodynamics of binding of ferric ion to human serum transferrin, particularly the C-site.

[1] T. Friganović, V. Borko, T. Šeba, R. Kerep, I. Biruš, T. Weitner, Zenodo, (2020) https://doi.org/10.5281/zenodo.4002005
[2] T. Štambuk, A. Cvetko, T. Weitner, Zenodo, (2020) https://doi.org/10.5281/zenodo.4006018
[3] L.-N- Lin, A. B. Mason, R.C. Woodworth, J. F. Brandts, Biochemistry, 32 (1993) 9398-9406
[4] L.-N- Lin, A. B. Mason, R.C. Woodworth, J. F. Brandts, Biochemistry, 30 (1991) 11660-11669

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Thermoanalytical approach to physicochemical compatibility evaluation of 5-aminosalicylates and folic acid

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Differential scanning calorimetry (DSC) is the first technique of choice when it comes to compatibility evaluation between components of physical blends in the development of pharmaceuticals. Its main advantage is fast acquisition of information regarding the potential interactions of components in blends which are manifested through changes in characteristic thermograms of blends compared to those of pure compounds. Physicochemical compatibility of folic acid (FA) and two 5-aminosalicylates (5-ASA), balsalazide (BSZ) and olsalazine (OSZ), used in the therapy of inflammatory bowel diseases was investigated using DSC and isothermal stress testing (IST), as a prerequisite to the development of 5-ASA/FA fixed-dose combinations.

Thermograms of pure compounds as well as their blends in various ratios (5-ASA : FA 10:1, 5:1, 2:1 and 1:1, *m*/*m*) were obtained on a Diamond DSC (Perkin Elmer Inc., Waltham, MA, USA) with a heating rate of 10 °C/min, under the atmosphere of pure nitrogen with the gas flow of 25 mL/min. IST was conducted on pure drug substances and their blends, in a ratio of 10:1, 5:1, 2:1 and 1:1 in favour of both 5-ASAs and FA, by keeping the samples at 50 °C for four weeks. IST was followed by chromatographic analysis of stressed samples using high-performance liquid chromatography.

OSZ and FA showed peaks that correspond to their melting, whilst BSZ showed no characteristic melting peak, however, one peak that occurred corresponds to its dehydration since it comes in the form of a dihydrate, which can provide relevant information regarding its physicochemical properties. DSC results implied compatibility between FA and two 5-ASAs (no notable shifts in peak temperatures, < 5°C). Results obtained by chromatographic analysis of samples subjected to IST showed that recoveries of both 5-ASAs and FA in all stressed samples did not markedly differ (97.9 – 103.0%, with the relative standard deviation not exceeding 2.4%).

Results obtained by DSC and IST imply that there was no notable change in the physical or chemical nature of 5-ASAs and FA when combined in the same blend. Although DSC measurements can sometimes be misleading due to the exposure of samples to extreme temperatures, it is always recommended to support those results by using other techniques, such as IST.

The effect of waste coffee ground on the porosity and structure of slip cast alumina ceramics

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Porous ceramics have been used in various industrial applications such as high temperature filtration, orthopaedic implants, thermal insulation, catalyst supports, lightweight structural components, etc. [1]. Porous ceramics can be obtained by the following methods: (i) replica template [1], (ii) sacrificial fugitives [2], (iii) direct foaming [3] and (iv) partial sintering [4]. In this work, porous alumina ceramics was obtained by the sacrificial fugitive method. This method is based on mixing appropriate amounts of sacrificial fugitives as pore-forming agents with raw ceramic powder and evaporating or burning them out before or during sintering to create pores.

This work presents the preparation of porous alumina ceramics by the addition of waste coffee grounds as an eco-friendly pore-forming agent. Green bodies of alumina ceramics were prepared by slip casting of 60 wt. % alumina suspensions containing different amounts of waste coffee grounds (0 wt. %, 1 wt. %, 5 wt., 10 wt. and 15 wt. %). The influence of waste coffee grounds amount in green alumina bodies on density, porosity and microstructure of sintered ceramics was evaluated. The viscosity of all suspensions was determined using a rotational viscometer. The sintering regime was determined according to the simultaneous differential thermal and thermogravimetric (DTA/TGA) analysis where thermal decomposition of waste coffee grounds was observed. The density and porosity of the obtained sintered samples were investigated and calculated. Microstructure and pore morphology were characterized by Scanning Electron Microscopy (SEM). It was found that the density of sintered ceramics decreased from 3.743 to 2.172 g/cm^3 as the amount of waste coffee grounds increased from 0 wt. % to 15 wt. %. Therewith, the porosity increased from 6.12 % to 45.52 % as the amount of waste coffee grounds increased from 0 wt. % to 15 wt. %.

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[1] Z. Švagelj, V. Mandić, L. Ćurković, M. Biošić, I. Žmak, M. Gaborardi, Materials, 13 (2020) 1
[2] R. M Mesquita, Bressiani, Adv. Sci. Technol. 63 (2010) 170
[3] Z. Du, D. Yao, Y. Xia, K. Zuo, J. Yin, H. Liang, Y.-P Zeng, Ceram. Int. 45 (2019) 2124
[4] F. Akhtar, P. O. Vasiliev, L. Bergstrom, J. Am. Ceram. Soc. 92 (2009) 338

Optimization of corrosion resistance of high purity alumina ceramics in nitric acid

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Developing ceramic materials with resistance to various chemicals as well as certain mechanical characteristics is of considerable importance for enabling a wider application of these ceramics [1]. Corrosion resistance depends on the purity and microstructure of the material along with the kind of the aggressive medium and temperature [2-4].

The corrosion behaviour of cold isostatically pressed high purity alumina ceramics (sintered in conventional - electrical kiln) in aqueous HNO_3 solutions in a concentration range of 0.5 mol dm^{-3}, 1.25 mol dm^{-3} and 2 mol dm^{-3} with different exposure times – up to 10 days – has been studied. The influence of temperature (25, 40 and 55 °C) on corrosion was also monitored. Corrosion resistance evaluation of Al_2O_3 ceramics was based on measurements of the mass concentrations of eluted Al^{3+}, Ca^{2+}, Fe^{3+}, Mg^{2+}, Na^{+} and Si^{4+} ions by inductively coupled plasma atomic emission spectrometry (ICP-AES) and density by Archimedes method.

Response surface methodology [5] was used for optimization of parameters within experimental "sample-corrosive media" area. Exposure to corrosive media was conducted according to the Box-Behnken design. After regression functions were defined, conditions to achieve maximal corrosion resistance of sintered ceramics were determined by optimization within experimental area.

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[1] L. Ćurković, M. Fudurić Jelača, S. Kurajica, Corros. Sci., 50 (2008) 872
[2] B. Wei, D. Wang, Y. Wang, H. Zhang, S. Peng, C. Xu, et al. RSC Adv., 8 (2018) 18163
[3] A. Nickol, A-K. Wolfrum, W. Kunz, A. Michaelis, M. Herrmann, Ceram. Int., 43 (2017) 15519
[4] S. Kurajica, L. Ćurković, E. Tkalčec, V. Mandić, J. Am. Ceram. Soc., 96 (2013) 92
[5] M. Mäkelä, Energy Convers. Manag, 151 (2017) 630

Heat capacity of the $Cu_{55}Hf_{45-x}Ti_x$ metallic glasses

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We were trying to connect their glass forming ability with feature called boson peak (BP) found in neutron scattering, Raman spectroscopy and heat capacity [1,2] and is close in energy to Debye energy of acoustic branch. BP is found to be characteristic feature of glasses in general, but can be found in some crystalline materials due to e.g. van Hove singularities in the acoustic phonon branch. The exact origin of such excess of vibrational modes is still not clear, so we were attempting to find out how we can control its eigenenergy and strength by varying the composition and studying as-cast and annealed samples of the ternary metallic glasses. Our results show that glass forming ability and BP are in no correlation, while energy of Debye and BP modes stay linearly connected, even after annealing which increases both. This strongly suggests that BP here is van Hove-like feature, with acoustic branch sticking to the excess modes of BP even after reducing disorder (by annealing). This goes in correlation with some crystals even though long-range (short wave vector) structure correlations are absent in glasses.

[1] G. D'Angelo, G. Carini, C. Crupi, M. Koza, G. Tripodo, and C. Vasi, Physical Review B - Condensed Matter and Materials Physics 79, 014206 (2009).
[2] A. P. Sokolov, A. Kisliuk, D. Quitmann, and E. Duval, Physical Review B 48, 7692 (1993)
[3] W. Weselowski, A. Kartuj, F. Laam, J. Therm. Anal. Calorim., 81 (2008) 1237

Low temperature properties of propyl, butyl and octyl based biodiesels and corresponding biodiesel-diesel blends

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Biodiesel, as a renewable source of energy, can be obtained through the transesterification reaction from natural feedstock, such as vegetable oils or animal fats, that react with an alcohol, most commonly lower alcohols like methanol or ethanol. Besides the main product that is biodiesel, also known as fatty acid alkyl esters, the transesterification reaction yields glycerol as a by-product [1]. In comparison to biodiesel, conventional diesel has different chemical structure, consisting of paraffinic, naphthenic and aromatic hydrocarbons. Therefore, when combined together, there is a change in certain fuel properties, including viscosity, heating value, density or cetane number. [2] In this study, different biodiesel-diesel blends were prepared, with the use of purified biodiesels that were synthesised from alcohols propanol, butanol and octanol. The temperature of crystallization, as well as the enthalpy of crystallization, were determined using DSC, while the cold filter plugging point for selected samples was determined by standardized test according to the standard HRN EN 116. In all cases, samples of biodiesel showed higher crystallization temperature and cold filter plugging point than the ones of mineral diesel and their blends. Cold filter plugging point of fatty acid butyl esters is lower than the one of fatty acid propyl esters. Furthermore, since the obtained results of the crystallization temperature and cold filter plugging point for blends and diesel are within the repeatability of these methods, it can be stated that the addition of biodiesel up to 10 vol% doesn't affect these low temperature properties.

[1] Y. Zhang, M. A. Dube, D. D. McLean, M. Kates, Biodiesel production from waste cooking oil: 1. Process design and technological assessment. Bioresour Technol 89 (2003) 1-16.
[2] M. Gülüm, A. Bilgin, Measurements and empirical correlations in predicting biodiesel-diesel blends' viscosity and density, Fuel 199 (2017) 567-577.

Effect of magnesium hydroxide addition on the mechanism of thermal degradation of poly(ethylene oxide)

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Poly(ethylene oxide) (PEO) is a semi-crystalline, biodegradable and water-soluble polymer of considerable industrial significance, which finds applications in many different branches of industry [1].

On the other hand, magnesium hydroxide ($Mg(OH)_2$) is a very important inorganic compound and it can be used as halogen-free flame-retardant for polymers. Simultaneously in polymer materials it acts as reinforcing agent, flame retardant, as well as smoke suppressant additive with low or zero emissions of toxic or hazardous substances [2]. Different methods for obtaining magnesium hydroxide are well known [3-4] but for this work, it has been synthesized via chemical precipitation method from sea bittern residual after production of sea salt from sea water. In order to obtain high purity magnesium hydroxide, clear limewater (γ = 1.54 gL^{-1}) as a precipitation agent was added in the sea bittern in a stoichiometric amount. The chemical reaction between magnesium ions from sea bittern and clear limewater produces magnesium hydroxide particles of fibre-like morphology (diameter ~ 10-20 nm; length ~ up to 400 nm) agglomerated into larger structures.

Thermal degradation and kinetic analysis of the thermal degradation of PEO have already been in focus of many studies and widely reported in the literature [5]. Likewise, the thermokinetic study of magnesium hydroxide obtained from seawater has also been performed [6]. However, no information about the kinetic analysis of the non-isothermal thermogravimetric degradation of PEO/$Mg(OH)_2$ composites couldn't be found in the literature.

Hence, the main goal of this work is to investigate the effect of $Mg(OH)_2$ addition on the mechanism of thermal degradation of PEO. The PEO/$Mg(OH)_2$ composites were prepared via hot melt extrusion. Non-isothermal thermogravimetry in an inert atmosphere at four different heating rates was performed. The obtained data were utilized for the kinetic analysis using the isoconversional Friedman method in combination with multivariate nonlinear regression method incorporated in the Netzsch Thermokinetics 3.1 software. The kinetic parameters (activation energy, pre-exponential factor and kinetic model) were calculated.

[1] F. Hassouna, S. Morlat-Thérias, G. Mailhot, J. L. Gardette, Polym. Degrad. Stab. 92 (2007) 2042-2050.
[2] D. Ghanbari, M. Salavati-Niasari, M. Sabet, Composites Part B: Engineering, 45(1) (2013.) 550-550.
[3] A. A. Pilarska, Ł. Klapiszewski, T. Jesionowski, J. Pow. Tec. 319 (2017) 373-407
[4] M. A. Shand, The Chemistry and Technology of Magnesia. New York, 2006, Wiley: 39-60.
[5] M. Erceg, I. Krešić, N. Stipanelov Vrandečić, M. Jakić, J. Therm. Anal. Calorim. 131 (2018) 325-334
[6]. J. Jakić, M. Jakić, M. Labor, J. Therm. Anal. Calorim. 142 (2020) 2099-2110

A thermodynamic characterization on the binding of oral chemotherapeutic drug imatinib to human α1-acid glycoprotein using isothermal titration calorimetry

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Binding of drugs to proteins influence their pharmacokinetic and pharmacodynamics action. In the blood, the drug is distributed in the body in the free form or bound to plasma protein. α1-acid glycoprotein (AGP, also known as orosomucoid) is an important plasma protein involved in the binding and transport of many drugs, particularly basic one such as imatinib (IMT), a selective tyrosine kinase inhibitor, successfully used for the treatment of chronic myelogenous leukaemia and gastrointestinal stromal tumors [1-2].

This research uses sensitive and modern isothermal titration calorimetry (ITC) technique for characterization of microscopic thermodynamic parameters that trigger the binding of drugs to AGP. ITC is a convenient and widely used experimental technique to directly measure released or absorbed heat during association processes such as protein-drug interaction and to quantitatively measure the binding affinity [3].

The main goal of this research is to quantitatively evaluate the interaction between imatinib mesylate and AGP to characterize the nature and forces underlying the formation of a protein-drug complex. The binding of basic drug imatinib displayed an exothermically driven binding interaction with AGP. Binding energy was guided by a combination of favorable (negative) enthalpy ($\Delta_r H$ = –4.21 kcal/mol) and favorable (positive) entropy ($\Delta_r S$ = 3.62 kcal/mol K) contribution to the Gibbs free energy ($\Delta_r G$ = –7.82 kcal/mol) with association constant ($K_A = 17.6\ x\ 10^{-2}\ \mu M^{-1}$). Enthalpy change is an important step in understanding the driving forces that characterize the protein-drug interaction information very much needed in the drug discovery process.

[1] ZH. Israili, PG. Dayton, Drug Metab. Rev., 33 (2001) 161-235
[2] M. Mic, A. Pîrnău, CG. Floare, M. Bogdan, Int. J. Biol. Macromol., 147 (2020) 326-332
[3] JX. Huang, MA. Cooper, MA. Baker, MAK. Azac, RL. Nation, J. Li, T. Velkov, J. Mol. Recognit., 12 (2012) 642–656

Thermal and magnetic properties of M-type hexaferrites

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Hexaferrites are a class of iron compounds which crystalize in a sandwich-like periodic stacking of iron-oxide layers containing different metal atoms. The simplest is the M-type with chemical formula $AB_{12}O_{19}$, where A = Ba, Pb … and B = Fe, Ti … [1]

Our recent measurements [2,3] with frequency-dependent magnetic susceptibility technique on various substitutions within the M-type hexaferrite ($Ba_{1-x}Pb_xFe_{12-y}Al_yO_{19}$) has shown signatures of exotic phenomena which point toward a general relaxational mechanism in ferrimagnetic semiconductors. Moreover, it was shown that activation energies of relaxation dynamics increase by adding aluminum.

Heat capacity measurements from room temperature down to liquid helium indicate that the whole temperature range can be fitted well by the Debye and Einstein contributions up to room temperature (Figure 1 (a)). From fitting results in Figure 1 (b), the energy of the lowest Einstein mode came close to the energy of the Debye mode.

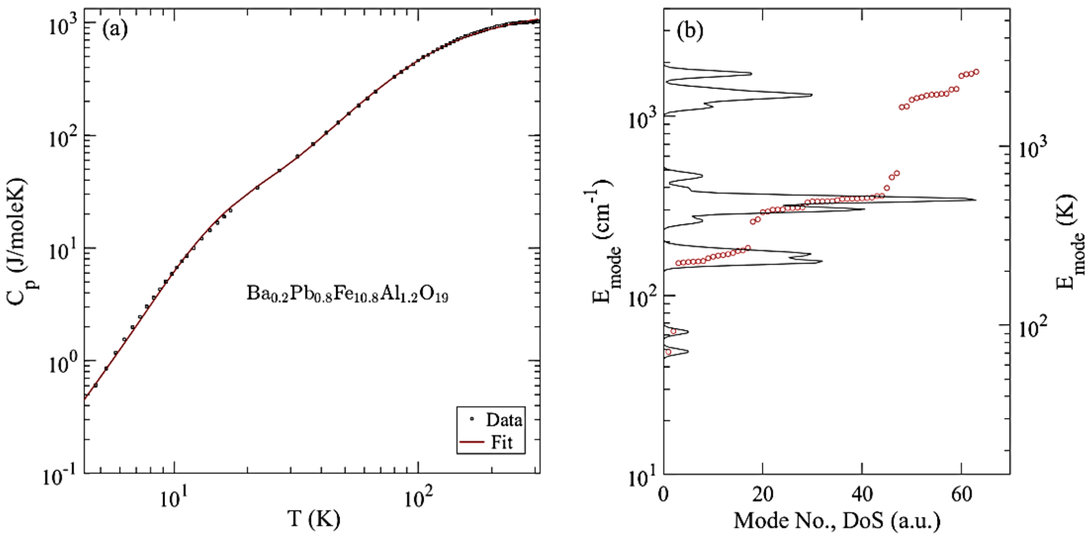

Figure 1. (a) Cp and fit (b) Extracted modes are marked with red circles. Black line represents estimated density of states of Einstein modes.

[1] R. C. Pullar, Progress in Materials Science 57, 1191 (2012).
[2] L. N. Alyabyeva et al., New J. Phys. 21, 063016 (2019).
[3] Ž. Rapljenović et al., Persisting correlation between electrical transport and magnetic dynamics in M-type hexaferrites, arXiv:2104.06964v2, in review (2021).

Poly(ethylene oxide)-lithium bis(oxalato)borate based nanocomposite polymer electrolytes

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This work focuses on the characterization of series of solid nanocomposite polymer electrolytes consisting of poly(ethylene oxide) (PEO), aminopropyl hepta isobutyl polyhedral oligomeric silsesquioxane (APHIB POSS) and lithium bis(oxalato)borate (LiBOB). Nanocomposite were prepared by melt intercalation method with different EO:Li molar ratios and at different APHIB POSS loadings. Differential scanning calorimetry (DSC) shows that an addition of LiBOB and APHIB POSS causes an important decreases of the crystallinity and melting temperatures of PEO, while the glass transition temperatures show higher values. The influence of LiBOB and APHIB on the PEO crystallinity was also confirmed by Fourier transform infrared spectroscopy (FTIR). Thermal stability as one of the key issues of the polymer electrolytes was investigated by the non-isothermal thermogravimetry. Thermogravimetric analysis (TGA) shows a more complex degradation of prepared samples compared to pure PEO. However, polymer electrolytes remaind thermally stable enough for their suitable applications in the electrochemical devices. Electrochemical impedance spectroscopy (EIS) reveals that LiBOB and APHIB POSS incorporation have positive influence on the ionic conductivity of PEO at room temperature. Considering the ionic conductivity of nanocomposites the optimized system was determinated.

Thermal stability and utilisation of 1D-nanostructured Co_3O_4 rods derived by simple solvothermal processing

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Gas sensors require materials with vapour sensitive surface, photocatalytic systems require materials with oxygen sensitive surface, photovoltaic devices require materials with photon sensitive surface [1]. For all of the mentioned purposes, different metal oxides forming semiconducting materials are found to be convenient due to their sometimes very unique specific properties but also ability to conduct a low price synthesis, to derive a robust material, which undergoes reactions over known mechanisms and thereof are widely applicable. N-type semiconductors are known for somewhat faster reactivity leading to considerably lower amount of p-type semiconductor-related reports. Among those, a cobalt oxide spinel is found. Here, a simple solvothermal method was applied to derive Co_3O_4 nanomaterial using cobalt nitrate and ammonia as precursors.

Structurally monophasic Co_3O_4 nanoparticles with spinel structure were indicated by powder X-ray diffraction crystallisation of while the presence of traces of organic phase residuals in otherwise chemically homogeneous material was observed by Fourier-transformed infra-red spectroscopy. Scanning electron microscopy further shows that the observed fine nanoparticulate matter forms agglomerates with possible presence of rod-like formations. Interestingly, using transmission electron microscopy it was possible to reveal that the agglomerates of the fine nanoparticulated material is actually nanostructured, i.e. the presence of 1D-shaped Co_3O_4 rods embedded in fine nanoparticulated matrix are confirmed. In conjunction with the N_2 adsorption/desorption isotherms, the discussion about the orientation, exposure of nanostructured rod domains and derivative geometry parameters was possible. The nanostructured Co_3O_4 material was shown to be stable up to 800 °C whereat the decomposition to CoO takes place. The specific surface area of nanostructured sample was raised, so it was interesting to investigate photocatalytic efficiency. For that matter just a simple degradation tests using the basic model pollutant methylene blue were performed; results suggest that the degradation performance of prepared nanostructured Co_3O_4 photocatalyst having above-mentioned properties is worth deeper investigation.

[1] F. Xia, E. Ou, L. Wang, J. Wang, Dyes and Pigments, 76 (2008) 76-81
[2] J. Kaczmarczyk, F. Zasada, J. Janas, P. Indyka, et. al., ACS Catal., 6 (2016) 1235-1246

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Influence of molar mass and styrene on thermal stability and phase transitions of methacrylate based polymer additives for lubricating oils

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Polymers based on alkyl methacrylates are widely used as additives for modifying the rheology of lubricating oils, where they serve as viscosity thickeners, viscosity index improvers and pour point depressants. It was established that methacrylates with medium size lateral alky groups (C_{10}-C_{14}) enhance viscosity index and those with the long chain groups (C_{16}-C_{18}) mostly contribute to the lowering of the pour point of solutions, whereas the methyl group contributes to the stiffness of the polymer chain. Also, polymers for lubricating purpose should have high shear stress stability over broad temperature range as the conditions found in lubricating environment require. Thus, to have multiple functionalities, additives should have high thermal and oxidative stability which can be achieved by addition of styrene comonomer units. [1,2]

Free radical polymerizations of monomers were carried out at 95 °C in mineral base oil using *tert*-butyl-peroxy-2-etilhexanoate as initiator and n-dodecyl mercaptane as chain transfer agent. There are two groups of polymers containing same comonomers: *N,N*-dimethylaminoethyl methacrylate (DMAEMA), dodecyl methacrylate (DDMA) and octadecyl methacrylate (ODMA) differentiating in one comonomer: styrene (ST) and methyl methacrylate (MMA). Synthesized polymers of different molar mass and composition were analysed using differential scanning calorimetry to determine phase transitions (glass transition temperature, melting point and crystallization temperature). Also, thermogravimetric analysis was carried out to investigate thermal and oxidative stability.

[1] I. Šoljić, A. Jukić, Z. Janović, "Terpolymerization kinetics of N,N- dimethylaminoethyl methacrylate/alkyl methacrylate/styrene systems", Polym. Eng. Sci: 70:577–584 (2010)
[2] A. Jukić, E. Vidović, Z. Janović, "Alkyl methacrylate and styrene terpolymers as lubricating oil viscosity index improvers", Chem. Technol. Fuels Oils 43, 386–394 (2007)

Adulteration of monofloral honey with fructose syrup and possibility of detection by differential scanning calorimetry

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Adulteration of honey with sugar products, especially cheap syrups, has been a problem in the honey industry for years. In this work, differential scanning calorimetry (DSC) was used for the possibility of detecting adulteration in Croatian honeys.

The aim of this study was to investigate the possibility of detecting fructose syrup in monofloral honeys of known botanical origin (5 acacia and 5 chestnut samples) using DSC technique. DSC scans were used to determine the thermal behaviour of syrup, honeys with known sugar composition, and artificially adulterated honeys over a very wide temperature range (from -100 to 220 °C, 10 °C min^{-1}), i.e., as a basis for determining onset and midpoint glass transition temperatures (Tg_0 and Tg_m), change in specific heat capacity (Δc_p), and enthalpy of fusion (ΔHf).

There was a significant difference in Tg temperatures between syrup and pure honey samples (13-22 °C). The results of thermal analysis showed a statistically significant difference between authentic and artificially adulterated honeys. Adulteration of honeys from 5 to 20% fructose syrup addition caused changes in both Tg temperatures (decreasing values up to 6 °C) and ΔHf (increasing values up to 29 Jg^{-1}).

The role of thermal processing for achieving homogeneity of magnetron sputtered AZO films

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Transparent conductive thin-films have received much attention due to their high conductivity and transmittance as well as broad areas of use (optoelectronic devices, e.g. solar cells). In comparison to the widely used indium tin oxide (ITO) films, aluminium doped zinc oxide (AZO) films represent a low cost alternative that can be easily deposited by a variety of chemical and physical methods [1,2].

In order to determine the optimal conditions for obtaining films that can be used as transparent conductive oxide layers (TCO) we investigated the course of preparing AZO films by DC magnetron sputtering using two source targets: zincite (ZnO) and aluminium (Al). DC power was varied during the deposition on glass substrates and derived films were subsequently thermally treated.

All films display hexagonal wurtzite structure of zincite regardless of the deposition parameters as shown by X-ray diffraction analysis (XRD). The average transmittance of the films was more than 85% in the visible range (400 to 800 nm). The Al content and thermal treatment were responsible for variations of the average grain size and achieved morphology, which was confirmed by electron and atomic force microscopies (SEM and AFM) as well as synchrotron radiation scattering experiments (SAXS). Finally, solid state dielectric spectroscopy measurements (SS IS) described the development of electrical conductivity with temperature in the prepared thin-films. It was found that the optimisations of the thermal processing play a key role in tailoring of layers with advanced charge transport functionalities.

The investigation brings to conclusion that application of the subsequent thermal processing can improve both electrical and optical properties of the AZO films derived by magnetron sputtering.

[1] B. Sarma, D. Barman, B. K. Sarma, Appl. Surf. Sci., 479 (2019) 786-795
[2] K. E. Lee, M. Wang, E. J. Kim, S. H. Hahn, Curr. Appl. Phys., 9 (2009) 683-687

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Thermal properties of PEO/NaAlg blend film complexed with LiBOB

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Development of Li-ion battery (LIB) with solid-state polymer electrolyte (SPE) drew many scientists' attention as the challenge of finding the material that will fulfil all the necessary demands to be considered as SPE in LIB. One of the promising polymers for the polymer electrolyte is poly(ethylene oxide) (PEO). Its main advantage lies in the broad range of complexation with different salts and electron-rich ether group facilitating the salt dissociation [1]. However, its lower ionic conductivity at room temperature needs to be improved, and one way is to blend PEO with other polymers to enhance the ion migration by crystallinity reduction of PEO. A smaller amount of crystalline phase will favour faster ion transport through the amorphous phase, which would mean higher conductivity [2]. Sodium alginate (NaAlg) as polyelectrolyte with the possibility of forming hydrogen bonds between its hydroxyl groups and ether oxygen in PEO was proved to be a good choice for preparation of miscible blend with PEO that has an excellent film-forming ability and good thermal properties [3]. Lithium *bis*(oxalato)borate (LiBOB), as salt for the preparation of SPE, has its advantages, primarily as environmentally friendly salt with high thermal stability and bulky anion size [2].

This investigation is focused on the preparation of flexible and freestanding solid-state polymer electrolyte film based on PEO/NaAlg/LiBOB composite by solution cast technique. The aim was to prepare film with good thermal properties and thermal stability for solid-state lithium polymer batteries. First, the structural and morphological features of the casted polymer composite films have been investigated by using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). In addition, thermal properties and thermal stability were investigated by using differential scanning calorimetry (DSC) and thermogravimetry (TG). Investigation revealed changes in structure incorporating LiBOB salt in PEO/NaAlg blend film and variation of salt concentration. The addition of LiBOB salt has a complex effect on PEO thermal properties in PEO/NaAlg/LiBOB film, with a reduction in PEO crystallinity. PEO/NaAlg film degrades in three degradation stage, while PEO/NaAlg/LiBOB films have more complex degradation with up to eight degradation stages depending on the composite composition. The primary influence of the salt incorporation in PEO/NaAlg film is the reduction of the PEO degradation rate with the increase of LiBOB content.

[1] A. Arya, A. L. Sharma, Macromolecular Research, 27 (2019) 334
[2] A. Arya, A. L. Sharma, Ionics, 23 (2017) 497
[3] S. Perinović Jozić, A. Sesar, Z. Grubač, B. Andričić, Kemija u industriji, 69 (2020) 503

Thermal properties of different poly(alkymethacrylate) additives and their influence on low temperature properties of mineral diesel fuel

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Mineral diesel fuel is one of the main products of crude oil refining. It is obtained by mixing petroleum fractions and light gas oil fractions with a boiling range 130 - 370 °C and used in an internal combustion diesel engine where compression causes self-ignition of a mixture of fuel and air. [1,2] Diesel fuel contains a substantial amount of paraffin waxes that begin to crystallize at low temperatures and tend to agglomerate. The big wax crystals can plug filters affecting the cold flow plugging point (CFPP) and also the pour point (PP) of diesel fuel. [3] In this study, the low temperature properties of non-additivated mineral diesel fuel with the addition of poly(alkyl methacrylate) (PAMA) additives A1 - C3 were investigated. Thermal transitions temperatures were determined using the differential scanning calorimetry (DSC) for pure polymer additives and for diesel blends with up to 2000 ppm of additives. Standard tests for low-temperature properties (HRN EN 116 for CFPP and ASTM D 5950 for PP) have shown that they lower the temperature of CFPP up to 10 °C and PP up to 30 °C.

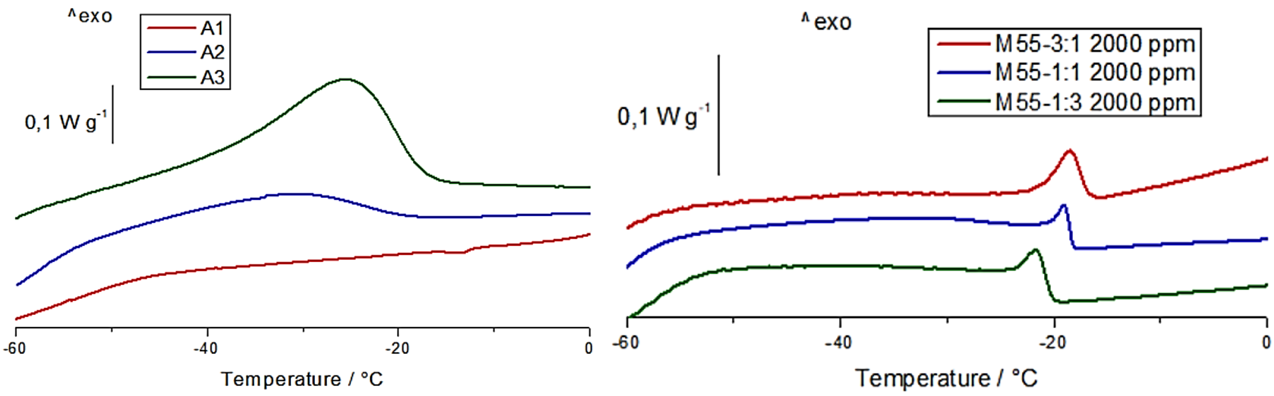

FIGURE 1. DSC thermal transitions of pure additives (left) and additive/diesel blends (right)

[1] Fayyazbakhsh, A., Pirouzfar, V., Renewable and Sustainable Energy Reviews 74 (2017), 891–901.
[2] Liu, H., Ma, J., Dong, F., Yang, Y., Liu, X., Ma, G. Yao, M., Energy Conversion and Management 171 (2018), 1787–1800.
[3] Xu, G., Xue, Y., Zhao, Z., Lian, X., Lin, H., Han, S., Fuel 216 (2018), 898–907.

Reactive spark ablation deposition and subsequent thermal conversion of copper oxide porous thin-films

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Spark ablation is a powerful new, clean and efficient method capable of controlled nanoparticle preparation **[1]**. Copper oxide (Cu_xO_y) nanostructured thin-films are inexpensive, chemical stable and non-toxic, and thereof recently applicable for energy conversion, gas sensing and optoelectronics circuits **[2]**.

Among stable crystalline Cu_xO_y phases; Cu_2O (cuprite) and CuO (tenorite) are found while among metastable only Cu_4O_3 (paramelaconite) **[3]**. Coupling the spark ablation nanoparticle generator to impaction deposition chamber we were able to produce porous Cu_xO_y thin-films on glass substrates.

The thin-films were characterized as prepared and after thermal treatment at 500 °C. The development of crystalline phases was monitored by grazing incidence diffraction using synchrotron radiation; to confirm ability to derive cuprite and paramelaconite by ablation at ambient conditions, and their conversion to monophasic tenorite upon thermal treatment. Microscopic characterisation by scanning and transmission electron microscopy as well as Kelvin probe force microscopy revealed the morphology behind the particulate domains forming thin-film is quite complex. The preparing of such Cu_xO_y thin-films with high specific surface area in highly demanding. These characterisations provided valuable insight into the phase evolution and nanostructuring mechanisms of the as prepared and thermally annealed Cu_xO_y thin-films, to foster the utilisation of this chemical system and deposition method.

[1] E.A.J. Rennen, M.F.J. Boeije, A. Schmidt-Ott, “Spark Ablation: Building blocks for Nanotechnology”, Jenny Stanford Publishing Pte. Ltd. (2020) 223-245
[2] H. Soonmin, A review on copper oxide thin films, Int. J. Recent. Sci. Res. 7 (2016) 11914-11918
[3] J. Li, G. Vizkelethy, P. Revesz, J.W. Mayer, K.N. Tu, Oxidation and reduction of copper oxide thin films. J. Appl. Phys. 69 (1991) 1020-1029

This work has been supported by the projects UIP-2019-04-2367 of the Croatian Science Foundation and PZS-2019-02-1555 in Research Cooperability Programme funded by the European Union from the European Social Fund under the Operational Programme Efficient Human Resources 2014-2020.

Influence of molar mass and styrene on thermal stability and phase transitions of methacrylate based polymer additives for lubricating oils

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Polymers based on alkyl methacrylates are widely used as additives for modifying the rheology of lubricating oils, where they serve as viscosity thickeners, viscosity index improvers and pour point depressants. It was established that methacrylates with medium size lateral alky groups (C_{10}-C_{14}) enhance viscosity index and those with the long chain groups (C_{16}-C_{18}) mostly contribute to the lowering of the pour point of solutions, whereas the methyl group contributes to the stiffness of the polymer chain. Also, polymers for lubricating purpose should have high shear stress stability over broad temperature range as the conditions found in lubricating environment require. Thus, to have multiple functionalities, additives should have high thermal and oxidative stability which can be achieved by addition of styrene comonomer units. [1,2]

Free radical polymerizations of monomers were carried out at 95 °C in mineral base oil using *tert*-butyl-peroxy-2-etilhexanoate as initiator and n-dodecyl mercaptane as chain transfer agent. There are two groups of polymers containing same comonomers: *N,N*-dimethylaminoethyl methacrylate (DMAEMA), dodecyl methacrylate (DDMA) and octadecyl methacrylate (ODMA) differentiating in one comonomer: styrene (ST) and methyl methacrylate (MMA). Synthesized polymers of different molar mass and composition were analysed using differential scanning calorimetry to determine phase transitions (glass transition temperature, melting point and crystallization temperature). Also, thermogravimetric analysis was carried out to investigate thermal and oxidative stability.

[1] I. Šoljić, A. Jukić, Z. Janović, “Terpolymerization kinetics of N,N- dimethylaminoethyl methacrylate/alkyl methacrylate/styrene systems”, Polym. Eng. Sci: 70:577–584 (2010)
[2] A. Jukić, E. Vidović, Z. Janović, “Alkyl methacrylate and styrene terpolymers as lubricating oil viscosity index improvers”, Chem. Technol. Fuels Oils 43, 386–394 (2007)

Determination of human alpha-1-acid glycoprotein–drug binding constants using microscale thermophoresis

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After the drug is administrated to the blood stream, it usually binds to certain plasma proteins. Alpha-1-acid glycoprotein (AGP) is an important plasma protein involved in the binding and transport of many basic and neutral drugs. The extent of this association at equilibrium determines the concentration of unbound drug. Only the free fraction of the drug (unbound drug) is available for active uptake or diffusion into the surrounding tissue according to the "free drug principle". Due to their high concentration, the plasma proteins control the free drug concentration, thus influencing the drug potency in vivo.[1] Clinically, this buffering effect should be considered when adjusting the dosage of a drug as well as in assessing the toxicity of the administered drug which is often complicated by changes in patient's protein-binding capacity.[2] For that reason, data obtained from the binding constant measurements is crucial for the calculation of free drug concentration in plasma in order to predict/modify the dosage needed.

In this study, a novel method Microscale Thermophoresis (MST) was applied in the investigation of molecular interaction between human plasma protein AGP and five drugs from four different drug classes. Thermophoresis describes a direct movement of molecules through a temperature gradient and is one of the two main factors contributing to the measured MST signal, the other being TRIC (Temperature-Related Intensity Change). AGP-drug binding constants are listed in the Table 1.

Table 1. Drugs, drug classes and their respective binding constants on native human AGP.

Drug	**Drug Class**	K_d **/ M**
Carvedilol	Antihypertensive	$1.13\cdot10^{-4} \pm 6.69\cdot10^{-6}$
Dipyridamole	Antithrombotic	$2.96\cdot10^{-6} \pm 3.48\cdot10^{-7}$
Imipramine hydrochloride	Antidepressant	$1.61\cdot10^{-3} \pm 1.88\cdot10^{-4}$
Propranolol hydrochloride	Antihypertensive	$1.03\cdot10^{-3} \pm 5.04\cdot10^{-5}$
Vinblastine sulfate	Cytostatic	$3.14\cdot10^{-4} \pm 2.10\cdot10^{-5}$

[1] G. L. Trainor, Expert Opin. Drug Discov., 2(1) (2007) 51-64
[2] J. M. Kremer, J. Wilting, L. H. Janssen Pharmacol Rev.. 40(1) (1988) 1-47

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Development of polymer nanocomposites with enhanced thermal conductivity

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Thermal conductivity is an important property of the material, especially in certain industrial products. Polymer materials usually have very low thermal conductivity, which determines them in some applications. Namely, heat wastage during the operation of electrical equipment is crucial for extending their lifespan, especially for polymer insulation materials that are prone to thermal aging. In the scope of the KK.01.2.1.02 project, Končar GIM and the Faculty of Chemical Engineering and Technology are developing an improved insulation system. It is based on impregnation resin with enhanced thermal conductivity achieved by the incorporation of oxide nanoparticles. The effect of nanofiller particle size and concentration on the thermal conductivity of cured nanocomposite resin was measured with the transient hot bridge method. The thermal conductivity increased up to 11% with 5 wt% of nanofiller. Further, the thermal stability of resin nanocomposites showed a minor increase as was determined by thermo-gravimetric analysis (TGA). In addition, the curing process effectiveness was evaluated by differential scanning calorimetry (DSC).

Synthesis and characterization of cellulose/PDMAEMA copolymers and nanocomposites with SiO_2

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In this work cellulose/poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) copolymers were synthesized. The nanofiller SiO_2 was added in order to construct nanocomposites. The polymer films were casted directly after synthesis, while the nanocomposites were casted after mixing in the SiO_2 filler and additional exposure of the mixture to an absorbed dose (100 kGy) of γ-rays from a ^{60}Co source. Finally, water responsive cellulose/poly(2-(dimethylamino)ethyl methacrylate) and cellulose/poly(2-(dimethylamino)ethyl methacrylate)/SiO_2 nanocomposite hydrogels and films were successfully prepared.

The chemical reaction of cellulose and 2-(dimethylamino)ethyl methacrylate (DMAEMA) (ratio 1:1; 1:3 and 1:5 mol/mol) was carried out in the solvent *N,N*-dimethyl acetamide/LiCl with a peroxide initiator at 90 °C and using *N,N*-methylene-*bis*-acrylamide as a crosslinker.

The microstructure and properties of prepared hydrogels and films were investigated by scanning electron microscopy, water contact angle, thermogravimetric analyses (TGA), while the swelling ability was followed gravimetrically. The prepared hydrogels displayed high degree of swelling, between 600 and 900 %. All hydrogels showed hydrophilic surfaces whereat with increasing share of PDMAEMA the contact angle increased from a minimum of 40° for sample from the 1:1 series to a maximum of 53° for sample from the 1:5 series. Based on SEM micrographs the SiO_2 nanofiller were well dispersed as no agglomerates were visible. The TGA reveals that all samples display the main mass loss at temperatures above 300 °C where amorphous cellulose and second PDMAEMA mass losses add up. A significant signal in the 1-5 series recorded around 430 °C corresponds to the third mass loss of increased share of PDMAEMA. At temperatures up to 600 ° C the samples show high residue content common to amorphous cellulose.

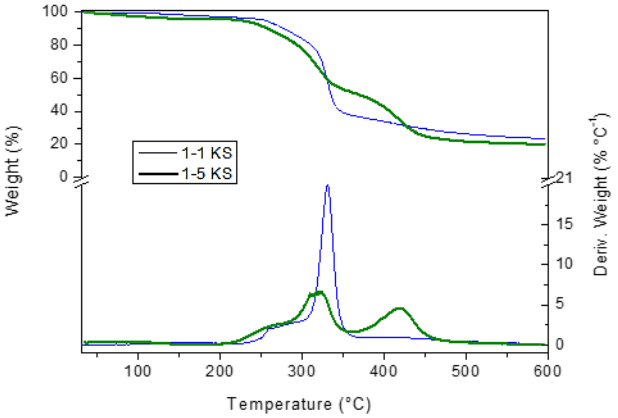

Figure 1 TG and DTG curves for 1-1 and 1-5 cellulose/PDMAEMA copolymers

Porous SnO_2-modified cellulose photocatalysts derived by non-hydrolytic sol-gel freeze-drying

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Upgrades of designing the synthesis pathways for preparing advanced nanocomposites based on semiconducting materials are essential for improving their functional performance in fields of optoelectronics, sensing, catalysis, etc. Thus, semiconducting oxides with facile synthetic routes are found suitable for further application. TiO_2 (bandgap of ~3.2 eV) is up to date the most investigated photocatalyst, whereas SnO_2, despite a similar bandgap of 3.6 eV has not yet reached similarly wide applicability. Therefore, exploring synthetic routes to extrapolate the range of functional SnO_2 nanocrystals and nanostructures is vastly interesting. To overcome the discrepancies related to the separation of particulate photocatalysts from the reaction suspension, the preferred photocatalysts are commonly immobilised. For immobilised photocatalysts, the high specific surface plays a major role, hence foam-type catalysts, monolithic aerogels, graphene and carbon foam composites have emerged. Here we investigate the synthetic strategy to derive a candidate for an immobilised SnO_2-based photocatalyst with enhanced availability of the reaction surface. As a tool to boost the porosity of SnO_2 material, cellulose, as the most abundant, biocompatible and renewable natural polymer on Earth, was used to form a composite with SnO_2. This work focuses on the course of non-hydrolytic sol-gel freeze-drying synthesis in combination with reductive mineralization of cellulose necessary for deriving chemically and morphologically homogeneous high-porosity composites.

The resulting composites were thoroughly characterised using Fourier transformed infrared and Raman spectroscopies and diffraction analysis, which show the level of chemical and structural homogeneity in the derived composites. Thermal and thermogravimetric analysis reveals thermal stability while N_2 adsorption/desorption isotherms and electron microscopy analyses suggest morphologic and surface geometry. Finally, photocatalytic degradation was investigated using a model micropollutant. Overall, the composites show performance value for the immobilised photocatalyst.

[1]A. Aboulaich, B. Boury, P.H. Mutin, Eur. J. Inorg. Chem. 24 (2011) 3644-3649
[2]A. Beltran, J. Andres, J. R. Sambrano, E. Longo, J. Phys. Chem. A. 112 (2008) 8943-8952
[3]C. Antonini, T. Wu, T. Zimmermann, A. Kherbeche, et. al., Nanomaterials 9 (2019) 1142

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Thermodynamic Properties of Two Maleic Anhydride Derivatives: Experimental and Computational Approaches

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Maleic anhydride derivatives are among the compounds that constitute the monomeric units of stimuli-responsive polymers most referred to as *smart materials*.[1] Such polyanhydrides have also been shown to present enormous potential in the development of drug delivery systems.[2] Acknowledging that the observed properties of a polymer are hugely determined by the properties of its monomers, the reliable establishment of the fundamental properties of the monomer molecule is crucial. In this work, we studied the structural and energetic properties of two maleic anhydride derivatives — 1-cyclohexene-1,2-dicarboxylic anhydride (CDA) and 1,2,4,5-cyclohexanetetracarboxylic dianhydride (HPMDA) — by experimental methods in tandem with high-level computational studies.

The experimental part involved techniques as combustion calorimetry, Calvet microcalorimetry, and Knudsen effusion to, respectively, determine the standard ($p^{\circ} = 0.1$ MPa) molar energy of combustion in the crystalline phase, $\Delta_{\mathrm{c}}U_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})$, the standard molar enthalpy of sublimation, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$, and the vapor pressure at different temperatures for both compounds. These data led to the derivation of the standard molar enthalpies of formation in the crystalline and gaseous phases, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})$ and $\Delta_{\mathrm{f}}\mathrm{H}_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g})$, respectively.

For the computational part, several methods at different levels of theory were used: methods at the DFT level, and high-level methods using variants of the G3 level and the G4 level. This multi-level computational study had as main objective the estimation of the gas-phase enthalpies of formation for each level of theory, as well as comparing the results obtained from the different methods. We observed a very good agreement between our computational and experimental results.

[1] M. Schwartz, Smart Materials—Encyclopedias, John Wiley and Sons, Inc., New York 2002 (ISBN: 0-471-17780-6).
[2] J. Tamada, R. Langer, The development of polyanhydrides for drug delivery applications. J. Biomater. Sci., Polym. Ed. 3 (1992) 315-353.

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Characterisation of the fire behaviour of wood: From pyrolysis to fire retardant mechanisms

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Abstract

Wood is undeniably the most useful and readily available natural raw material. However, the susceptibility of wood products to fire is one of the crucial challenges faced in the wood industry. The fire behaviour of wood is a very complex phenomenon due to the different constituents and their independent reactions to fire. This article presents a thorough overview of the flammability stages of wood. It covers pyrolysis, thermal oxidative decomposition, ignition, combustion and heat release as well as flame extinction mechanisms. In the area of flame retardancy, conventional wood fire retardants, nanocomposites fire retardants and wood modification processes are investigated. Factors such as wood species, moisture content, density, experimental conditions, external heat flux, heat exposure time, wood permeability and porosity are some of the deterministic parameters characterising the fire behavior. This paper is a one-stop-shop for researchers analysing wood flammability since it includes all aspects pertaining to the burning of wood.

Keywords: Wood, fire behavior, pyrolysis, ignition, combustion, flame retardancy, wood modification.

Low-temperature DSC for investigation of hyaluronic acid interaction with collagen-containing materials

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Collagen is the basis of the body's connective tissues, it maintains their strength and elasticity. Collagen-containing materials (bone and cartilage tissue, connective tissue fragments of tendons - peritenons) in some form are used in the manufacture of implants in reconstructive medicine. However, the problem of perfect biocompatibility of materials and technologies still exists. For example, serious problems arise with the calcification of collagen-containing implants in cases where this is undesirable (pericardial implantation). In addition, the problem of the destruction of the implanted material during cryopreservation is urgent. Researchers actively seek for chemical agents that ensure the preservation of elasticity and other physicochemical properties of collagen-containing compositions. One of these is hyaluronic acid. Due to its water-holding and structure-forming properties it affects the water clusters and osteogenesis precursors in collagen compositions.

Low-temperature DSC makes it possible to investigate the state of water in the microchannels of collagen fibers. In this work, we investigated the effect of hyaluronic acid (2% sodium hyaluronate stabilized in 0.5% of mannitol solution in the composition of the medicine "Gilarten"). DSC analysis was carried in the temperature range 20 ...- 40 ... 50 ° C with the heating rate of 0.5 K/min. Native and hyaluronate-treated collagen in the composition of peritenons (young tissue) and tendon filaments (old tissue), as well as collagen gel (dermal equivalent used in clinical practice for the treatment of burns), were selected as the test samples. In ultrathin channels of collagen filaments, water is in a clustered form and its freezing point is below 273 K due to adsorption interactions with biological tissues. On the basis of DSC analysis shift (up to 2 °C) of the water crystallization temperature to the low-temperature region was observed in the samples treated with hyaluronic acid. Moreover, an increase in the exposure time of samples in hyaluronate (up to 3 days) leads to an increase in the magnitude of the shift. In addition, thermal behavior of the hyaluronate-treated samples changes in the range of physiological temperatures. The results obtained are important for analyzing the prospects for using hyaluronic acid to prevent dehydration and destruction of implanted biological tissues.

Thermophysical behavior features of water structured into fibrillar collagen of hyaluronic acid treated tendons

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Tendons contain at least 90% of type 1 fibrillar collagen, which, according to various sources, contains 60-70% water. In the polypeptide structure of fibrillar collagen water is present within the interchain and interdigitating spaces. The diameter of the interchain channels reaches 10 nm, the interdigiting ones vary within 2 nm. The indicated dimensional ratios assume the presence of several water subsystems with different structural properties. Anatomical peculiarities are no less important, and in particular the fact that the tendons are functionally heterogeneous tissue: the closer to the outer sheath (peritenon), the higher the histogenetic potential that implements physiological remodeling and post-traumatic fiber regeneration. The role of water structured into fibrillar collagen in these processes in general and, in particular, modulated by hyaluronic acid remains largely unknown. Purpose of the work: to clarify the features of the thermal behavior of the tissue water of tendons treated with hyaluronic acid. Sources of samples: outer sheaths of paravertebral tendons of Wistar rats and the medicine "Gilarten" as a donor of hyaluronic acid. The duration of hiaulronate treatment is up to 3 days in *in vitro* and *in vivo* experiments. Thermal analysis (TG, DTG, DTA) was performed in a temperature range from room temperature to 600 °C at an air flow rate of 50 ml/min (STA 409 PC LUXX derivatograph (NETZSCH, Germany).

According to the data of TG, DTG and DTA, in the samples of hyaluronic acid treated peritenons multidirectional changes in the thermophysical parameters of the aqueous and dense phases of the tendon tissue were found. In the aqueous phase: the temperature, the rate of mass loss and the energy of endothermic effects of water boiling increase. In the dense (organic and mineral) phase the rate of weight loss decreases, the energy of exothermic effects decreases, and the peak temperature values decrease. The progressive increase in the boiling point indicates the strengthening of bonds and the thermal stability of the aqueous phase which may be due to the ordering effect of hyaluronate on the structure of hydrogen bonds in sorbed water. Acceleration of weight loss during boiling in combination with an increase in the absorbed energy of the aqueous phase indicates a decrease in the viscosity of the liquid fraction of the extracellular matrix due to a decrease in the ability of hyaluronic acid to self-association. Thus, high-temperature thermal analysis leads to a conclusion that hyaluronic acid enhances the lubricating properties of tissue fluid and increases the regenerative functionality of the tendons.

Poster session 2

Influence of temperature and composition on excess thermodynamic properties. Statistical processing of experimental data using the MLR method

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Pharmaceuticals and cosmetics contain a wide range of substances, which differ in terms of physical-chemical properties and which may have a strong impact on the environment [1]. The presence of such substances in surface waters negatively impacts living organisms and, if they get into the human body, they may cause various diseases. The main sources of contamination with such products are represented by domestic, urban, hospital and industrial wastewater [2]. In an attempt to mitigate these negative effects on the environment, numerous groups of researchers have focused on studying the behaviour of liquid mixtures of substances. Good knowledge of the thermodynamic properties for liquid systems is very important in engineering, as they provide important experimental data for the design of fractional distillation separation plants used in chemical engineering [3, 4]. The following properties were assessed in our paper: surface tension and refractive index in a composition range influenced by component miscibility and four temperatures: 20, 30, 40 and 50°C, for binary and ternary systems of benzyl alcohol, hexanol and water. Both benzyl alcohol and hexanol are emerging pollutants that reach surface waters because they are contained in pharmaceuticals and in personal care products. Considering that the refractive index is determined much easier and with a lower consumption of substances than the surface tension, in our paper we used the statistical processing of experimental data using the multiple linear regression (MLR) method, which generated the following model:

$\boldsymbol{\gamma^{exc} = 478.5+101.514*X_1+58.389*X_2+47.083*(T/298.15)-416.897*n}$**.** It correlates excess surface tension (γ^{exc}) with composition (X_1 and X_2), normalized temperature and refractive index (n). The correlation coefficient for this model is 0.895 and the standard deviation is 5.92.

[1] P. Rzymski, A. Drewek, P. Klimaszyk, Limnol Rev. 17 (2017) 97
[2] L. Spessato, A. L.Cazetta, S.Melo, O.Pezoti, J.Tami, A.Ronix, J.M. Fonseca, A.F.Martins, T.L. Silva, V.C.Almeida, J. Mol. Liq. 300, (2020) 112282
[3] S. Bretsznajder, „Prediction of transport and other physical properties of fluids", First English edition, Pergamon Press, Oxford (1971) 408 pp
[4] C. Lisa, M. Ungureanu, P.C. Cosmatchi, G. Bolat, Thermochim. Acta 617 (2015) 76

Optical characterization of some common polymers and metal nanoparticles dispersion

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This paper brings together the optical techniques and chemical properties of some common polymers and metal nanoparticles dispersed in these polymers, in order to create a data base with their refractive index, at different temperatures.

Refractive index and size are important parameters to many gold nanoparticle for diverse applications, such as biomedical imaging,[1] drug delivery[2] or clinical diagnosis.[3] Gold nanoparticles can also be used as DNA biomarker selection, which highly depends on the diameter and refractive index of gold nanoparticles.[4] As a result, the determination of diameter and refractive index of gold nanoparticles is becoming increasingly important.

Given the above, we have studied the behavior of the refractive index in binary polymer system with nanoparticles at normal body temperature and in case of fever (considering the multiple applications in medicine of metal nanoparticles dispersed in polymers solutions, used in disease diagnosis and therapy).

The polymers that we choose to study have multiple applications in industry, pharmacy and biomedicine.

As a first conclusion, we calculated interferometricaly the refractive index for three polymers intensive used as excipients in various pharmaceutic formulations (PEG, PVP and CMC) and compared also with the results obtained with the Abbe refractometer. The refractive index of these polymers is decreasing with the increasing temperature.

In the second part of the paper, we studied refractive index dependence of temperature for gold/silver nanoparticles in polymer aqueous solution.

[1]. Zdenka Kolska, Petr Valha, Petr Slepicka, Vaclav Svorcik, Refractometric study of system water-poly(ethylene glycol) for preparation and characterization of Au nanoparticles dispersion, Arabian Journal of Chemistry, 12, 5019-5027, 2019

[2]. M. Tajdidzadeh, A. B. Zakaria,Z. Abidin Talib, A. S. Gene, and S. Shirzadi, Optical Nonlinear Properties of Gold Nanoparticles Synthesized by Laser Ablation in Polymer Solution, Journal of Nanomaterials, Article ID 4803843, 2017.

[3]A. C. Templeton, J. J. Pietron, R. W. Murray, P. Mulvaney, Solvent refractive index and core charge influences on the surface plasmon absorbance of alkanethiolate monolayer-protected gold clusters, Journal of Physical Chemistry B, 104(3), 564–570, 2000.

[4]. M. Faraday, The bakerian lecture: experimental relations of gold (and other metals) to light, Philosophical Transactions of the Royal Society of London, 147, 145–181, 1857.

Thermal, optical, spectral, adhesive and biological properties of some ethers with chlorine, with two azo groups, of the anthracene

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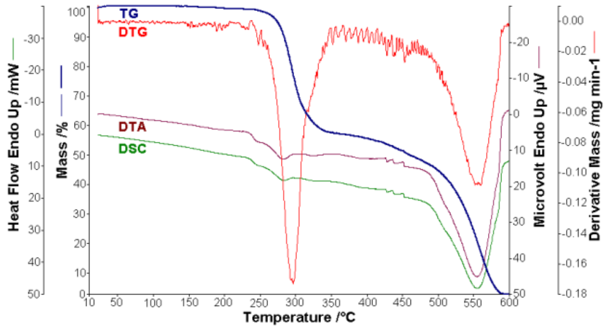
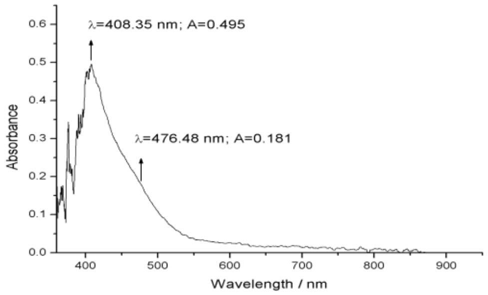
Bis (phenylazo) phenyleneoxymethylene] anthracene (BPBA) and its four derivatives were prepared by condensing of 9,10-bis (chloromethyl) anthracene with the sodium salts of 4-hydroxy-4’-(3,4-dichloro-phenylazo)-diphenyl, 4-hydroxy-4’-(4-chloro-phenylazo)-diphenyl, 4-hydroxy-4’-(4-methyl-phenylazo)-diphenyl, 4-hydroxy-4’-(2-chloro-phenylazo)-diphenyl and 4-hydroxy-4’-phenylazo-diphenyl [1].

Anhydrous sodium salts were prepared by reacting 4-hydroxy-4'-phenylazo-diphenyls with sodium hydroxide in an ethanol-benzene medium (1:1 by volume). In addition, the nucleophilic attack of the phenoxy anion on the bischloromethylate derivative results in the formation of the bisazobisester [2]. The results of spectral analyzes (in visible and IR) confirmed the composition and structure of the studied compounds [1].

The study extends to three chlorinated compounds, determining the thermal stability, physical properties and biological activity of the compounds. The measurements focused on atomic fluorescence, UV spectroscopy and AFM. The birefringence of the compounds in polarized light was determined. Their thermal analysis was performed over the temperature range RT-600 °C. The measurements were performed in air at a heating rate of 10 K / min with a PerkinElmer DIAMOND TG / DTA thermobalance.





The analyzed compounds are stable up to a temperature of 250°C. Also, the antioxidant activity of the compounds and their interaction with some common proteins were determined.

[1] L. Ma, Z. Chen, J. Therm. Anal. Calorim., 87 (2009) 1567.
[2] A. Ionescu, V. Alecu, “Thermal properties of solids”, Expert PublishingHouse, (2008) 1356-1364.

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Exploring of thermal properties of plant-polymeric films for medical applications

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The concern to develop wound healing materials envisages the use of alternative to topical antimicrobial agents such as antibiotics. The use of animal-derived proteins and plant extracts for wound dressings is an environmentally friendly approach in terms of circular economy, as well as the regenerative, antimicrobial and biocompatibility properties. Plant extracts, in particularly essential oils constitute a promising replacement to synthetic drugs, due to their properties which include antibacterial, antifungal, anti-inflammatory, antioxidant, and insecticidal activity [1].

In this paper, plant-polymeric films were prepared by casting film-forming emulsions based on lemongrass (*Cymbopogon flexuosus*) essential oil/Tween80 dispersed into hydrolyzed collagen-chitosan and rabbit collagen glue-chitosan, respectively. The effect of composition on structural, morphological characteristics, oxidative degradation and antioxidant properties was studied.

The presence of lemongrass essential oil into collagen-chitosan films led to the formation of flexible films with improved antioxidant activity, as well as the thermal resistance, which recommends them for potential use in medical applications. The evaluation of isothermal and non-isothermal chemiluminescence reveals the generation of free radicals depicting the progress of oxidation for each material structure and formulation [2] in correlation with antimicrobial activity and the stability to sterilization final process.

[1] E. Mele. Electrospinning of Essential Oils. Polymers 12 (2020) 12, doi:10.3390/polym12040908
[2] T. Zaharescu, M. Rapa, V. Marinescu. J Therm Anal Calorim., 12 (2017) 185

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Thermal properties of electrospun bio-based polymers for food packaging applications

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Polymers derived from renewable resources have gained an increased consideration for our society shifting from linear to circular economy. Poly(lactic acid) (PLA) is a leading bio-based polyester on the market having application in various fields as: food packaging, medicine, sensors, automobile, etc. Beside beneficial features of PLA for packaging materials, some limitations such as the low barrier, mechanical and thermal properties [1] are exhibited. PLA's drawbacks can be exceeded by blending with other polymers like poly(hydroxybutyrate) (PHB). The evaluation of thermal behaviour of bio-based polymers is associated to the resistence of the materials for the induced degradation which limits their use for a particular application [2].

In this work, the durability of PLA and PLA/PHB nanofibers prepared by electrospinning technique was investigated using Differential Scanning Calorimetry (DSC) and chemiluminescence (CL) analyses. Isothermal (170, 180 and 190 °C) and nonisothermal chemiluminescence were the experimental procedures achieved in air. The morphology and chemical composition of the electrospun bio-based polymers were investigated using scanning electron microscopy (SEM) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FT-IR).

The thermal oxidative mechanism demonstrated the thermal resistance for PLA and PLA/PHB nanofibers, potentially used as support for encapsulation of bioactive agents for food packaging applications.

[1] R.N. Darie-Niță, M. Râpă, M. Sivertsvik, J.T. Rosnes, E E. Popa, R.P. Dumitriu, O. Marincaș, E. Matei, C. Predescu, C. Vasile. Polymers, 13 (2021) 1610
[2] T. Zaharescu, M. Rapa, V. Marinescu. J Therm Anal Calorim., 12 (2017) 185

Funding: This work was supported by a grant of the Romanian Ministry of Education and Research, CCCDI - UEFISCDI, project number PN-III-P2-2.1-PED-2019-2878, within PNCDI III" (BioMatFood), under the Contract No 379PED/2020.

Non-isothermal degradation kinetic study of new multicomponent polymer systems for flame retardant coatings

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There were obtained three phosphorus containing flame retardant semi–interpenetrating polymer networks (S–IPNs) having as linear component an aromatic oligophosphonate and as cured matrix an epoxy resin crosslinked with three different curing agents: 4,4’–diaminodiphenylsulfone, 1,3–bis(aminomethyl)cyclohexane and octamethylene diamine.

For the non–isothermal kinetic studies there were recorded TGA curves at three different heating rates of 10, 20, 30 ^{o}C min^{-1} in nitrogen atmosphere.

The non–isothermal global kinetic parameters of the thermal degradation processes were obtained with the aid of the Friedman (FR) and Ozawa–Flynn–Wall (OFW) isoconversional methods. The variation of the global non–isothermal kinetic parameters showed that the structures thermally degraded following two or three stage complex mechanisms, depending on the hardener’s chemical structure. By using the experimental TGA heating curves and 18 kinetic mathematical models in the “Netzsch Thermokinetics–3” software, the individual kinetic parameters per each stage were calculated. In order to find the kinetic model which best describes each stage of thermal degradation a multivariate non–linear regression (MNR) method was used. The MNR compared the experimental curves to software simulated ones. After the testing of all 18 kinetic models, there were found the kinetic equations which most accurately described each thermal degradation stage through the obtaining of correlation coefficients close to the value 1.

Acknowledgment

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Thermal characterization of bio–based epoxy resins crosslinked with curing agents from raw renewable resources

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Thermosets based on epoxidized vegetable oil (EVO) and biobased crosslinking agents are normally soft owing to their flexible structure. In order to compensate the soft behaviour, it is necessary for a part of the biobased crosslinking agents to be replaced with small molecular crosslinking agents. The presence of small molecular crosslinking agents can enhance the thermal properties of the obtained thermoset. The aim of this research is to study the thermal characteristics of a green thermoset based on EVO crosslinked with castor oil maleic anhydride derivative (COMA) and methyl nadic anhydride (MNA). The presence of MNA increases the glass transition temperature and the hardness of the obtained thermoset. The crosslinking and thermal decomposition mechanisms of the biobased thermoset were obtained using the simultaneous TG/FT-IR/MS and differential scanning calorimetric (DSC) analysis. The kinetic parameters (activation energy and pre-exponential factor) as well as the curves shape of the variation of activation energy versus conversion degree were obtained both for the crosslinking process and for the thermal decomposition process using the multivariate linear regression method (MLR) from “Thermokinetics–3” software. Based on the variation of curves shape of activation energy versus conversion degree for both crosslinking and thermal degradation processes as well as from the shape of the DSC and DTA curves, it can be accepted that both processes occur in multi-step kinetics. The multivariate linear regression method (MLR) from “Thermokinetics-3” software, allows estimating the most probable thermal mechanisms associated with the bio-based thermosets.

Acknowledgment

This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PN-III-P1-1.1-TE-2019-0604, within PNCDI III

Thermal, morphological and rheological properties of the MRF122 magnetorheological fluid

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Magneto-rheological fluids (MRF) are composite materials in the form of suspensions of micron-sized magnetic particles, dispersed in organic dielectric liquids, which possess remarkable properties, comparing them with other materials. Recent research on the properties of magneto-rheological fluids, performed with high-performance equipment, has led to their improvement and allowed their use in many applications. Much information about the behavior of fluids is obtained by thermal and rheological measurements. Data on changes in the viscosity of the rheological fluid, for a wide range of shear rates, and on the viscoelastic properties and some mechanical properties of the rheological fluid can be obtained using the Anton Paar rheometer. Thermal (using PerkinElmer DIAMOND TG/DTA), morphological and rheological measurements were performed on the MRF122 magneto-rheological fluid. The results of the thermal and rheological measurements are in Figures 1 and 2.

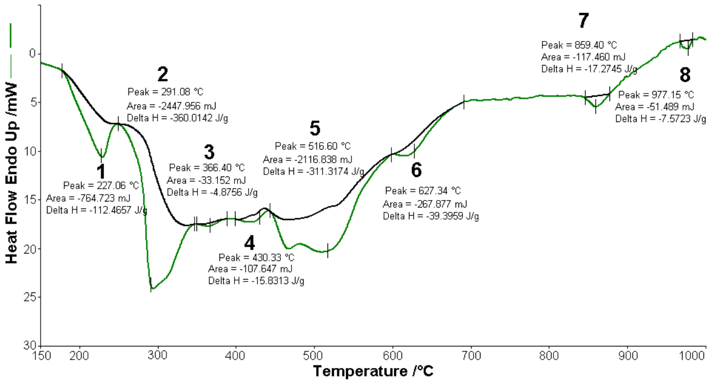

Fig.1 Thermal analysis of MRF122

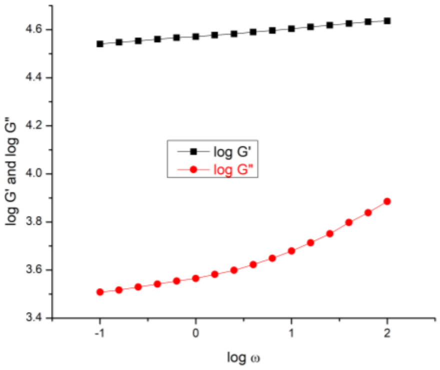

Fig.2 Log G' and log G" vs. log ω

Vaporization and decomposition of hydrocarbons, in which iron particles are suspended, occurs with a total exothermic effect (**1** and **2**) of -472.48 J g^{-1}. During the temperature range 349-445 °C, the iron structure is rearranged, with a minor exothermic thermal effect (**3**) of -4.88 J g^{-1}. From over 387 °C and up to 1000 °C the iron oxidizes and binds carbon dioxide, with the accumulation of exothermic effects **4-8**, at the values of -391.39 J g^{-1}. Over the entire temperature range analyzed, the total thermal effect was -868.75 J g^{-1}.

For MRF122, G' > G" over the whole angular frequency range, which confirms its non-Newtonian fluid behavior, well organized at the microscopic level. Representation of Storage modulus (G') and of Loss modulus (G") according to Angular frequency (ω) indicates that the elastic properties of MRF122 increase as the angular frequency increases, in the same way as the tangent of the loss factor (tan δ) increases.

Thermal, morphological and rheological properties of the energized MRF122 magnetorheological fluid

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Based on the ability of magnetorheological fluids to change their viscosity when a magnetic field or external action is applied to them, the ability to provide a response in a short time, the reversibility and redispersibility of suspended particles, magnetorheological fluids can be used in applications of braking or clutch, of transmitting force or torque in valves, of damping vibrations in car shock absorbers, in the manufacture of medical devices such as orthopedic joints, in industrial devices such as hyper-redundant arms, etc. The characterization thermal and rheological of the magnetoreological fluid is essential for the choice of the appropriate fluid for the application and for the optimization of the properties of the rheological fluid for later use.

The sample was prepared by "energizing" the magnetoreological fluid MRF122. The energization consisted in exposing the fluid, for 5 days, in a magnetic field of magnetic induction B = 0.37 T, produced by a permanent ferrite magnet. At 2 hour intervals the fluid container was stirred vigorously for rehomogenization. Energized MRF122 sample was investigated with a horizontal DIAMOND TG/DTA/DSC programmable device from PerkinElmer Co. by heating with 10 °C min^{-1} from room temperature up to 1000 °C under dynamic air atmosphere (150 cm^3 min^{-1}). The rheological properties of the energized fluid MRF122 were determined with Magneto-Rheological Device: TwinGap ™ Geometry (MRD / TG), from Anton Paar Comp. In Figures 1 and 2 are only two examples of results of thermal and rheological measurements.

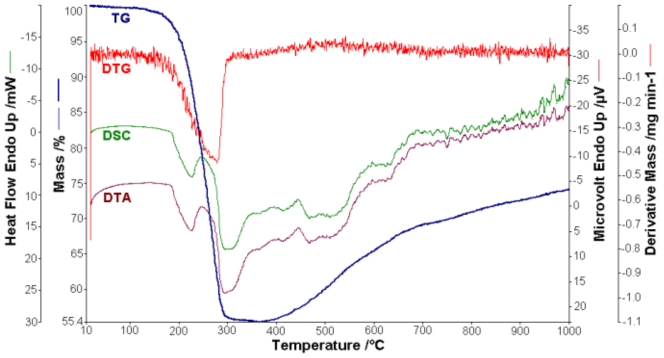

Fig. 1 Thermoanalytical curves of energized MRF122

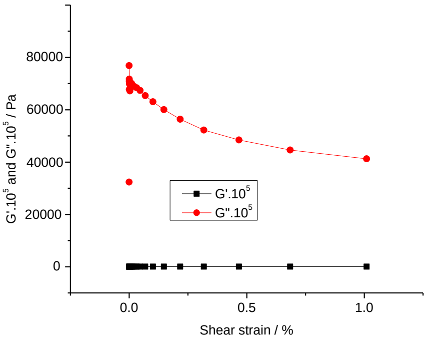

Fig. 2 G’ and G” for energized MRF122

Because G” is much larger than G’ the energized MRF122 sample deviates from the ideal fluid behavior. In energized MRF122 the plastic properties predominate, to the detriment of the elastic ones (non-Newtonian fluid).

Core–shell structured $Fe_3O4@SiO_2@OSO_3H$ magnetically recoverable nanocatalyst for the synthesis of glycerol acetals

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Recent developments in the scientific world have been increasingly interested in nanotechnology for the last decades [1]. Magnetite nanoparticles as a class of nano-sized materials have received great attention due to their wide range of usages in various fields such as medical applications, drug delivery, remediation, catalyst, industry [2].

Magnetite nanoparticles supported silica sulfonic acid ($Fe_3O_4@SiO_2@OSO_3H$) catalyst was successfully designed and synthesized, being characterized and confirmed by different techniques such as FT-IR spectroscopy, scanning electron microscopy, X-Ray diffraction, X-Ray fluorescence spectroscopy and Dynamic light scattering (DLS). The application of $Fe_3O_4@SiO_2@OSO_3H$ as an efficient catalyst in the synthesis of glycerol acetals was evaluated by the reaction of furfural and glycerol, under solvent-free conditions with high yields. $Fe_3O_4@SiO_2@OSO_3H$ nanocatalyst was readily recovered using an external magnet and could be reused several times without significant loss of its reactivity.

[1] M. Abboud, S. Youssef, J. Podlecki, R. Habchi, G. Germanos, A. Foucaran, Mat. Sci. in Semicon Proc, 39 (2015) 641-648
[2] M. A. Ghasemzadeh, Quim. Nova, 40, 1 (2017) 47-53

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Preparation of Fe_3O_4/PVA magnetic nanofibers via electrospinning composite processing

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Magnetic nanoparticles (MNPs) have attracted a great deal of interest because of their potential for different applications including many important catalytic processes [1], fuel cell, targeted drug delivery, water treatment [2], but they are prone to agglomerate, diminishing their activities. Magnetic fibers has attracted more and more attention because of the large surface area and overcoming the disadvantages of easy agglomeration and difficult separation.

This study is focused on preparation of composite fibers of uniformly dispersed Fe_3O_4 MNP in polyvinyl alcohol (PVA) via electrospinning technique and by combining in-situ composite method with electrospinning technology. The morphology and stability of the fibers were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), thermogravimetric analysis (TGA) and BET.

This work provided a versatile strategy for further design and development of magnetic nanofiber-nanoparticle composites towards various applications.

[1] K. Yi, A. Lin, M.T. Yang, J.T. Lin, Y.Du, Chemosphere, 208 (2018), 502-511
[2] S. Shi, C. Xu, X. Wang, Y. Xie, Y. Wang, Q.Dong, L. Zhu, G. Zhang, D. Xu, Mat. Des. 186 (2020) 108298

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Thermal decomposition of some chemotherapeutic drugs as gemcitabine and paclitaxel

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Thermogravimetry, differential thermal analysis and differential scanning calorimetry (TG/DTA and DSC) are widely used thermal analysis techniques for qualitative and quantitative drugs or other organic compounds characterization [1-3]. Solid state reactions and decomposition reactions of Gemcitabine (GCT) and Paclitaxel (PTX), two chemotherapeutic drugs, were studied by thermal analysis.

A Diamond Thermogravimetric/Differential Thermal Analyzer (TG/DTA) Perkin Elmer was used. All tests were performed under identical conditions; small drug samples (2-4 mg) were introduced into the work platinum crucible and heated from room temperature (*RT*) to 1000 °C, under atmospheric pressure with a heating rate of 10 °C $\mathrm{min^{-1}}$. The decomposition processes were carried out in dynamic inert atmosphere of nitrogen gas, this atmosphere was ensured by purging the nitrogen gas in the circuit at a constant flow of 150 $\mathrm{cm^3}$/min. [1-3].

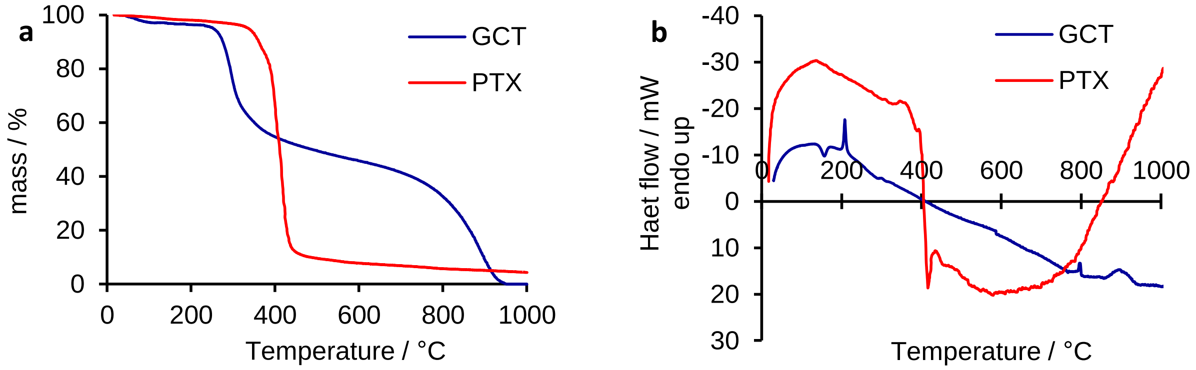

Figure 1: Thermoanalytical curves (a-TG and b-DSC) recorded for Gemcitabine (GCT) and Paclitaxel (PTX) chemotherapeutic drug.

Thermal behavior of the two drugs is quite different implying both, mass loss and calorimetry. TG and DSC of GCT and PTX indicate that the melting point occurs with mass loss. Most likely, this thermal effect is due to the evaporation of water present as moisture [1-4]. In the case of GCT there are two decreases in mass in the temperature ranges 220-350 and 750-920 °C while PTX shows a single mass loss in the temperature range of 350-430 °C. The calorimetric results obtained contributed to the development of a mechanism of thermal degradation of drugs.

[1] A. Samide, B. Tutunaru, J. Therm. Anal. Calorim., 127 (2017) 597
[2] A. Samide, B. Tutunaru, J. Therm. Anal. Calorim., 127 (2017) 863
[3] A. Samide, G.E. Iacobescu, B. Tutunaru, S. Iordache, J. Therm. Anal. Calorim., (2021) DOI: 10.1007/s10973-020-10444-0

Study on thermal and electrochemical stability of Captan fungicide

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Pesticides are widely used in agriculture and the food industry, but their usefulness can also have negative effects on the environment and thus on human health. Consequently, the analysis of pesticides and their degradation / elimination is a matter of global interest. Captan is a fungicide used to control diseases on some fruits and vegetables and was cited by US Environmental Protection Agency as o probable human carcinogen. Thermal and electrochemical stability of Captan (® 80 WDG) fungicide was studied.

Thermoanalytical curves of Captan were obtained using a Diamond Thermogravimetric/ Differential Thermal Analyzer (TG/DTA), Perkin Elmer. All tests were carried out under atmospheric pressure conducted by Pyris software. An small amount of 2-4 mg from sample were heated between room temperature (RT) and 600 °C, at a heating rate of 10 °C/min. [1-4]. Work and reference crucibles were identical and manufactured from platinum. The decomposition processes were carried out in dynamic inert atmosphere by purging the N_2 gas at a constant flow of 150 cm^3/min. [1-4].

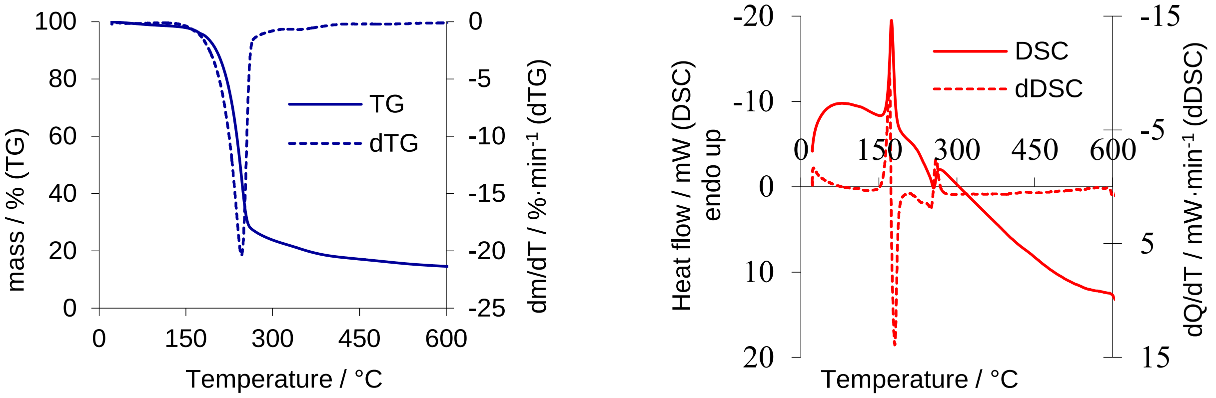

Figure 1: Thermoanalytical curves (a-TG/dTG and b-DSC/dDSC) recorded for Captan fungicide.

The results obtained by thermal analysis indicate a significant decrease in the mass, at temperatures higher than 175 °C. The DSC analysis shows an endothermic effect at 173 °C corresponding to the melting point of Captan. At temperatures above 175 °C, both TG and DSC analysis indicate pyrolysis of the pesticide molecule. The presence of the exothermic effect at 255 °C (DSC curve) indicates the pyrolysis of thermal degradation intermediates, at the experiment final (600 °C), when a residue about of 15% remained.

[1] A. Samide, B. Tutunaru, J. Therm. Anal. Calorim., 127 (2017) 597
[2] A. Samide, B. Tutunaru, J. Therm. Anal. Calorim., 127 (2017) 863
[3] A. Samide, B. Tutunaru, C. Merisanu, N. Cioatera, J. Therm. Anal. Calorim., 142 (2020) 1825
[4] A. Samide, G.E. Iacobescu, B. Tutunaru, S. Iordache, J. Therm. Anal. Calorim., (2021) DOI: 10.1007/s10973-020-10444-0

Thermal behaviour and fungal protection of composites based on wood and natural and synthetic epoxy resins cured with a rosin acid derivative

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Novel biocomposites were designed through the thermal curing of diglycidyl ether of bisphenol A (DGEBA)/epoxidized vegetable oils (EO) (grapeseed, soybean, corn)/ maleopimaric acid (MPA) in the presence of triethylbenzylammonium chloride (TEBAC) and coated on wood surface. The curing agent was a rosin acid derivative. The biocomposites were characterized in terms of coating properties, chemical resistance, thermal stability and non–isothermal degradation kinetics, morphological study and behaviour to microbiological exposure. The results demonstrated that all coatings showed increased hardness and very good adhesion to the substrate.

The thermal degradation of the coatings and biocomposites (WECs) was conducted with the aid of thermogravimetric analysis (TGA). Global non–isothermal degradation parameters were determined. By observing the shape of the activation energy curves as a function of conversion, it was shown that the samples undergo a complex thermal decomposition process occurring in a minimum of two stages through successive or parallel reactions. For the anti–fungal testing of the WECs there were used the strains of *Aspergillus brasiliensis, Penicillium chrysogenum* and *Cladosporium cladosporioides*. The monitoring of the crystallinity index values of coated and non–coated wood was made with wide angle X–ray diffractometry (WAXD). It was demonstrated that coated wood presented enhanced thermal stability and anti–fungal resistance due to the coated wood surface blocking moisture and fungi access. Mass loss and moisture increase depended on fungi nature and were significantly higher for the untreated wood. The fungal attack led to a decrease in the cristallinity index for the non–coated wood. For the coated wood the increase in crystallinity index was much lower due to polymer mass loss.

Acknowledgment

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Investigation of hydration thermodynamics by differential scanning calorimetry

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The present work was aimed at the calorimetric investigation of hydration thermodynamics of different materials, such as natural zeolites, BaZr1–xYxO3–x/2 and BaCo1–x*RE*xO3–δ (RE – rare-earth element).

Calorimetric measurements were performed with an original heat-flux differential scanning calorimeter (DSC). The calorimetric cell consisted of two identical alumina crucibles with a thermopile in the form of 16 (8 on each crucible) K-type thermocouple junctions rigidly mounted on crucibles' sides. Two platinum crucibles, one of which empty and another one containing around 0.5 g of sample, were inserted into the alumina ones. The calorimetric cell was then placed in a furnace and held at a given temperature in 50 ml/min flow of dry ($\lg(pH_2O)=-4.0$ atm) gas for at least 48 h to achieve equilibrium water content in the sample. The inlet gas was dried by passing it through the column with pre-annealed zeolites. The enthalpies were measured during the sample hydration, which followed the abrupt switching of the feed gas flow from dry to wet ($\lg(pH_2O)=-1.8$ atm) gas. The humidification of the dry gas, resulting in the wet gas flow with stable humidity, was performed by passing it through the water inside a small Peltier-controlled thermostat. The particular values of water vapor partial pressure before and after the switching experiment were measured with factory-calibrated SHT31 (Sensirion, Switzerland) relative humidity sensors. The sensors were mounted on a Peltier element to control their temperature, significantly enhancing their humidity measurement range. The DSC hydration experiment was repeated, at least, 3 times at each temperature. The heat sensitivity of DSC setup was calibrated using standard metals' heats of fusion in scanning mode with various heating rates, and the sensitivity coefficient extrapolated to zero heating rate was used to calculate the heat of hydration.

Temperature-dependent equilibrium water content in samples in dry and wet atmospheres was measured by thermogravimetry using CI Precision (UK) microbalances.

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Thermal analysis of Co-Zn ferrite synthesis from milled powders

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Cobalt-zinc ferrite $Co_{0.5}Zn_{0.5}Fe_2O_4$ (Co-Zn) is a soft magnetic ferrite. Because of its excellent magnetic and electrical properties, it is widely used in different electrical devices such as generators and transformer cores. Magnetic properties of spinel ferrites depends on many parameters, such as morphology, especially from crystallite size, so in biomedical and modern data storage application we need to closely control the particles morphology and decrease their size[1].

The solid state synthesis is conventional way to produce ferrites, which involves the formation of single-phase product (via solid-state reaction between oxides). Because of complex composition of reaction mixtures, repeated alternation of grinding and thermal treatment operations is often performed for completeness of solid-phase reactions, thereby significantly increasing the time of synthesis. Moreover, low temperature techniques such as chemical co-precipitation and hydrothermal synthesis were used by some researchers to obtain the Co-Zn ferrites. However, these chemical methods contain a large number of parameters, including: pH, reaction time, atmosphere, temperature, reaction rate, washing and drying methods, etc., which must be controlled during the synthesis of the powder. It is known, that high-energy planetary mills widely used such as the perspective method to increase the reactivity of reagents in initial mixtures. Moreover, it was shown, that the mechanical activation initial mixture in high-energy mills makes it possible to obtain ferrite materials with a homogeneous phase composition. In addition, the use of mechanical activation increases the rate of solid-phase interaction reactions in the production of ferrite materials [2, 3].

In this study, the formation of spinel phase of $Co_{0.5}Zn_{0.5}Fe_2O_4$ from mechanically milled mixture (Fe_2O_3-ZnO-Co_3O_4) was investigated. The initial mixture was milled with using the Retsch E_{max} high energy ball mill at different regimes. XRD analysis of initial and synthesized mixtures was studied by powder diffractometer ARL X'TRA (Switzerland). The formation of spinel phase was detected by thermomagnetometry method, which is thermogravimetric analysis in magnetic field. Thermal analysis of the samples was carried out using analyzer STA 449C Jupiter (Netzsch, Germany). It was established that preliminary ball milling of the initial reagent mixture allows to accelerate the solid-phase reactions. Moreover, the magnetization of the samples increases with an increase in the rotation speed of vials, milling time and diameter of the milling balls.

This research was supported by the Russian Science Foundation (Grant no. 19-72-10078).

[1] M. Noor Ismai, M. Hashim, A. Hajalilou, I. Ismail, M. Zulkimi. J. Supercond. Novel Magn. 27 (2014) 1293–98.
[2] N. Obradović, W.G. Fahrenholtz, S. Filipović, S. Marković, V. Blagojević, S. Lević, S. Savić, A. Dordević, V. Pavlović. J. Therm. Anal. Calorim. 140 (2020) 95-107.
[3] T.T. Parlak, F. Apaydin, K. Yildiz. J. Therm. Anal. Calorim. 127 (2017) 63-9.

Investigation of interactions in the mechanically activated Fe_2O_3-Li_2CO_3 reagents by thermal analysis

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Fe_2O_3 and Li_2CO_3 powders are of considerable interest for electronic engineering for the production of ferrites with various target functions, catalysts, solid-phase oxide electrodes, etc.

When Fe_2O_3-Li_2CO_3 powder mixture is heated, a solid-phase interaction of lithium carbonate and iron oxide occurs. This process starts at a temperature 200 °C lower than the melting point of Li_2CO_3 (725 ° C), since iron oxide reduces the decomposition temperature of lithium carbonate. As the temperature rises to 900 °C, the formation of lithium ferrite $Li_{0.5}Fe_{2.5}O_4$ occurs when a molar ratio of 5:1 in the Fe_2O_3-Li_2CO_3 is used [1].

Mechanical grinding of reagents in ball mills is widely used in the manufacture of ferrite materials. At the same time, during the grinding process, the powder reagents are activated depending on the processing conditions, including the grinding medium, the material and diameter of grinding balls, and the rotation speed of vials. The study of the effect of mechanical activation on the reaction of lithium ferrite formation showed that the initial temperature of Fe_2O_3-Li_2CO_3 interaction is greatly reduced, which makes it possible to synthesize ferrites at a temperature of 600 °C [2, 3].

In this work, a TG/DSC analysis of Fe_2O_3-Li_2CO_3 mixture preliminarily milled using different energy intensities was carried out. The formation of the magnetic ferrite phase was controlled by TG analysis in a magnetic field. It was found that the reactivity of the initial reagents depends on the energy intensity of the grinding. With an increase in the rotation speed of vials from 1290 rpm to 2220 rpm, the end temperature of the reaction shifts to the region of lower temperatures. In this case, the magnetization of the powder mixture increases due to the formation of the ferrite phase in a large amount during heating in the oven of the thermal analyzer.

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[1] V. Berbenni, A. Marini, P. Matteazzi, R. Ricceri, N.J. Welham, J. Eur. Ceram. Soc., 23 (2003) 527–536.
[2] E.N. Lysenko, E.V. Nikolaev, A.P. Surzhikov, S.A. Nikolaeva, I.V. Plotnikova J. Therm. Anal. Calorim., 138 (2019) 2005–2013.
[3] E.N. Lysenko, E.V. Nikolaev, V.A. Vlasov, A.P. Surzhikov, J. Thermochimica Acta, 664 (2018) 100–107.

Thermal analysis of sintering Li-Ti-Zn ferrite from mechanically activated powders

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Ferrites belong to the category of promising magnetic materials. They are used in modern radio engineering and electronic devices. Moreover they are widely used as magnetic materials for circulators, high quality filters, rod antennas, and phased array elements [1]. Multicomponent $Li_{0.5+0.5t-0.5x}Fe_{2.5-1.5t-0.5x}Ti_tZn_xO_4$ (Li-Ti-Zn) ferrite has found application as discrete phase shifters due to its high initial permeability, high squareness of the hysteresis loop, low magnetic losses, and high electrical resistivity [2]. Traditionally, the manufacture of Li-Ti-Zn ferrite is carried out using the ceramic method, which includes sintering the synthesized powder at high temperatures to obtain high-density ferrite ceramics.

The mechanical activation of initial reagents prior to synthesis has been intensively studied. Here, the powder milling in a high-energy ball mill is used to increase the reactivity of the powders and to reduce the temperature of synthesis. As shown in [3], this procedure also allows to reduce the temperature of initial shrinkage of ferrite and accelerate its compaction during the sintering.

The aim of this study is to investigate the effect of ferrite powder mechanical activation on the sintering Li-Ti-Zn ferrite ceramics. For this, ferrite powder was prepared using different modes of mechanical processing. The mechanical activation of powder was carried out in a Retsch Emax ball mill using stainless steel vials and balls with different diameters (2 and 5 mm). The powder was divided into several parts and mechanically activated with different rotation speeds: 300, 600 and 1100 rpm. The mechanical processing time was 30 minutes. Then the powder was mixed with a 12% solution of polyvinyl alcohol and compressed into tablets with a diameter of 9 mm.

Sample compaction during the sintering was studied by the dilatometric analysis using a highly sensitive dilatometer DIL 402C. The samples were heated up to sintering temperature of 1010°C with a constant heating rate of 10°C/min. The bulk density of the samples was calculated before and after sintering.

It was found that the mechanical activation of the powder affects the sintering process of Li-Ti-Zn ferrite. The results from dilatometric analysis were used to determine the kinetic model and parameters of the sintering process. The calculated values of the kinetic parameters can be used to improve the technological process of sintering the multicomponent Li-Ti-Zn ferrite materials.

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[1] V. Verma, S.P. Gairola, V. Pandey, J.S. Tawale, H. Su, R.K. Kotanala. J. Magn. Magn. Mater. 321 (2009) 3808-3812.

[2] Dipti, P. Kumar, J.K. Juneja, Sangeeta Singh, K.K. Raina, Chandra Prakash. Ceram. Int. 41 (2015) 3293-3297.

[3] E.V. Nikolaev, E.N. Lysenko, A.P. Surzhikov, S.A. Ghyngazov, S.V. Bordunov, S.A. Nikolaeva. J. Therm. Anal. Calorim. 142 (2020) 1783–1789.

Thermal analysis of the lithium ferrite formation from $Sm_2O_3/Fe_2O_3/Li_2CO_3$ precursors

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Lithium and lithium-substituted ferrites are widely used in microwave and electronic technologies due to their good electric and magnetic properties. The studies of Li-ferrite substituted by different metal ions such as Ti, Zn, Ni, Mg, Mn, and Co were carried out by many researches. However, few studies resulted the effect of rare earth elements on properties of lithium ferrites were performed [1, 2]. At the same time, the introduction of rare earth elements, including Sm, can significantly affect the electro-magnetic properties of Li-ferrites.

It was shown in [2, 3], when Sm_2O_3 and Fe_2O_3 are used as raw materials for ferrite production, ferrite phases substituted with samarium and a certain amount of $SmFeO_3$ are formed as a result of the interaction of samarium oxide and iron oxide during synthesis. This conclusion was based on XRD analysis of samples. However, this control method is insufficient for correct phase analysis of the synthesized ferrites.

This study aims to investigate the effect of Sm additive on lithium ferrite formation by thermogravimetric (TG), differential scanning calorimetric (DSC) and X-ray diffraction analyses. $Sm_2O_3/Fe_2O_3/Li_2CO_3$ (4.7/87.1/8.2, 14.7/77.5/7.8 mass%) mixture was preliminarily mixed in a planetary mill. Both the raw reagents mixture and ferrite samples synthesized at 900 °C for 240 min were analyzed. TG/DSC measurements were performed using a STA 449C Jupiter thermal analyzer where the alumina crucibles and a heating rate of 10 °C/min were used. In addition, the magnetic ferrite phase formed was controlled by TG analysis in a magnetic field.

It was found that the heating of mixture leads to the formation of a two-phase product consisting mainly of $Li_{0.5}Fe_{2.5}O_4$ lithium ferrite and the $SmFeO_3$ phase, the amount of which depends on the content in the initial mixture. Thus, no substituted lithium ferrite phase is formed. The formation of pure lithium ferrite was confirmed by the Curie temperature measured using TG analysis in a magnetic field as well as by the presence of an endothermic peak at 750 °C on DSC curve, corresponding to the order-disorder transition in the $Li_{0.5}Fe_{2.5}O_4$ phase.

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[1] M.F. Al-Hilli, S. Li, K.S. Kassim, J. Magn. Magn. Mater. 324 (2012) 873–879.
[2] M. Mahmoudi, M. Kavanlouei, H. Maleki-Ghaleh, Powder Metallurgy and Metal Ceramics, 54(1-2) (2015) 31–39.
[3] S.S.R. Inbanathan, V. Vaithyanathan, J. Arout Chelvane, G. Markandeyulu, K. Kamala Bharathi, J. Magn. Magn. Mater. 353 (2014) 41–46.

Defect structure and thermodynamics of $RBaCo_2O_{6-\delta}$ (R = Sm, Eu) double perovskites

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The complex oxides $RBaCo_2O_{6-\delta}$ (R = Sm, Eu) belong to the family of A-site-ordered layered double perovskites. Since $EuBaCo_2O_{6-\delta}$ was found to possess giant magnetoresistance, it is more often subjected to magnetic properties investigations at low temperatures, whereas $SmBaCo_2O_{6-\delta}$, whose electrochemical performance is better, is regarded as a promising material for solid oxide fuel cell (SOFC) cathodes and oxygen-permeating membranes. This work is directed at filling some of the gaps in reported physicochemical properties of $RBaCo_2O_{6-\delta}$ (R = Sm, Eu), for which, so far, no data on either $pO_2 - T - \delta$ depencences, defect interactions, redox energetics or high-temperature thermodynamics are available.

$RBaCo_2O_{6-\delta}$ (R = Sm, Eu) powders were synthesized using the glycerol-nitrate technique with the final annealing temperature of 1373 K. Dense ceramic pellets that, when crushed, were used as samples for the drop calorimetry, were sintered at 1473 K. Phase-purity of the samples was confirmed by X-ray diffraction (XRD) with 7000S diffractometer (Shimadzu, Japan) in Cu Kα radiation.

The absolute oxygen nonstoichiometry in $RBaCo_2O_{6-\delta}$ (R = Sm, Eu) was found by reducing the samples at 1373 K in H_2/N_2 gas mixture in the thermogravimetric (TG) setup (STA 409, Netzsch, Germany). Equilibrium $pO_2 - T - \delta$ data was obtained between 623 K and 1023 K simultaneously with the values of the integral enthalpies of oxidation using Sensys 830 (Setaram, France), a symmetrical thermobalance coupled with Calvet-type differential scanning calorimeter. As a result, not only $pO_2 - T - \delta$ diagrams but also more than 30 distinct oxidation enthalpies at different T and $\Delta\delta$ were obtained for each oxide. For the first time, it was possible to fit the defect structure models for $RBaCo_2O_{6-\delta}$ (R = Sm, Eu) to either the thermogravimetric or the calorimetric data. Good agreement between the fitting results – the enthalpies and entropies of the defect interactions – was obtained; in other words, the defect structure models proposed were found to describe accurately both $pO_2 - T - \delta$ and the calorimetric data.

Finally, enthalpy increments were measured in the range (373 – 1273) K for $RBaCo_2O_{6-\delta}$ (R = Sm, Eu). The temperature dependences of the enthalpy increments showed the characteristic oxygen-exchange-related upward trend at higher temperatures. By subtracting the contribution of the oxide reduction, found using the defect structure models, from as-measured enthalpy increments, the increments for the constant-composition $RBaCo_2O_{6-\delta}$ (R = Sm, Eu) were obtained.

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Thermodynamic investigation of Te(IV) polybromides

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Tellurium halide complexes are of interest due to the variety of attractive physical properties of these compounds: luminescence, photochromism, semiconductor properties, etc. Recently, a family of polybromide complexes containing $\{Br\}^{n-}$ units was introduced [1-2]. Among them compounds, containing tetraalkylammonium cations $(Me_4N)_2\{[TeBr_6](Br_2)\}$ (**1**) and $(Et_4N)_2\{[TeBr_6](Br_2)\}$ (**2**), demonstrate the greatest stability. The octahedrons $\{TeBr_6\}$ are linked by bridging fragments $\{Br_2\}$ in the anionic part of these compounds (Fig. 1). The thermodynamic properties of these complexes have not been practically studied: only DTA/TG investigations have been carried out [2] which revealed their sufficient thermal stability up to 560 K.

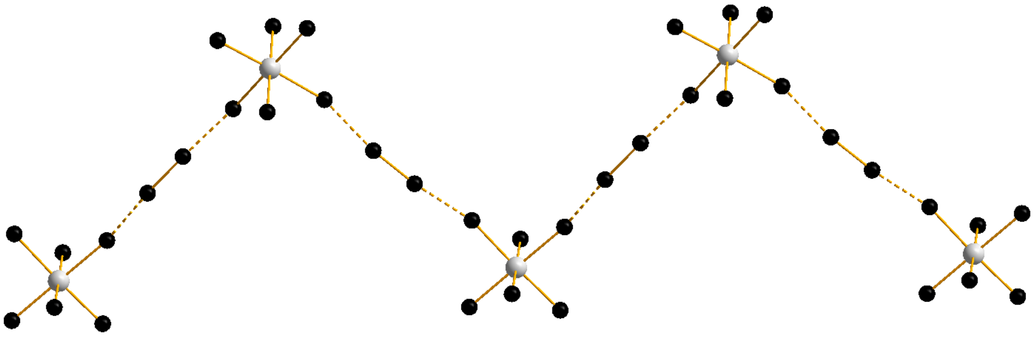

***Figure 1**. Structure of the anionic part in **1** and **2**. Te – grey, Br – black.*

Thermal behavior of these new complexes has been investigated by static method with glass (pyrex) membrane-gauge manometers [3]. The limiting uncertainties in measurement of pressure, temperature and solid phase composition on this set-up were 0.5 Torr, 0.5 K and 0.01 formula units, accordingly. The experiments have been carried out in the wide intervals of temperature ($298 \leq T/\mathrm{K} \leq 540$) and pressure ($0.3 \leq p/\mathrm{Torr} \leq 350$).

As a result of this study the fields of their thermal stability were established, the temperature dependences of bromine vapor pressure were obtained, the thermodynamic characteristics of the processes of Br_2 bridging fragments evaporation were calculated and the conclusions about the nature of interaction between bromine molecules and a matrix are made.

[1] A. Usoltsev, S. Adonin, A. Novikov, D. Samsonenko, M. Sokolov, V. Fedin. Cryst. Eng. Com. 39 (2017) 5934.
[2] A. Usoltsev, S. Adonin, P. Abramov, A. Novikov, V. Shayapov, P. Plyusnin, I. Korolkov, M. Sokolov, V Fedin, Eur. JIC. 27 (2018) 3264.
[3] L. Zelenina, T. Chusova, S. Sapchenko, E. Ukraintseva, D. Samsonenko, V. Fedin, JCT. 67 (2013) 128.

A thermogravimetric and DFT study of silver molybdate reduction by hydrogen

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Silver molybdate (Ag_2MoO_4) is a complex oxide composed from equimolar amounts of one easily reducible (Ag_2O) and one hardly reducible (MoO_3) component, Its thermally induced reduction in hydrogen atmosphere proceeds according to the equation:

$$Ag_2MoO_4 + 4H_2 = 2Ag + Mo + 4H_2O$$

and its final reduction product is a composite mixture of two mutually insoluble metals, Ag and Mo [1].

Having in mind that the formation of surface oxygen vacancies precedes the formation of H_2O molecules and, consequently, influences the reduction kinetics, we calculated the energy of oxygen vacancy formation ($E_f(O)$) in Ag_2O (3.37 eV), β-Ag_2MoO_4 (5.54 eV), MoO_3 (5.82, 6.99 and 5.74 eV) and MoO_2 (7.89 and 7.95 eV). For these calculations, Quantum ESPRESSO software and the equation

$$E_f(O)= E_{bulk} – E_{vac} - E_{isol}$$

were used, where E_{bulk} is computed total energy of bulk crystal, E_{vac} is computed total energy of crystal with one oxygen vacancy and E_{isol} is computed total energy of an isolated oxygen atom. A much stronger bonding Ag-O-Mo in Ag_2MoO_4 than Ag-O-Ag in Ag_2O implies significant retardation of reduction kinetics of Ag_2MoO_4 against that of Ag_2O, i.e. an almost simultaneous formation of Ag and MoO_2 at temperatures close to that of pure MoO_3 reduction.

To prove these predictions experimentally, we performed thermogravimetric investigations of Ag_2MoO_4 reduction in hydrogen stream (25 vol.% H_2 in Ar) at various heating rates (2.5-50 °C/min) within the temperature interval 25 – 1000 °C. The sample was synthesized by precipitation from neutral aqueous solution of silver nitrate and ammonium molybdate. The stable cubic β- structure of obtained Ag_2MoO_4 was evidenced by XRD.

At low heating rates (below 10 °C/min), the TG curves show that the reduction of Ag_2MoO_4 starts very close to the initial temperature of Ag_2O reduction, and the mass loss due to the water liberation looks like an almost monotonous process, similarly to that found elsewhere [2]. At high heating rates (equal to or higher than 10 °C, the reduction became more obviously a multi-step process, like to that predicted by DFT calculations. This means that not only vacancy formation, but also other factors, like catalysis by metallic Ag, or kinetics of phase transitions in solid state, should be considered too, in order to explain correctly the thermogravimetric behaviour of the observed system.

[1] J. Stolk and A. Manthiram, Metall. Mater. Trans. A, 31A (2000) 2396–98.
[2] J.C. Juarez and R. Morales, Metall. Mater. Trans B, 39B (2008) 738-745,

Thermal stability and antimicrobial properties of pure and modified pyrophyllite (PYRO/Ag) clay

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Clays, inorganic materials with a layered structure, possess good chemical inertness and biocompatibility, low toxicity, and have excellent physicochemical properties. They are widely used as pharmaceutical excipients and active substances. In recent years, clay minerals proved to be very interesting for the delivery of drugs. There are some reports that clay improves the stability of drugs, or even prevents or reduces side effects. For stability assessment, the thermal stability of clay is of great importance. The focus of this investigation is a potential pharmaceutical application of pyrophyllite clay, an alumosilicate mineral, $Al_2Si_4O_{10}(OH)_2$, that belongs to the same sub-clay group as talc, $Mg_3Si_4O_{10}(OH)_2$. In order to explore potential pyrophyllite application in the pharmacy field, having in mind talc problems associated with asbestos, thermal properties along with antimicrobial ones were tested. Simultaneously TGA/DTA was employed for thermal decomposition of pyrophyllite clay in dynamic (non-isothermal) regime with the following heating rates: 5, 15, and 30 °C/min in neutral (N_2) atmosphere. Detailed kinetic analysis, both isoconversional and model-fitting one, was performed. Pyrophyllite clay decomposition proved to be a two-step process. The first step presents dehydration process best described with nucleation and growth model (Ea=156,8 kJ/mol, A= $1.1416 \cdot 10^{12}$ s^{-1}, m=0.441 and n=1.073). It must be stressed that a strict separation between the first and second degradation stages does not exist, because the second stage almost continuous outputs from the first stage. The second stage is best described with distributive energy models (Discrete: Ea=177,4 kJ/mol, A=$5.9725\cdot10^8$ s^{-1} and Gaussian: Ea=209 kJ/mol (46.9%), 188 kJ/mol (26.92%), 175 kJ/mol (26.18%), A=$6.502\cdot10^9$ s^{-1}). Antimicrobial activity was tested on pure (PYRO) and modified pyrophyllite with silver (PYRO/Ag). Modified PYRO/Ag showed improved antimicrobial properties, providing sterile conditions against *Staphylococcus aureus* ATCC 25923 and *Escherichia coli* ATCC 25922. The minimum bactericidal concentration (MBC) of Ag was found to be 25 mg/ml. Ministry for Scientific and Technological Development, Higher Education and Information Society of Republic of Srpska supported this study (project No. 19.032/961-78/19).

[1] L.A. Rodrigues, A. Figueiras, F. Veiga, R. Mendes de Freitas, L.C.C. Nunes, E.C. Filho, C. M. Leite, Colloids and Surfaces B: Biointerfaces 103 (2013) 642–651
[2] J.K. Kang, C.G. Lee, J.A. Park, S.B. Kim, N.C. Choi, S.J. Park, Environ. Technol. 34, 2013, 703-710

Thermal characterisation and valorisation of cement kiln dust for production of traditional ceramic materials

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Cement kiln dust (CKD) is a by-product of manufacturing of Portland cement, generated during the calcination process. This material is composed mostly of calcite, free lime, and other compounds such as SiO_2, Al_2O_3, MgO, and Fe_2O_3. Moreover, the contemporary usage of alternative fuels and wastes adds compounds with relatively high chloride content, as well as SO_3 and K_2O to the CKD mixture. From the aspect of sustainability and environmental impact, the science is urged to provide improved understanding of the potentials and offer tailored solutions for alternatives of CKD utilisation.

The aim of the research presented in this paper was to evaluate solutions for CKD reuse as a secondary raw material for environmental-friendly building materials (lightweight aggregate, bricks, and ceramic roofing tiles). It included the chain of activities: thermal and chemical-mineralogical characterisation, evaluation, and valorisation of the CKD potentials to be used as raw material for novel lightweight aggregates, bricks, and ceramic roofing tiles.

The results obtained include in-depth knowledge about the CKD with relevant details considering its chemical-mineralogical and morphological characteristics, particle size distribution, and potential dangers to human health and the environment. In the next step the research explored approaches to valorisation of the CKD in the production of traditional building materials. Different approaches were identified; however, some of them are time consuming or too expensive.

This paper presents a promising technology of lightweight ceramic aggregate production using combination of CKD (up to 30 mass %) with clay material and appropriate melting agent. Formation of new phases during the thermal treatment was followed by thermo-gravimetry with mass spectroscopy (TG-MS), and by DSC analyses of the CKD up to 1000°C. Based on the thermal characterisation, the maximal temperature of thermal treatment was set at 800°C as frontier parameter aiming not to exceed the temperature of the salt decomposition which could lead to release of harmful gasses to the atmosphere. The final products characteristics were evaluated, including thermal expansion, weight loss, porosity, microstructure, compressive strength, changes of morphology and colour, as well as leaching of soluble salts.

Key words: Cement kiln dust, environmental impact, thermal treatment, new phases, ceramic materials

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Study of bioactive glasses doped with Li_2O by thermal methods

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In the past, the basic research of glass and its applications was mainly concentrated on silicate and chalcogenide glasses. Nowadays, however, phosphate glasses are also very intensively studied, especially bio-glasses [1]. Bio glass can also be doped with various amounts of elements such as copper, zinc, or strontium, that facilitate the growth and formation of healthy bones [2]. An important characteristic of the glass phase is its behavior (so-called relaxation) near the glass transformation temperature, when the driving force of the ongoing processes is the effort of the system to reach the equilibrium state from which it was deflected by the previous temperature history or by the external forces.

Thermal properties were studied on bioglasses ($Na_2O \cdot CaO \cdot P_2O_5 \cdot SiO_2$) doped with Li_2O. The composition of prepared glasses was determined by XRF. The corresponding structural information was obtained by means of Raman spectroscopy. The base glass transition characteristics – coefficients of thermal expansion in glass and undercooled liquid α_g and α_l, difference between the heat capacities of glass and undercooled liquid Δc_p, and glass transition temperature T_g – were determined using the thermomechanical analyser (TMA) and differential scanning calorimetry (DSC). Main focus of the present study was the description of the enthalpy relaxation in terms of the Tool-Narayanaswamy-Moynihan (TNM) model [3]. Constant ratio and constant heating rate DSC cyclic experiments were used to determine the activation energy of the enthalpy relaxation processes Δh^*. In addition, the newly developed simulation-comparative method was used to estimate the non-linearity (x) and non-exponentiality (β) TNM parameters. Consequently, the compositional dependences of the TNM parameters were interpreted in regard to the structural information.

[1] F. Baino, S. Hamzehlou, S. Kargozar: Bioactive glasses: Where are we and where are we going? Journal of Functional Biomaterials 2018, 9 (1), 25.
[2] Rahaman, M (2011). "Bioactive glass in tissue engineering". Acta Biomaterialia. 7 (6): 2355–2373. doi:10.1016/j.actbio.2011.03.016. PMC 3085647. PMID 21421084.
[3] C. T. Moynihan, A. J. Easteal, M. A. DeBolt, J. Tucker, J. Am. Ceram. Soc. 59 (1976) 12.

Thermodynamic model and identification of the surface-active components of barium crystal glass

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Surface tension of 15 glassforming melts with the composition derived from the barium crystal glass ($10.49\ Na_2O\cdot 2.36\ K_2O\cdot 9.06\ CaO\cdot 0.78\ ZnO\cdot 2.44\ BaO\cdot 0.85\ Al_2O_3\cdot 74.02\ SiO_2$) by increasing/decreasing the content of each oxide was measured by the sessile drop profile analysis. The drop profiles recorded at 1190°C were analysed by the numerical integration of Laplace's equation using the experimentally determined melt density [1-2]. It was found that the surface tension is significantly decreased by increasing the content of K_2O, ZnO, Al_2O_3, and SiO_2.

The Shakhmatkin and Vedishcheva thermodynamic model (TDM) [3] was evaluated for each glass melt at the glass transition temperature. The total number of 58 components was considered in TDM. Only 23 components were present with not negligible equilibrium amount. The surface-active components (i.e. components that decrease the surface tension) were identified by correlation analysis, by the statistically significant negative value of particular correlation coefficient. Finally, the surface tension was approximated by multilinear function of equilibrium amounts of statistically independent not negligible components of the TDM.

[1] J. Hlavač, Glass Science - The Technology of Glass and Ceramics, Elsevier S.Co. (1983).

[2] M. Chromčíková, B. Hruška, R. Svoboda, M. Liška, A. Nowicka, E. Bruneel, K. De Buysser: Identification of surface active components in glass forming melts by thermodynamic model, J. Non-Cryst. Solids. 551 (2021) 120415.

[3] B.A. Shakhmatkin, N.M. Vedishcheva, M.M. Shultz, A.C. Wright, The thermodynamic properties of oxide glasses and glass-forming liquids and their chemical structure, J. Non-Cryst. Solids. 177 (1994) 249–56.

Relation of the phase change temperature of polycrystalline PCMs to the profile of heat capacity peaks

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We developed a theoretical description of enthalpy, h, and heat capacity, c_p, of phase change materials (PCMs) [1] in which a change between two phases is used to store/release thermal energy. The description uses results of a rigorous statistical mechanical theory of first-order phase transitions [2]. We were able to fit experimental data on the jumps and peaks that h and c_p exhibit near such a phase change. In addition, it was possible to separate the sensible heat from the latent heat of the phase change. We applied the results to three selected PCMs for which thermal hysteresis and supercooling were absent and the measurements were carried out in quasi-equilibrium conditions (i.e., kinetic effects were negligible) by adiabatic scanning calorimetry. Even for PCMs with such a plain behaviour, h and c_p show a jump and peak that are not infinitely sharp but of finite width (i.e., a mushy region is distinct). Therefore, we interpreted them as purely equilibrium (finite-size) effects that occur in PCMs due to their ‘polycrystalline’ microstructure.

We have proposed an improved version of this description [3] with the aim to plausibly determine the temperature of a phase change. However, the results are calculated in a numerical form. A better understanding of the problem would require to develop explicit mathematical relations between the considered quantities that would be applicable at least in special cases. This is the goal of this contribution. The main result is a relation for the phase change temperature whose predictions for the three PCMs are compared with the values obtained in [3] by numerical calculations.

[1] I. Medved, A. Trnik, L. Vozar, Int. J. Heat Mass Transf. 107 (2017) 123-132.
[2] C. Borgs, R. Kotecky, J. Stat. Phys. 79 (1995) 43-115.
[3] I. Medved, M. Jurci, A. Trnik Int. J. Heat Mass Transf. In preparation.

Effect of the powder processing methods on the densification behaviour, grain growth and mechanical properties of zirconia toughened alumina

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Zirconia and alumina – based ceramics are commonly used in the manufacturing of biomedical implants due to their outstanding strength, wear resistance, and biocompatibility [1,2]. Among several different types of ceramics, zirconia toughened alumina (ZTA) have demonstrated their effectiveness for orthopedic applications [1]. However, several variables like initial powders' characteristics and processing of ZTA ceramics can affect the microstructure, mechanical performance and the lifetime of ZTA ceramics [1,3,4]. In this work, the effects of powder processing methods, mixing commercial powders vs coprecipitation methods, stabilizing dopant and zirconia's particle size on the densification behavior, grain growth, and fracture toughness have been studied. The role of powder properties on the tetragonal to monoclinic phase transformation of zirconia upon fracture has been investigated and critically discussed.

[1] V. Naglieri, Paola Palmero, L. Montanaro, J. Chevalier, "Elaboration of Alumina-Zirconia Composites: Role of the Zirconia Content on the Microstructure and Mechanical Properties", Materials, 6 (2013) 2090-2102.
[2] P. Tan, Y. Yang, Y. Sui, Y. Jiang, "Influence of CeO_2 addition on the microstructure and mechanical properties of Zirconia-toughened alumina (ZTA) composite prepared by spark plasma sintering", Ceramics International, 46 (2020) 7510-7516.
[3] H. L. Calambás Pulgarin, M. P. Albano, "Three different alumina–zirconia composites: Sintering, microstructure and mechanical properties", Materials Science and Engineering: A, 639 (2015) 136-144.
[4] E. B. Benalcazar Jalkh, K. Nunes Monteiro, P. Francisco Cesar, L. Antonio Genova, E.T.P. Bergamo, A. Coelho de Oliveira Lopes, E. Lima, P. Noronha Lisboa-Filho, T. Moreira Bastos Campos, L. Witek, P. G. Coelho, A. Flavia Sanches Borges, E. A. Bonfante, "Aging resistant ZTA composite for dental applications: Microstructural, optical and mechanical characterization", Dental Materials, 36 (2020) 1190-1200.

Study of thermal properties of nanocomposite inorganic-organic xerogels based on TEOS and OTES precursors

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The hybrid, inorganic-organic materials represent the materials which combine properties of inorganic and organic components [1]. For preparation of hybrid materials, the sol-gel method is very suitable, because it can use the nano building blocks (NBB) approach for the controlling of reactions of hydrolysis and condensation of precursors, such as alkoxides and mono-substituted organo-alkoxysilanes [2, 3]. For achievement of the desired properties of hybrid materials, it is needed to understand and observe which processes take place during thermal treatment of these materials.

Nanocomposite inorganic-organic xerogels, dried at 80 °C, were prepared from sol in "tetraethoxysilane - triethoxy(octyl)silane - distilled water - nitric acid - isopropyl alcohol" system. Using NBB approach, six sols were prepared by three different procedures of mixing of initial precursors at different temperatures (room temperature and boiling temperature of isopropyl alcohol). DTA/TG analysis at heating rates of 10 and 2 °C/min in the air was used for study of processes which take place during the thermal treatment process of xerogels.

Based on the results, it can be concluded that the thermal behaviour of the prepared xerogels is a multistep process which very strongly depends on mixing procedure as well as temperature during the sol preparation.

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[1] C. Sanchez, B. Julián, P. Belleville, M. Popall, J. Mater. Chem., 15 (2005) 3559
[2] G. Kickelbick, "Hybrid materials", Wiley, (2007)
[3] H. Mori, Int. J. Polym. Sci., 2012 (2012) 173624

Using biopolymers as a fillers in polymer blends

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Biopolymers are renewable source of raw materials of plant and animal origin. Recently, they have been used as potentially suitable fillers in polymer blends, as a substitute of inorganic fillers mainly due to their biodegradation, their positive impact on the environment and the improvement of polymer blends properties. The most common biopolymers with interesting properties, which have been used as filler, are the cellulose, chitosan, galactomannan, starch and soya protein isolate [1-3].

For polymeric materials, the resistance to elevated or reduced temperatures is important. The thermal stability of a polymer determines its functional usability, and it is defined as a range of temperature, in which the polymer retains its elastic properties [4].

In this work, the influence of amount of filler as well as the type of filler on properties of polymer blends were studied. The thermogravimetry was used for determination of thermal stability of biopolymers filled polymer blends. For observation of structural changes after the addition bio-fillers to polymer blends, the infrared spectroscopy was used.

Natural rubber (NR) was blended with galactomannan (LBG), cellulose (CEL), chitosan (CHI) or soya protein isolate (SPI) as a filler in amount 0, 30 and 55 phr. The results indicate that the thermal degradation of NR/CE, NR/CHI, NR/SPI and NR/LBG polymer blends in nitrogen is a three–step process. The first step is assigned the destruction of biopolymers. The second step is assigned to the decomposition of double bonds of methylene groups in polyisoprene molecules, i.e. to the decomposition of natural rubber. The third step is the carbonization of natural rubber. When the cellulose, chitosan, soya protein isolate or galactomannan are used as the filler in polymer blends, the thermal stability of filled polymer blends decreases when the amount of given filler increases.

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[1] J. Johns, V. Rao, International Journal of Polymer Anal. Charact., 13 (2008) 280
[2] L. Jong, Industrial Crops and Products, 65, (2015) 202
[3] E. Abraham, M.S. Thomas, C. John, L.A. Pothen, O. Shoseyov, S. Thomas, Industrial Crops and Products 51 (2013) 415
[4] P. Rybiński, A. Kucharska-Jastrząbek, G. Janowska, Polymer Science Ser. B 56 (2014) 477

Structural and thermal properties of elastomeric blends filled with modified cellulose

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Nowadays, almost every area of industry is placing increasing emphasis on the search for alternative raw materials, method and procedures to reduce the negative impact on the environment. Natural polymers are one of the alternative options and are gaining more and more prominence in various fields of application. The main advantage of natural polymers is their biodegradability and the ability to obtain them from available natural sources. Research into new possibilities for the use of natural polymers in elastomeric blends is still ongoing in the rubber industry. One of the biopolymers often used as a filler in elastomeric blends is cellulose [1- 4].

This work is focused on preparing elastomeric blends filled with cellulose, which was modified chemically with SiO_2 (CEL_{sil}) and physically with plasma (CEL_{plasma}). Impact of physically modified cellulose as a filler was studied on thermal properties of elastomer blends. Natural rubber (NR) blends with different amount (30; 35; 40; 45; 50 and 55 phr) of cellulose (CEL) were prepared. On prepared blends thermal properties were studied. Physical-chemical properties were evaluated, too.

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[1] P. Skalková, A. Čížová, I. Sroková, Fibres and Textiles, 17 (2010) 3
[2] P. Skalková, K. Csomorová, M. Brezina, M. Kapusnak, Inter. Multidisc. Sci. GeoConf. Surveyin Geology and Mining Ecology Management, SGEM, 1 (2014) 253
[3] K. Van de Velde, P. Kiekens, Polymer Testing, 21 (2002) 433
[4] D. Santos, F.A., Iulianellig, C.V, Tavares, Mat. Sci. and Appl. 7 (2016) 257

Thermal behaviour and photoluminescence properties of Er^{3+} doped ytterbium-aluminate glasses

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The Yb_2O_3-Al_2O_3 glass with two different compositions (49.9 mol. % Al_2O_3, 50.1 mol. % Yb_2O_3, and 79.4 mol. % Al_2O_3, 20.6 mol. % Yb_2O_3) doped by 3 and 5 mol. % of Er_2O_3 were prepared by a combination of sol-gel Pechini method and flame synthesis in the form of glass microspheres (particle diameter ≈ 15 μm) [1]. The prepared glasses were characterized by SEM, SEM EDX, XRD, DSC analysis. Emission spectra in VIS and NIR region were also measured. All samples consisted of only fully re-melted spherical particles. A more detailed examination by SEM revealed the presence of a small portion of partially or fully crystallised microspheres. The EDX SEM analysis confirmed high homogeneity (even distribution of Er^{3+} ions throughout sample volume) of prepared systems. Subsequent examination by XRD showed the presence of traces of $Yb_3Al_5O_{12}$ phase in X-ray diffraction patterns of all prepared systems and also traces $Er_3Al_5O_{12}$ phase in samples with higher Er_2O_3 content. DSC analysis in temperature interval 35-1200°C with heating rate 10°C/min in nitrogen atmosphere was performed to study the thermal behaviour of prepared glasses. Two exothermic effects (at ≈ 919°C, and ≈ 939°C), which can be attributed to the crystallisation of $Yb_3Al_5O_{12}$ [1] and $Er_3Al_5O_{12}$ phase, were observed for all prepared compositions. A comparison of the peak areas indicated different thermal behaviour depending on the Al_2O_3 content. The red emission band centred at 665 nm ($^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition) and green one at 557 nm ($^2H_{11/2} \rightarrow {}^4S_{3/2}$) was observed in upconversion spectra of all prepared samples. A band centred at 1530 nm was observed in NIR spectra of all prepared systems [2-3]. Crystallisation at temperatures 1000°C and 1500°C with dwell times 20 and 120 min resulted in a small increase of intensities of individual bands with Stark splitting due to $Yb_3Al_5O_{12}$ and $Er_3Al_5O_{12}$ phase crystallisation.

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[1] A. Prnová, K. Bodišová, R. Klement, M. Migát, P. Veteška, M. Škrátek, E. Bruneel, I. Van Driessche, D. Galusek, J. Ceram. Int., 40 (2014) 6179–6184
[2] Ch. Xu, Q. Yang, G. Ren, Y. Liu, J. Alloys Compd, 503 (2009) 82-85
[3] T. Hlásek, K. Rubešová, V. Jakeš, O. Jankovský, J. Oswald, J. Eur. Ceram. Soc., 34 (2014) 3779-3782

Crystallization kinetics of Bi-doped 2CaO-Al$_2$O$_3$-SiO$_2$ glasses

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2CaO-Al$_2$O$_3$-SiO$_2$ (gehlenite) glasses doped with different concentration of Bi^{3+} (0.5, 1, 3 mol. %) were prepared by conventional melting. The prepared samples were X-ray amorphous expect of the sample with the highest content of Bi^{3+}, for which XRD records revealed traces of crystalline gehlenite.

The thermal properties of prepared glasses were studied by differential thermal analysis (DTA), performed at 5 different heating rates (2, 4, 6, 8, 10 °C/min) in nitrogen atmosphere. The DTA records of all studied glasses contained one exothermic peak attributed to crystallization of the gehlenite phase [1], whereas the XRD patterns of all samples after DTA analysis contained gehlenite (01-074-164 COD) as the main phase. Increasing content of the Bi^{3+} ions caused a decrease of the maxima of the peaks from 982 °C to 925 °C, measured at a heating rate of 10 °C.min^{-1}. The Johnson-Mehl-Avrami-Kolgomorov model was used for examination of crystallisation kinetics and the kinetic triplets (frequency factor A, apparent activation energy E_{app}, and the Avrami coefficient m) were determined using of RSS, R$^2_{adj}$, AIC and W$_{AIC}$ criteria [2]. Based on the kinetic parameters, it can be assumed that the nucleation rate is linear, the movement of the growth zone is controlled by diffusion and one-dimensional crystal growth is prevalent in the studied systems, irrespective of the Bi content.

Tab.1. Kinetic parameters of Bi-doped 2CaO-Al$_2$O$_3$-SiO$_2$ glass

Sample	***m***	***A* ± *SD* [min^{-1}]**	**E_{app} ± *SD* [kJ mol^{-1}]**
GBi0.5	1.5	(6.44 ± 3.06) × 10^{28}	695.1 ± 4.0
GBi1.0	1.5	(2.71 ± 0.64) × 10^{27}	659.9 ± 2.2
GBi3.0	1.5	(7.05± 1.65) × 10^{22}	538.0 ± 2.1

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[1] A. Malecki et al. Kinetics and mechanism of crystallization of gehlenite glass pure and doped with Co^{2+}, Eu^{3+}, Cr^{3+} and Th^{4+}. J. Non-Cryst. Solids. 212 (1997) 55-58

[2] A. Prnova et al. Crystallization kinetics of binary Yb$_2$O$_3$-Al$_2$O$_3$ glass. J. Therm. Anal. Calorim. 142 (2020) 2141-2148

The crystallization of anorthite in a system of illite/smectite and $CaCO_3$ mixture

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Traditional ceramic products are still widely used even though there has been recently an extensive progress in the field of advanced ceramic materials. The progress in the production technology of these materials can bring about considerable financial savings for producers as well as for consumers. Advances in this area can be achieved, for example, by a modification of the composition of raw ceramic mixtures or by the use of waste materials. Nowadays, many studies deal with the production of ceramic materials with additions of various waste materials, which are characterized by a high content of calcium oxide (CaO). The most frequently used waste materials are fly ash [1, 2] or waste limestone [3–5]. The addition of waste materials with high content of CaO into clays is often connected with a formation of anorthite ($CaO\cdot Al_2O_3\cdot 2SiO_2$), which, evidently, accounts for an improvement of the material properties. From the technological point of view, this mineral is interesting because it increases mechanical strength [6]. Because of these properties, it can be suitable for the production of tiles, paves, and porcelain [7]. The production of ceramic materials based on illitic clays is not specifically focused to support crystallization of anorthite. However, an increase of anorthite content improves the final properties of ceramic materials.

The aim of this paper is to study the crystallization of new phases in a system of illite/smectite and laboratory $CaCO_3$ and illite/smectite and wollastonite mixture. It is necessary to understand processes which take place in the raw input materials during their thermal treatment. To investigate these effects, differential scanning calorimetry (DSC), thermogravimetry (TG), termodilatometry (TDA), and X-ray diffraction analysis (XRD) is used. The temperature and the enthalpy of crystallization of new phases is determined by the DSC method. The amount of new phase (e.g. anorthite) is estimated from the measured enthalpy of the reaction.

[1] R. Sokolář and L. Vodová, Ceram. Int. 37 (2011) 2879–2885.
[2] T. Húlan, A. Trník, T. Kaljuvee, M. Uibu, I. Štubňa, U. Kallavus, and R. Traksmaa, J. Therm. Anal. Calorim. 127 (2017) 79–89.
[3] L. Vodová, R. Sokolář, and J. Hroudová, Int. J. Civil, Environ. Struct. Constr. Archit. Eng. 8 (2014) 717–720.
[4] R. Sokolář, L. Vodová, S. Grygarová, I. Štubňa, and P. Šín, Ceram. Int. 38 (2012) 6607–6612.
[5] I. Štubňa, A. Trník, R. Podoba, R. Sokolář, and P. Bačík, J. Ceram. Soc. Japan 120, (2012) 351–354.
[6] S. N. Monteiro, L. A. Peçanha, and C. M. F. Vieira, J. Eur. Ceram. Soc. 24 (2004) 2349–2356.
[7] S. Kurama and E. Ozel, Ceram. Int. 35 (2009) 827–830.

Prehistoric ceramics: analysis of late Neolithic / Eneolithic pottery and clay samples from the Foeni Tell-Orthodox Cemetery (Timis County, Romania) using complementary techniques

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The study aims to analyze prehistoric ceramics consisting of pottery samples from the archaeological site Foeni Tell – Orthodox Cemetery (Foeni, Timiş county, Romania), a late Neolithic/early Eneolithic multi-stratified site (4720-4457 cal BC), also inhabited during the early Bronze Age and Middle Ages.

The analyzed samples come from 19 pottery sherds, belonging to the Foeni cultural group (4920/4675-4580/4460 cal BC, corresponding to the Vinča culture, from the end of phase C to the end of phase D), and are representative of the categories (black, red, painted) and types (fine, semifine, coarse) pottery associated with the cultural group. Also analyzed were clay samples from the site, in order to ascertain a connection between local sources and the pottery [1-4]. The analysis was conducted using complementary techniques (TG/HF, FT-IR, XRD, SEM, XRF and LIBS) in an effort to uncover details regarding production technology and origin of the raw materials used in making the pottery [1, 5, 6].

The results indicate slight differentiation between categories and a more pronounced difference between types, indicating a preferred method for each type, regardless of category. The results also show a high probability that the local clay was indeed used as the primary source of raw material for the pottery. With one exception (much higher temperature), the results indicate the firing temperature was the same regardless of category or type, while also indicating a secondary thermal treatment of painted pieces.

[1] Vlase D., Rogozea O., Moșoiu C., Vlase G., Lazău R., Vlase T. Thermoanalytical investigations of some ceramics dated from the Neolithic period, discovered at Oxamplatz, Sânandrei, Romania. J Therm Anal Calorim 2019; DOI: 10.1007/s10973-019-08767-8
[2] Lazaraovici G. The absolute and relative chronology and evolution of the Zau Culture. Acta Musei Porolissensis, 2012; 34: 55-71.
[3] Drașovean, F., Die Petreşti-Kultur im Banat. Praehistorische Zeischrift, 1997; 72: 54-80.
[4] Drașovean, F., Transylvania and the Banat in the Late Neolithic. The Origins of the Petreşti Culture. Antaeus, 2004; 27: 27-36.
[5] Shoval S, Beck P. Thermo-FTIR spectroscopy analysis as a method of characterizing ancient ceramic technology. J of Therm Anal Calorim, 2005; 82: 609–616. DOI: 10.1007/s10973-005-0941-x
[6] Ouahabi M. El, Daoudi L, Hatert F, Fagel N. Modified mineral phases during clay ceramic firing. Clays and Clay Minerals, 2015; 63(5):404–413. DOI: 10.1346/CCMN.2015.0630506

Chemical and thermal analysis for different waste substrates – comparative scenario analysis

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Abstract

In the context of continuous growing of energy demand, new solutions must be found relative to waste capitalization and energetic potential for different substrates that can presently be found in large quantities and are not used in their entirety.

The present material presents a comparative analysis between two different types of waste materials, one with a high organic content and one with high mineral content, in terms of their physical and chemical properties and their further applicability for co-firing processes.

Correlations were made in terms of physical and chemical parameters of studied materials, together with calorific values for determining energetic potential and thermogravimetric analysis for identifying the specific points under nitrogen conditions. Also ash melting behavior analysis was made for better understanding the residual ash behavior inside a burning chamber, during firing processes.

Interpretations are made relative to the gathered data from laboratory analysis and overall conclusions are going to be traced relative to possible applications of the analyzed materials.

[1] A. E. Cioabla, N. Pop, G. Trif-Tordai, D. G. Calinoiu, J. Therm. Anal. Calorim.,127 (2017)515.
[2] A. E. Cioabla, N. Pop, G. Trif-Tordai, D. G. Calinoiu, J. Therm. Anal. Calorim., 121(2015)421.

Verification of the increase of the thermal stability of a polyurethane matrix as a result of its nanomodification with a layered silicate by performing thermogravimetric analyzes

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A nanocomposite is a solid multiphase material wherein one of the phases has one or all of the three dimensions of the particles that make it up of the order of magnitude of max 100 nm. This phase is homogeneously dispersed in a matrix which in it confers new properties [1].

Polyurethane matrix nanocomposite is a new material, obtained by a process of modifying the polyurethane matrix with a chemical entity with a special molecular structure.

A polyurethane macromolecule is obtained by a polyaddition reaction in the strongly isocyanate unsaturated group – N=C=O, wherein the carbon atom is hybridized sp of a strongly acidic group respectively –OH, – NH_2 .

The chemical entity with which the nanomodification is performed is a layered aluminosilicate.[2]

Its structure allows the construction of polyurethane macromolecules between its layers so as to obtain a nanomodification at the molecular level.

To study the increaseing of thermal stability of the polyurethane macromolecular structure which would result from nanomodification ***thermogravimetric analyzes were performed*** [3,4] in parallel to an unmodified polyurethane sample considered a control sample and samples of polyurethane obtained from polyadditions of polyether polyols 2 and polyether polyols 3 nanomodified 2-6% by weight with aluminosilicate The results showed a substantial increase in temperature values from which molecular degradations begin.

[1] Marin Laurentiu CERCETARI PRIVIND OMITEREA EFECTELOR DE PRIZĂ DINTRE SUPRAFEȚELE METALICE ȘI NEMETALICE PRIN INTERMEDIUL PELICULELOR DE GRAFIT teza doctorat UTM, pag. 57;

[2] Theng, B.K.G. 1979. Formation and Properties of Clay Polymer Complexes. Developments in Soil Science 9. Elsevier, Amsterdam, ISBN 0-444-41706-0;

[3] Guyonnet, Dominique; Gaucher, Eric; Gaboriau, Hervé; Pons, Charles-Henri; Clinard, Christian; Norotte, VéRonique; Didier, GéRard (2005).

[4] Geosynthetic Clay Liner Interaction with Leachate: Correlation between Permeability, Microstructure, and Surface Chemistry". *Journal of Geotechnical and Geoenvironmental Engineering* 131 (6): 740. DOI:10.1061/(ASCE)1090-0241(2005)131:6(740)

Poster session 3

Effects of two size fractions of platinum nanoparticles on properties of soil organic matter

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Nowadays, nanoparticles can be seen as a new type of pollutant which may have a negative effect on the environment compartments, including soil. Currently, there is only a limited number of studies investigating the effect of nanoparticles on soil properties. On the contrary, numerous articles reported the impacts on soil biota. Therefore, the aim of this study is to investigate how the 3 and 200 nm platinum nanoparticles affect selected properties of water and soil organic matter dried at various relative humidity (43, 75, and 95 %). These particles were selected due to their presence in the exhausting gases, where they are released from automotive catalysts. In this work, we determined the stability of water molecular bridges (proportional to structure rigidity), water holding capacity, evaporation enthalpy of water (the strength of water binding), the stability of aliphatic crystals (microbiological persistent fraction) in soil were studied using differential scanning calorimetry.

It was discovered that 3 nm platinum nanoparticles generally increased the strength of water molecular bridges, which implies a higher soil structural rigidity. It was therefore confirmed that these nanoparticles act as kosmotropic agents (structure-forming) in water molecular bridges. On the other hand, 200 nm nanoparticles exposed to 75% relative humidity decreased the water molecular bridges stability. Also, effect of 3 nm Pt nanoparticles on water evaporation enthalpy which represents the strength of water binding, was observed. Generally, evaporation enthalpy decreased, which can lead to soil desiccation. In this situation, nanoparticles act as chaotropic agents (i.e. water structure breaking). Contrary to the previous observations, 200 nm Pt nanoparticles exposed to 75% relative humidity increased evaporation enthalpy; however, at 92% relative humidity the effect was identical to 3 nm Pt nanoparticles (i.e. higher evaporation enthalpy). Additionally, 3 nm Pt nanoparticles decreased the water content at the highest relative humidity and high nanoparticles concentration which was not observed for 200 nm Pt nanoparticles. The smaller Pt nanoparticles also induced the aliphatic moieties' crystallization, whereas the 200 nm Pt nanoparticles had practically no effect.

These observations confirmed that nanoparticles can pose potential risks to environment, in this case to soil. It was also discovered that the effect of size of the same nanoparticles is significant. The smaller nanoparticles seem to have a greater effect to soil organic matter properties than the larger ones, although observed changes of properties for 200 nm Pt nanoparticles are not negligible.

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TG study on the influence of PET and tyre-based microplastics on soil properties

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Nowadays, the problems with microplastics, i.e. small plastic particles contaminating the environment, is a subject of heated discussions. The literature data suggest that the microplastics from conventional plastics are not as inert as anticipated, but instead, they impact all environmental compartments including soils. In particular, many studies describe negative effects of microplastics on soil fauna and flora. However, the effects on soil abiotic properties and soil quality have not been sufficiently addressed. In this work we present results from the short- and medium-term experiments. We studied the effects that have microplastics from polyethylene terephthalate (PET) and from car tyres on properties of water and soil organic matter in three different soils including chernozem, cambisol and phaeozem. We analysed changes in soil organic matter thermal properties, soil respiration, amount of water and soil aggregation over the period of 15 months to observe their transformation and effects on soil properties.

The results revealed that the effect of microplastics on soil properties are soil-type and microplastic-type dependent. Also, it was confirmed that the microplastics were not inert but influenced all the measured parameters. Probably the most important observation was the effect of microplastics on soil organic matter stability. The contamination influenced the soil microbiological activity, which led to the decomposition of soil organic matter and loss of organic carbon. In addition, contaminated soils appeared to have an adverse effect on water holding capacity. Therefore, the microplastics based on non-biodegradable polymers influence significantly the soil ecosystem functions.

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Application of High Pressure Thermogravimetry as a perfect tool to study catalyst performance

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Thermogravimetric analysis (TGA) is typically used to determine the thermal stability of materials by applying a temperature gradient to the sample and detecting weight changes due to processes such as drying, evaporation, oxidation, decomposition or pyrolysis. However, when a TGA setup can be operated at elevated pressures and with a reactive gas atmosphere, catalytic gas reactions can be performed in the high pressure TGA instrument as well. The change of the catalyst weight can provide online data on processes such as catalyst activation, oxidation, coking or other ways of catalyst deactivation.

A combination of this instrument with an online mass spectrometer (MS) for evolved gas analysis can additionally provide information on conversion and product yields of the reaction depending on temperature and pressure.

How to transform a waste material into a resource: the thermal evolution of spent LDHs (layered doubled hydroxides) after the absorption of Cr (VI)

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Layered doubled hydroxides (LDHs) belong to a class of 2D materials, also known as anionic clays, with general formula: $[M_{1-x}^{2+}N_x^{3+}(OH)_2]^{x+}(A_{x/n}^{n-})^{x-} \cdot mH_2O$.

Where M and N are respectively a divalent and a trivalent cation, A is an anion with n charge, x is the molar ratio N/(M+N) and m is a value between 1 and 4. The cations are arranged in the structure layers of octahedral $M(OH)_2$ similarly to hydrotalcite. The anion is hosted in the interlayer.

The interlayer is very flexible and could host different compounds as anions, cations and not charged ones. Owing to the whide range of possible combination of M,N and A these materials are interesting as catalyst and anionic sponge [1,2]. LDHs are also promising materials for energy storage systems in particular in supercapacitors [3] and metal ion batteries [4].

Goal of this work is a thorough investigation on the structural transformation of the MgAl-NO_3 LDH, a promisig material for the absorption of the toxic Cr(VI)[5], before and after the chromium recovering process. By means of Differential Thermogravimetry (DTG), Differential Scanning Calorimetry (DSC) and X-ray powder diffraction (XRPD) it's possible to understand the precise adsorption mechanism. Furthermore, only a deep knowledge of the LDH evolution under heating, after the recovering routine, can allow to plan an set up the better circular process starting from a polluted water and ending to a product with an economical interest such as the formation of a Cr-spinel with interest as catalyst.

[1] Li F., Duan X. Applications of Layered Double Hydroxides. 2006 Layered Double Hydroxides. Structure and Bonding, vol 119. Springer, Berlin, Heidelberg. https://doi.org/10.1007/430_007
[2] Cardinale A.M.; Carbone C.; Consani, S.; Fortunato M.; Parodi N. Layered Double Hydroxides for Remediation of Industrial Wastewater from a Galvanic Plant. *Crystals* 2020, *10*, 443.
[3] Liu H., Yu T., Su D., Tang Z., Zhang J., Liu Y., Yuan A., & Kong Q. Ultrathin Ni-Al layered double hydroxide nanosheets with enhanced supercapacitor performance.2017 Ceramics International, 43(16), 14395–14400. https://doi.org/10.1016/j.ceramint.2017.07.207
[4] Shi L., Chen Y., He R., Chen X., & Song H. Graphene-wrapped CoNi-layered double hydroxide microspheres as a new anode material for lithium-ion batteries. 2018 Physical Chemistry Chemical Physics, 20(24), 16437–16443. https://doi.org/10.1039/c8cp01681j
[5] Chao, H. P., Wang, Y. C., & Tran, H. N. (2018). Removal of hexavalent chromium from groundwater by Mg/Al-layered double hydroxides using characteristics of in-situ synthesis. *Environmental Pollution*, *243*, 620–629. https://doi.org/10.1016/j.envpol.2018.08.033

Sol-Gel synthesis, thermal, spectroscopic and morphological characterization of bioactive titania

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Titanium dioxide (TiO_2) is frequently used in the industrial and environmental applications for its photocatalytic activity, chemical stability and anticorrosive properties. TiO_2 particles synthesized by the sol–gel method [1,2] were characterized with particular reference to their structure, thermal analysis and antimicrobial properties. In particular, this characterization aims at verifying the possibility to use these materials to prevent infections after implantation.

The physico-chemical and morphological characterization, carried out using FTIR, SEM and BET analyses, revealed that even though the particles size is non-uniform, an average value is found corresponding to about 700nm. Aggregation of particles are not clearly visible, because of the presence of both water molecules and hydroxyl group, confirmed also by FTIR analysis. Furthermore, both the FTIR spectra and TG experiments suggest that the thermal treatment at 60°C does not completely remove the water and residue solvents. As a confirmation, the EDX analysis showed both the peaks of Ti and O, as well as those of Carbon. TG experiments revealed that in spite of the thermal pre-treatment at 60°C, a significant mass of water physically or weakly bound to the material was released at low temperature. The occurrence of processes accompanied by mass losses can be excluded at temperature higher than 900 K.

As far as the biological characterization is concerned, the Kokubo test confirmed that the formation of hydroxyapatite layers occurs after 21 days in simulated body fluid (SBF), thus suggesting that the TiO_2 particles synthesized in this study are bioactive.

The antibacterial activity of TiO_2 particles was assessed using *Escherichia coli* and *Enterococcus faecalis*. Finally, the bioactivity of TiO_2 particles were estimated by soaking them for 21 days in simulated body fluid with the view to evaluate their bioactivity.

[1] M Catauro, E Tranquillo, G Dal Poggetto, M Pasquali, A Dell'Era, S. Vecchio Ciprioti, Materials, 11 (2018) 2364.
[2] M. Catauro, G. Dal Poggetto, R. Risoluti, S. Vecchio Ciprioti, J. Therm. Anal. Calorim., 142 (2020) 1767-1774.

A TGA/DTA/EGA study on the thermal degradation of an intermediate compound of TiO_2 nanopowders production

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N-doped TiO_2 nanoparticles are considered very efficient photocatalysts for coating applications [1]. The preparation of the anatase-N-doped crystal is a very complicated operation passing through a series of heating steps [2].

This contribution aimed to highlight the thermal transformations of the intermediate compound obtained via the neutralization with ammonium citrate of the TiO_2 precipitate in HCl media [3].

TGA-DTA measurement (Netzsch STA 449F3) were coupled with IR analysis of the evolved gases at each temperature. DTA curve shows two main endothermic peaks (below 100°C, and at 220.9°C) and three main exothermic peaks (317.9°C, 494.8°C, 592°C), and all except the last one are associated to some weight loss. The first two endothermic peaks should correspond to water loss and to a first citrate derivatives decomposition. The first two exothermic peaks should correspond to further citrate derivatives decomposition, while the last one is probably due to the anatase-rutile transformation.

The FTIR spectrum recorded at 324°C shows the presence of CO_2 and H_2O, with small amounts of CO. CO is not detected anymore in the spectrum recorded at 462°C, while CO_2 and water are still present. This suggest that the remaining organics undergo to a combustion reaction as temperature increase, given also the corresponding exothermic peaks seen in DTA at the same temperatures. Despite thermal decomposition of NH_4Cl in NH_3 and HCl should occur, the presence of these two gases was not evident due to the high concentration in the gas phase of CO_2 and H_2O.

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[1] R. Asahi, T. Morikawa, H. Irie, T. Ohwaki, Chem. Rev., 114, (2014) 9824.
[2] S. A. Ansari, M. M. Khan, M. O. Ansari, M. H. Cho, New J. Chem., 40, (2016) 3000.
[3] G. Baldi, L. Niccolai, M. Bitossi, V. Dami, A. Cioni, Nitrogen-doped TiO_2 nanoparticles and the use thereof in photocatalysis, Patent, (2019), WO2019/211787A1.

Clay nanoparticles as pharmaceutical carriers to enhance anticancer treatments

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The appealing properties of different clay minerals were investigated to propose an effective delivery system for chemotherapeutic poorly soluble drugs. This represents a serious pharmaceutical concern due to the low bioavailability and low dissolution profile in biological fluids [1-2], making it necessary to administer high oral doses with severe adverse effects. To increase the solubility and bioavailability of these drugs and modulate the release profile, a drug-carrying, able to release the drug slowly, and to provide muco-adhesiveness to the pharmaceutical formulation, making it able to cross the gastrointestinal barrier and to mediate gastrointestinal disturbance, is required. The structural and chemical-physical properties of nanolayered silicates have long been exploited as effective nanocarriers for the loading and the controlled release of several classes of drugs [3].

In the present work, the Nile Red (NR) dye was used as a model for chemotherapeutic drugs to explore the drug loading and release property of drug/clays nanodevices. According to literature [4], the choice was dictated by the structural similarity between NR and these drugs and its peculiar spectroscopic sensitivity to the medium environment.

More in detail, the adsorption and release of NR, from different clays (namely kaoline, montmorillonite, and sepiolite) were investigated by changing external and internal parameters such as the nature of clay, pH, adsorption protocols, adsorbent, and adsorbate doses.

NR/clays hybrid nanocomposites were characterized through TGA, FTIR, and XRD measurements.

The obtained results allow us to propose nanodevices based on montmorillonite clay as efficient carriers for the administration of chemotherapeutic lipophilic drugs.

[1] S. Senapati, A. K. Mahanta, S. Kumar, e P. Maiti, Signal Transduct. Target. Ther., 3, (2018) 7.
[2] A. G. Abd-Elsatar, M. M. Farag, H. F. Youssef, S. A. Salih, M. M. Mounier, e E. El-Meliegy, Prog. Biomater., 8 (2019) 101.
[3] R. De Melo Barbosa, M. Alcântara, L. Meirelles, N. Zorato, e F. Raffin, Nanoclays in drug delivery systems (2020)185.
[4] S. L. Kurtz e L. B. Lawson, Sci. Rep., 9 (2019) 11810

Synthesis and characterization of Carbon Fiber Precursors coupled to a chemical oscillator

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The radical species formed during the Belousov-Zhabotinsky (BZ) reaction [1] were properly exploited to obtain, via a reaction of radical polymerization, the polymer poly(acrilonitrile) (PAN) and its bock copolymers with poly(ethylene glycol) (PEG), which are the most important and promising precursor for high-performance carbon fibres [2-3].

The synthesis was carried out by adding the monomer acrylonitrile (AN) to the unperturbed and PEG-perturbed BZ system after the onset of the oscillations, in the absence and presence of increasing amounts of the anionic surfactant sodium dodecyl sulphate (SDS). The potentiometric technique was utilized to detect the dynamics of the oscillatory reaction.

Preliminarily, the response of the BZ system on the monomer addition was investigated. Additional information was provided from the study of the effect of the SDS and PEG concentration on the dynamics of the BZ reaction during AN polymerization.

The viscosimetric characterization of the polymers and copolymers synthesized in the different emulsion evidenced that the polymer molecular weight depends on surfactant and PEG concentration. The true copolymeric nature of the prepared polymers was verified throw melting point and FT-IR characterization.

The fibres precursors were stabilized by heating the powder samples in an air oven at 50, 100 and 150 °C for 30 minutes. XRD patterns of the prepared polymers and copolymers were performed to determine the fibers crystal structure, the degree of crystallinity and the size of crystallites.

Results here obtained reveal that the proposed synthetic protocol represents a valuable alternative to conventional methods to produce high-performant precursors of carbon fibres.

[1] A. Cassani, A. Monteverde, e M. Piumetti, *J. Math. Chem.*, 59 (2021) 792.
[2] J. Hao, W. Li, X. Suo, H. Wei, C. Lu, e Y. Liu, *Polymer*, 157 (2018) 139.
[3] G. Chen *et al.*, *Polymer*, 186 (2020) 122012.

A greener path by hydrothermally processing apatite

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Hydrothermal processes are so common in nature: there are plenty of minerals that form dense solids near room temperature under mild pressures, including carbonates and phosphates [1, 2], and the principles of it have been used to develop new low-energy sintering strategies like reaction hydrothermal liquid-phase densification and cold sintering process. In nature, hydrothermal conditions prevail in at least two situations: the transformation of sediments into sedimentary rocks, and the formation and crystallization of magmas [1, 2]. Therefore, it is interesting to see if these formation-transformation phenomena could be used to form apatite from calcium carbonate and tricalcium phosphate powders, as they both are members of main skeletal inorganic solids [3] that can be used to develop different biomaterials. There have been attempts to hydrothermally sinter apatite [1], but this study leads to a greener, "no waste" phase formation strategy for producing apatite.

Calcium carbonate and tricalcium phosphate powders were synthesized using the wet precipitation method and freeze-dried. Characterization was done by XRD and FTIR to determine its structure and inherent functional groups. Both powders were thermally crystallized in air by heating at a phase transition temperature determined by DTA. Dry powders were mixed and ground in a mortar. The mixed powder was uniaxially pressed at 500 MPa load under hydraulic press in a die to obtain green body pellets in a size of diameter 13 mm and 1,6-1,7 mm thick. The green body pellet was then put into a hydrothermal vessel at 180 ℃ for 19 h with an amount of water creating 1,0026 MPa water vapor pressure. Pellets were structurally characterized by XRD and FTIR to determine if apatite was formed. Bulk density of green body pellets and hydrothermally processed ones were calculated.

This technique proves to be effective in the formation of apatite from two crystalline phases. XRD patterns showed apatite phase. This way hydrothermal sintering can be used to not only densify materials but also form apatite through a green, "no waste" sintering path.

[1] A. Ndayishimiye, M. Y. Sengul, S. H. Bang, K. Tsuji, K. Takashima, T. H. de Beauvoir, C. A. Randal, J. Eur. Ceram. Soc., 40 (2020) 1312-1324
[2] E. D. Eanes, "Amorphous Calcium Phosphate: Thermodynamic and Kinetic Considerations", Calcium Phosphates in Biological and Industrial Systems, (1998) 21– 39
[3] S. Mann, Endeavour, 15 (1991) 120-125

The effect of mechanochemical treatment on the structure of silica gel waste

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Waste management and recycling are the priority areas of environmental protection in Lithuania and the European Union. These areas are stated and their importance is declared in the Environmental Strategy and the EU Waste Statistics Action Plan (EU Implementation of the Circular Economy Action Plan) [1]. According to Eurostat, the European Union generates ~190 million tons of industrial waste every year, including ~3 million tons in Lithuania [2]. However, it is preferable to store the waste materials in landfill sites, where they occupy large areas and become concentrated sources of air, groundwater, and soil pollution [3]. Therefore, the search for attractive and profitable industrial waste recycling treatment, which could valorise them into products of high value [1-3].

The cement industry and similar spheres require a certain amount of SiO_2 which is mostly available as quartz (sand) for silicate (calcium, sodium, potassium, etc.) production [4]. As low-lime binders are getting more attention as a climate friendlier material than ordinary Portland cement (OPC), the demand for sand should increase as well to maintain an even output of the production [5]. Since the silica gel-waste (SGW) consists mainly of amorphous, fine, and porous SiO_2 which makes it more reactive compared to quartz. The SGW could be an excellent additive or replacement of sand in the silicate industry; however, it requires some further processing to reduce the F^- content which reduces the application of SGW [6].

Therefore, the aim of this work was to investigate how various methods of mechanochemical treatment influences the properties of silica-gel waste: structure, hydration capacity, particle size, and fluoride ion content.

The silica-gel waste was processed by disintegration, ultrasonication, centrifugation dynamic filtration, and application of alkalis. The refined material was later investigated by DSC, STA, XRD, BET, XRF, and chemical analysis. The obtained results proved to be successful in reducing F^- ion content by >90% as well as hydration capacity. The treatment also reduced the aggregation of SiO_2 particles which now tented to form ~0.5–1 μm sized spheres.

[1] EU Circular Economy Action Plan [interactive]. [viewed 2020-02-07]. Access: https://ec.europa.eu/environment/circular-economy/

[2] Waste statistics [interactive]. 2019. [viewed 2020-02-07]. Access: https://ec.europa.eu/eurostat/statistics-explained/index.php/Waste_statistics

[3] J. Malinauskaite, H. Jouharab, D. Czajczyńska, et al., Energy. 141 (2017) 2013–2044

[4] T. Shams, G. Schober, D. Heinz, S. Seiferta, Constr. Build. Mater. 272 (2021) 122014

[5] S. Siddique, A. Naqi, J. G. Jang, Cem. Concr. Compos. 111 (2020) 103616

[6] A. Iljina, K. Baltakys, A. Bankauskaite, A. Eisinas, S. Kitrys, J. Therm. Anal. Calorim. 127 (2017) 221-228

The effect of Cu^{2+} ions concentration on the adsorption capacity of synthetic mayenite and its thermal stability

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Mayenite ($C_{12}A_7$) has been recently stimulating research interest because of its superior accelerator effect-rapid hardening activity [1], oxygen mobility, ionic conductivity and catalytic properties in comparison with other calcium aluminates [2, 3]. The application of mayenite depends on the employed method of synthesis. There are three basic ways to produce it: solid, sol–gel or co-precipitation methods (primary soluble compounds are used), and thermal decomposition of synthetic CAH precursors.

In previous work [4], it was observed, that in unstirred $CaO–Al_2O_3–H_2O$ suspensions, when CaO/Al_2O_3 molar ratio of primary mixture was equal to 2.8, after 4 h of isothermal curing at 130 ºC temperature katoite was formed. It is worth mentioning, that synthetic katoite at 350 °C temperature fully recrystallized to mayenite. Also, the calcination temperature of products greatly affected their adsorption capacity for cooper ions when the primary aqueous solution containing 0.5 g/l of Cu^{2+} ions. For this reason, the main objective of the present work was to determine effect of Cu^{2+} ions concentration on the adsorption capacity of synthetic mayenite and its thermal stability.

The synthesis of compounds has been carried out in unstirred suspensions (CaO/Al_2O_3 = 2.8, w/s = 10) within 4 hours at 130 ºC. The synthesis product were calcined in different temperature (1 h): CA1 - (350 °C temperature), CA2 - (550 °C temperature), CA3 - (900 °C temperature) and was used as the adsorbent to removal of Cu^{2+} ions from differences concentration solutions. The results demonstrated that, the amount of adsorbed Cu^{2+} ions depends from mayenite structure and initial concentration of copper ions in solution. It should be mentioned that mayenite also adsorbed SO_4^{2-} anions, because they were determined in products after all experimental conditions. It was determined that, after adsorption process, mayenite fully recrystallization and new crystallinity phases formed. It was proved that these phases are stable still 350 °C, whereas at a higher temperature fully decomposed. It is likely, that when the temperature of calcinations was increased to 800 °C, amorphous structure compounds started recrystallize to tricalcium aluminate, ye'elimite and calcium copper oxide.

[1] K. Kurashige, Y. Toda, et. al., Cryst. Growth Des. 6 (2006) 1602.
[2] S. Fujita, H. Nakano, et. al., Catal. Lett. 106 (2006) 139.
[3] C.S. Li, Y. Yamamoto, et. al., J. Therm. Anal. Calorim. 95 (2009) 991
[4] A. Eisinas, K. Ruginyte, et. al., Ceram. Int. 46 (2020) 29429

The effect of synthetic katoite additive on the hydration of calcium aluminate cement

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Calcium aluminate cement (CAC) has advantages such as early compressive strength, due to the fast hydration of CAC can attain a very dense matrix compared to the Ordinary Portland Cement (OPC) [1, 2]. The initial hydration products of CA and CA_2 are calcium aluminate hydrate (CAH_{10} or C_2AH_8) with aluminium gel. These reaction products can be divided into two groups of hydrates, i.e. metastable (CAH_{10}, C_2AH_8) and stable (C_3AH_6, and AH_3) [3, 4]. Hydration products of CAC are primary calcium aluminate hydrate, which are a mixture of poorly crystallized particles. Thus, the properties of these gels are important for the mechanical and chemical properties of cement based materials. Presumably, that the synthesized C_3AH_6 additive induced the early stage of CAC hydration.

For this reason, the synthetic katoite (was synthesized under hydrothermal conditions in the primary mixture, $CaO/Al_2O_3 = 2.8$, w/s = 10, 4 h, 130 °C) was added as a partial replacement of calcium aluminate cement (Gorkal 70 (Gorka Cement, Poland)), at levels of 5, 10, 15 and 25% by weight of the total cementitious material. The rate of the heat evolution and the total amount of the released heat (TAM Air III (TA Instruments, New Castle, USA) calorimeter) was used to investigate the heat evolution rate were calculated based on the unit weight of cement.

It was determined that in the first stage of hydration the heat evolution rate increases (from 0.012 till 0.025 W/g) with increasing the amount of the katoite additive (25 %) in the cement samples. It was noticed that the second exothermic reaction beginning after 7.0 h hydration in pure systems, however, the samples with additive effect begins earlier: from 1.45 h in the samples with 25 % mentioned additive. At later stages of hydration, the calorimetric curve of all samples showed the slower continued reaction, because the rate of heat evolution was decreased. The higher values of cumulative heat were reached in all the samples with additive compared to pure cement sample (336 J/g).

[1] P. Gu, Y. Fu, et. al., Cem. Concr. Res. 24 (1994) 682.
[2] R.R. Lourenço, R.S. Angélica, et. al., Mat. Res. 16 (2013) 731.
[3] M.P. Adams, J.H. Ideker, Cem. Concr. Res. 100(Supplement C) (2017) 284.
[4] B. Pacewska, M. Nowacka, et. al., J. Therm. Anal. Calorim. 109 (2012) 717.

Thermal stability of synthetic kuzelite in the temperature range of 30-1250 °C

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The calcium monosulfoaluminate 12-hydrate (Ms12) or the naturally occurring mineral kuzelite ($C_4A\hat{S}H_{12}$) is a widespread crystalline hydrate phase of cement that forms during the hydration of Portland cement and calcium aluminate cement-based systems. [1]. Generally, the crystal structure of kuzelite consists of a positively charged main layers $Ca_2[Al(OH)_6]$ and a negatively charged interlayers $[SO_4 \cdot 6H_2O]$ [2]. However, the water content of the interlayer of monosulfoaluminate may vary, from 0 to 10 molecules, depending on the exposure of temperature and relative humidity [3]. The dehydration process of Ms12 was investigated widely by H. Pöllmann (1984) [4]. He demonstrated that water released from the interlayer is subdivided into different dehydration processes in the temperature range of 25-200 °C (different hydration states of monosulfoaluminate hydrates). However, there is presently no systematic approach to assessing the thermal stability range of different hydration states of monosulfoaluminate hydrates and the subsequent influence of elevated temperature on the crystalline phases.

This work presents novel results of the formation processes of kuzelite under hydrothermal synthesis conditions and its thermal stability. In order to produce kuzelite, the mixture of analytical grade CaO, Al_2O_3, and $CaSO_4 \cdot 2H_2O$ were used. The molar ratio of mentioned compounds corresponds to 3:3:1, respectively. The prepared initial mixture was treated mechanochemically (milled at 900 rpm with on-off cycles of 10 min respectively for 30 min) and then hydrothermally in an unstirred suspension under saturated steam pressure in a 130-200 °C temperature range for 1, 4, 8, 24, 72 h. The thermal stability of the synthesis products was evaluated by applying the In-situ X-ray diffraction method, which was performed in a modular temperature chamber at the temperature range of 30-1250 °C.

It was obtained that, most conducive synthesis conditions for kuzelite were at 130 °C for 8 h, because the initial compounds were fully reacted, and kuzelite dominated in the products. Meanwhile, the increment of hydrothermal synthesis temperature or duration negatively affected the stability of the presented compound. The examination of thermal stability demonstrated that the interlayer water of synthetic kuzelite gradually removes (observed 4 different hydration states of monosulfoaluminate) in the temperature range of 30-350 °C. Also, in the final stage of thermal treatment, the crystallization of ye`elimite was observed. The previous results were confirmed by XRD, STA, FT-IR, and SEM analysis.

References

[1] Matschei, T., Lothenbach, B. & Glasser, F. P. Cem. Concr. Res. 37 (2007) 118.
[2] Ahmed, S. J.; Taylor, H. F. W. *Nat.* 215 (1967) 622.
[3] Baquerizo, L. G., Matschei, T., Scrivener, K. L., Saeidpour, M. & Wadsö, L.. Concr. Res. 73 (2015) 143.
[4] Pöllmann, H. Cementitious Materials: Composition, Properties, Application. Cementitious Materials: Composition, Properties, Application (2017).

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Thermal and adsorption study of hydrothermal charcoals obtained from agricultural residues

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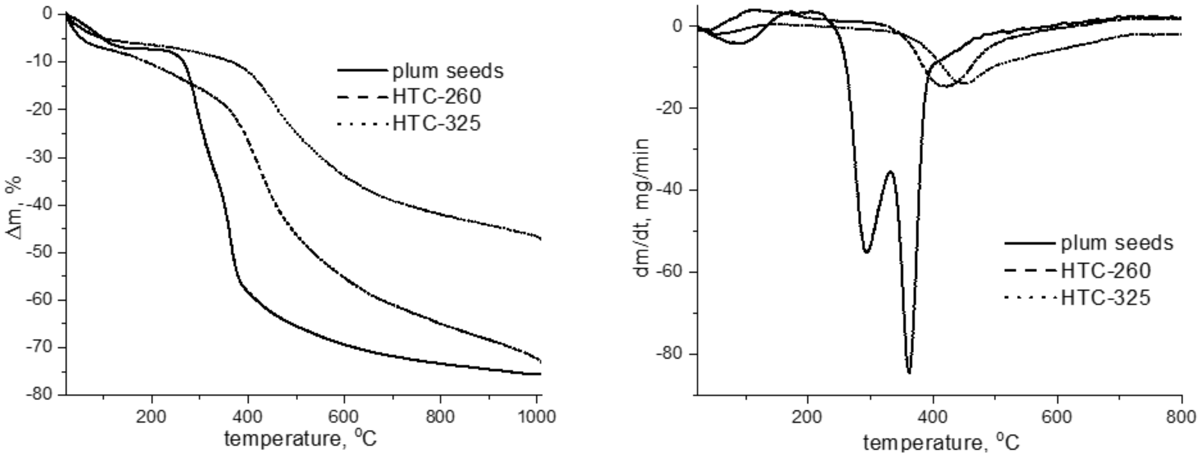
Hydrothermal carbonization processes (HTC) is a thermal conversion method that occurs at relatively low temperatures (150-350 ºC) in closed systems under self-generated pressures. The HTC process can be classified as ‘‘green’’ since it does not involve organic solvents, catalysts or surfactants. During HTC, the carbohydrate components from biomass are broken up and dissolved in the water, following a complex cascade of aldol-reactions, cycloadditions and condensations, a carbon rich solid product is obtained. Thus, the hydrothermal method has the potential to obtain adsorbents at low temperatures, but also catalysts by introducing metal ions and heteroatoms into the carbon structure.

In this study a series of charcoals were obtained by the HTC method in the temperature range 260-325 ºC. The plum seeds were used as raw material. The yield of charcoal varied from 43.5% at 260 ºC (HTC-260) to 36.9% at 325 ºC (HTC-325). Thermal analysis of the samples was performed in nitrogen atmosphere at a heating rate 10 ºC / min.



a b

Figure 1. TG (a) and DTG (b) curves of plum seeds and hydrothermal charcoals obtained at 260 and 325 ºC

The thermal analysis showed that for the charcoal samples obtained by the hydrothermal method, even at low temperatures (260 ºC), the characteristic peaks of cellulose and hemicellulose decomposition are not observed, and the thermal stability of the sample becomes higher. This is explained by the structure of the char obtained due to the high pressures and the formation of a thermally stable condensed structure.

Acknowledgements. This research was carried out with the financial support of the institutional project “The reduction of the environmental and health impact of toxic chemicals through use of adsorbents and catalysts obtained from local raw material” DISTOX, No 20.80009.7007.21.

Thermal behaviour of Mn(II) mono- and trinuclear coordination compounds based on 2,6-diacetylpyridine and isonicotinic acid hydrazide

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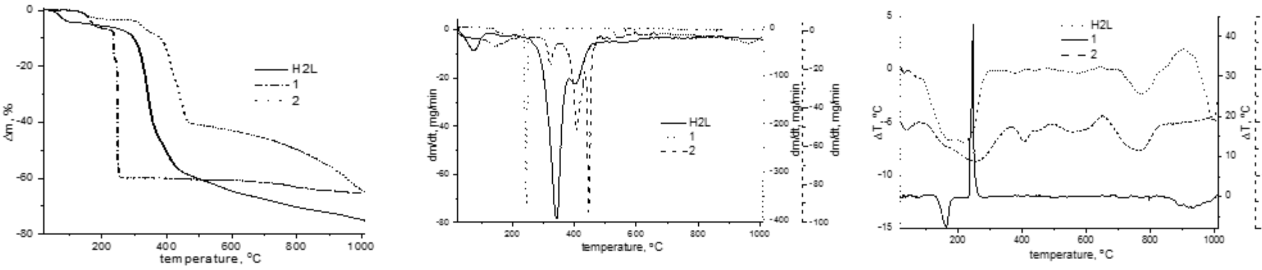
One-pot synthesis of Mn(II) salts, 2,6-diacetylpyridine and isonicotinic acid hydrazide (H_2L) in ethanol and reaction conditions afforded mononuclear $[Mn(H_2L)_2(H_2O)_2](NO_3)_2$ (**1**) [1] and trinuclear $[Mn_3(H_2L)_2(NCS)_2Cl_4(H_2O)_2]$ (**2**) complexes. The synthesized compounds were investigated in the solid state by IR spectroscopic method, X-ray diffraction and thermogravimetric analysis under inert atmosphere.

The compound **1** begins to decompose at 110 °C by removing water molecules, the mass loss being 5.93% (5.84% calc.). The process is accompanied by endothermic effect in the range of 110-190 °C. In the range 220-280 °C there is an oxidative thermal degradation with a strong exothermic effect. This is explained by the presence of nitrate anions in the structure. The mass loss at this stage is 53.9% and as a result, a mixture of carbonaceous residue and Mn(III) oxide is obtained. Up to 840 °C the residue formed is stable and in the interval 840-995 °C on the TG curve a decrease of the mass is observed as a result of the transformation of the oxide of Mn(III) into Mn_3O_4. The process is accompanied by a weak endothermic effect, possibly due to the fact that the more reactive organic part of the ligand (aliphatic chains) has been oxidized by the nitrate ions and the aromatic residue is not oxidized during this temperature range (Figure).

Compound **2** is thermally stable up to 110 °C; subsequent heating leads to the loss of two coordinated water molecules, a process that ends at 180 °C. The mass loss represents 2.85% (2.85% calc.). Up to 290 °C this compound does not undergo other transformations, and in the range 290-377 °C there is a mass loss of 6.7%, which corresponds to the elimination of two inaH molecules (6.8% calc.). In the range 377-434 °C has observed another 18.1 % mass loss, a process caused by the thermal degradation of the H_2L^1 ligand. Heating to 480 °C leads to a total loss of 40.5%, and the residue formed gradually degrades to 1000 °C. In the DTA curve at 654 °C is observed an endothermic effect without a mass change, which can be explained by the melting of Mn(II) chloride obtained at the decomposition of compound **2**.



(a) (b) (c)

Figure 1. TG (a), DTG (b) and DTA (c) curves for ligand H_2L, compounds **1** and **2**.

In all cases, thermal degradation of the Schiff bases occurs in two stages followed by exothermic decomposition with the formation of the manganese oxide as the final product.

Acknowledgment
The authors thank for the support of projects: *20.80009.5007.28* and *20.80009.7007.21)*, financed by National Agency for Research and Development of Republic of Moldova.

[1] Cocu M., Croitor L., Bourosh P., Titica T., Danilescu O., Bulhac I. *A XXXV-a Conferință națională de chimie*, 02-05 octombrie 2018, Călimănești-Căciulata, județul Vâlcea, România P.S.II, p. 6.

Effect of MgO and CaO addition on the silicate-phosphate glasses forming ability

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The present study aimed to investigate how the kind of alkaline-earth network modifier influences glass forming ability of sulfur-bearing silicate-phosphate glasses from SiO_2-P_2O_5-K_2O-MgO/CaO-SO_3 systems.

To date it has been established, that although sulfate solubility in silicate melts is limited due to poor polymerization compatibility between [SiO_4] and [SO_4] structural units [1], it may be significantly enhanced by increasing the modifier content in the glass composition [2]. Certain tendency has also been reported in the literature, according to which the region of glass formation increases with the size of monovalent or bivalent modifier cation [3]. Given that, an improved sulfate solubility should be expected from CaO-containing system.

To verify such theory glasses from studied systems were synthesized by traditional high-temperature melting of the glass batches. Silicon dioxide, ammonium dihydrogen phosphate, calcium carbonate, potassium carbonate, magnesium oxide and potassium sulfate, as high purity raw materials, were mixed in proper quantities in a mortar with a pestle to achieve the desirable homogeneity. Gained batches were melted in a ceramic crucible inelectrically heated furnace at 1450^{o}C and quenched by pouring the melt on a steel plate, after which the amorphous nature of samples was verified by XRD method, while the content of the amorphous phase was found by applying the internal Al_2O_3 standard. On that basis it has been demonstrated, that, while in the MgO-containing system as much as 3 mol% of SO_4^{2-} can be loaded within the base glass to obtain fully amorphous materials, in those with CaO and with the simultaneous presence of MgO and CaO, only glass-crystalline samples may be acquired. Furthermore, regardless of the studied system, appearance of the crystallization product in the form of K_2SO_4 has been revealed, when the molar content of SO_3 incorporated into the structure of MgO, CaO, MgO+CaO-containing system reaches 5, 3 and 3%, respectively. In order to verify the actual SO_3 content retained within the analysed materials, and subsequently - precisely determine the inherent sulfate-capacity of the given systems, the XRF method has been applied. Additionally, by means of the SEM-EDS investigation, changes manifesting themselves on the surface of studied materials and resulting from an incorporation of increasing amounts of sulfur into their structure, have been demonstrated, as well as the homogeneity of the surface was confirmed.

The present study constitute a step towards gaining a greater understanding of the nature of sulfur-bearing systems.

Acknowledgements:

This work was financed by the National Science Centre, Poland, project number 2018/31/D/ST8/03148

[1]R. K. Mishra *et al.*, “Role of sulfate in structural modifications of sodium barium borosilicate glasses developed for nuclear waste immobilization,” *J. Am. Ceram. Soc.*, vol. 91, no. 12, pp. 3903–3907, Dec. 2008, doi: 10.1111/j.1551-2916.2008.02773.x.
[2]P. A. Bingham *et al.*, “Modelling the sulfate capacity of simulated radioactive waste borosilicate glasses,” *J. Alloys Compd.*, vol. 695, pp. 656–667, 2017, doi: 10.1016/j.jallcom.2016.11.110.
[3]P. Bingham, R. Hand, and -r O R, “Sulphate incorporation and glass formation in phosphate systems for nuclear and toxic waste immobilization,” 2007, doi: 10.1016/j.materresbull.2007.07.024.

Thermal and structural investigations on P_2O_5-SiO_2-K_2O-MgO-CaO-Co_2O_3 glass crystalline materials

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Phosphate glasses has received a great attention since 1970. Because of extensive studies carried out on these materials, various applications were pointed out in case of not only fully amorphous compounds but also related glass-ceramics. Among them, bioglasses or bioglass ceramics, laser host materials, sealants, solid electrolytes, waste storage can be highlighted [1]. However, the data on the structural role of cobalt ions and their influence on the properties of phosphate glasses and glass based materials is limited.

Taking these into consideration it was decided to prepare glass crystalline materials from the P_2O_5-SiO_2-K_2O-MgO-CaO-Co_2O_3 system with the amount of cobalt ions incorporation expressed in oxide with accordance to the glass technology practice, set as not less than 30 mol%. Materials were subjected to the XRD analysis in order to identify corresponding crystalline phase – which occurred to be cobalt diphosphate ($Co_2P_2O_7$). Further studies were carried out via Raman spectroscopy, which have revealed their highly depolimerized character and via DSC, which led to the designation of the characteristic parameters such as temperature of glass transition (T_g), crystallization effects (T_c), change of specific heat (Δc_p) and thermal stability (ΔT).

Additionally, the transition at around 245°C were recognized and connected to the associated phase ($Co_2P_2O_7$). The further details of the transition was obtained by high-temperature XRD, Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT), dilatometry and Laser Flash Analysis.

Performed study allowed to characterized cobalt-rich glass crystalline materials and shed a light onto the nature of phosphate glasses family and associated materials.

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[1] F. Muñoz, J. Rocherullé, I. Ahmed, L. Hu, (2019), “Phosphate Glasses” In.: J. D. Musgraves, J. Hu, L. Calvez, (Eds.), “Springer Handbook of Glass”, Springer Nature Switzerland AG, 553 – 594.

Thermal and spectroscopic studies of multicomponent glasses from P_2O_5-SiO_2-K_2O-MgO-CaO-Co_2O_3 system

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Phosphate glasses are a group of materials characterized by broad ability to be accommodated by extensive amount of transition metal ions and simultaneously maintaining fully amorphous structure [1]. The alterations of their chemical composition affects the structural and therefore physical properties. The establishing of this connection is important for application purposes. Bioactive calcium or magnesium phosphate glasses for biomedical usage [2] and phosphate glasses with control release rate with various compositions as agro-fertilizers [3, 4] can be mentioned as the results of such considerations.

Phosphate-based multicomponent glasses from P_2O_5-SiO_2-K_2O-MgO-CaO system, with molar ratio of P_2O_5 and SiO_2 set as 41 : 6 and Co_2O_3 addition incorporated at the expense of MgO and CaO content, were prepared via melt-quenched technique and subjected to the thermal and structural studies.

DSC method was used for describing phase transitions occurring in glasses during heating. The compositional dependent parameters, such as glass transition temperature (T_g), change of specific heat (Δc_p), temperature of crystallization effects (T_c) and thermal stability (ΔT) were assigned. The impact of increasing addition of cobalt ions was reflected in noted changes of values of designated thermal parameters. DSC analysis was combined with XRD method, which also allowed to perform of identification of peculiar crystallization phases. Results were confronted and found to be consistent with the effects of Raman and FTIR studies which once again confirmed the correlation of physics properties to the glass structure.

Performed study shed a light into a structure of cobalt phosphate silicate glasses – material which can be considered as scientific novelty with various potential applications.

Acknowledgement: The work was supported by the Faculty of Materials Science and Ceramics AGH — University of Science and Technology No. 11.11.160.617 and the EU Project POWR.03.02.00-00-I004/16

[1] E. Metwalli, M. Karabulut, D.L. Sidebottom, M.M. Morsi, R.K. Brow, J. Non-Cryst. Solids 344 (2004) 128
[2] M.A. Karakassides, A. Saranti, I. Koutselas, J. Non-Cryst. Solids 347 (2004) 69
[3] M. Szumera, I. Wacławska, J. Sułowska, J. Mol. Struct. 1114 (2016) 78
[4] H.-K. Lee, S.-J. Hwang, W.-H. Kang, Mater. Sci. Forum Vols 486-487 (2005), 407

Common Nettle (Urtica dioica L.) as an Essential Filler of Natural Rubber Biocomposites

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Common nettle, as a natural fibrous filler of polymeric materials, represents the global trend of producing biocomposites with the addition of substances of plant origin. The aim of the study was to investigate and explain the effectiveness of *Urtíca Dióica L.* - as separate parts of seeds, leaves, stems (branches) and roots as a source of active functional compounds for the effective modification of elastomer composites based on natural rubber.

Common nettle represents an interesting alternative for commercial fillers and could be applied as a low-cost additive, which improves several properties of natural rubber vulcanizates. The work carried out included the characteristics of both lignocellulosic fillers and elastomer composites. The analysis of the particle size of the fillers as well as the UV-Vis absorption spectra and the FTIR spectra of *Urtíca Dióica L.* (stems, leaves, roots, seeds) was performed. The structural, morphological and dispersion properties of both *Urtíca Dióica L.* and new composite systems have been determined by spectroscopic (FTIR) and scanning electron microscopy (SEM) analysis. The rheometric properties of the elastomer blends were investigated, as well as the thermal properties (TGA, DSC) of the composites. Moreover, tests of mechanical properties (tensile strength and elongation at break) and changes in the color of vulcanizates were carried out, which allowed to determine the resistance of materials to simulated aging processes (thermo-oxidative, UV).

Application of Common nettle (*Urtíca Dióica* L.) for natural rubber composites, indicated high application level of those type of materials, due to the improvement of the performance properties. Additional ecological and economic benefits can be achieved by solving common agricultural problems by recycling ecologically clean and high-quality waste.

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The straw-clay fillers applied in elastomer composites

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The great interest in the subject of polymer-based biocomposites production results from the global idea of "cleaner production" and green chemistry. Such bio-composites have satisfactory properties. In order to ensure above-average functional properties, natural plant fillers are used in combination with other functional additives. The aim of the study was to create biocomposites with various fillers, including straw and modified or unmodified montmorillonites. Three different modified montmorillonites were selected as components of the produced hybrid fillers. This research attempts to provide information on the effects of both physical and chemical modification of fillers on the elatsomer matrix (natural rubber). In-depth characteristics of the applied bio-additive were prepared based on a number of research techniques and methods such as: scanning electron microscopy (SEM), thermogravimetric analysis (TGA), microcalorimetry method (pyrolysis combustion flow calorimeter).

Elastomer composites were prepared as a function of straw/nano-clay fillers content (10-30 phr). Then, an analysis of their main functional properties was performed, including mechanical and thermal properties. The research allowed to emphasize the significant value of straw-montmorillonite fillers in its new role - as an active filler of elastomer biocomposites.

It has been shown that the addition of optimal amounts of biofillers can, inter alia, increase the tensile strength of the composite, improve thermal properties, extend the burning time of the material and affect the course of vulcanization or cross-linking density.

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Influence of alloying elements on thermal properties of polycrystalline γ′ strengthened Co-Al-W superalloys

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The recently developed Co-Al based alloys with the γ–γ′ microstructure have demonstrated comparable high temperature creep than the second generation Ni-Al based superalloys [1-3]. The aim of the study is to provide information concerning effect of different elements on thermal behavior of γ–γ′ superalloys based on Co-Al-W system.

In this work, the effect of various alloying elements (Ni, Al, W, REE) on thermal properties of Co-Al-W superalloys is investigated. The Co-xNi-9Al-9W (x=10, 20, 30, 40) alloys were investigated by means of differential thermal analysis (DTA), differential scanning calorimetry (DSC) and laser flash method (LFA). The first two methods were also applied for Co-xAl-xW (x=2, 5, 7, 9) and Co-9Al-9W-0.1REE (REE=La, Ce, Nd, Dy). The studies aimed in determination of thermal behavior of alloys up to 1200 °C. Furthermore, characteristic temperatures such as *solidus*, *liquidus,* and γ′ *solvus*, were determined.

The DSC measurements in the temperature range of 40–1200 °C were performed using multi-HTC high-temperature calorimeter from Setaram. The measurements were performed under Ar protection; the heating rate was 5 °C min^{-1}. The DTA studies were carried out using the NETZSCH STA 449 F3 Jupiter thermal analyzer. The phase composition of alloys was determined using the Panalytical Empyrean X-Ray Diffractometer.

The increasing Al and W content stabilized fcc structure of Co solid solution at room temperature and improved ability to form γ′-Co_3(Al, W). Moreover, Ni improves γ′ *solvus* temperature. Rare earth elements affected solidus temperature by formation of intermetallicphases of melting temperature lower than that of γ and γ′.

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[1] K. Tanaka et al., Philos. Mag. 92 (2012) 4011-4027
[2] M.S. Titus et al., Scr. Mater. 66 (2012), 574-577
[3] M.S. Titus et al., Superalloys (2012) 823-832.

Temperature dependence of structural and magnetic transformations in Finemet amorphous alloy with Fe substituted for La

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Alloys, like $Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$ classical Finemet, appear primarily in amorphous-magnetic phase, which after appropriate thermal or mechanical treatment, are transformed into the phase, when iron-silicides and iron-borides magnetic nano-crystals are embedded in an amorphous residual matrix [1]. For practical purpose, in order to obtain soft magnetic properties of the material, it is important that the size of nano-crystals, during primary crystallization, is smaller than the exchange-correlation length.

So far, many different modifications of the basic FeSiB composition were analysed while searching for better technical properties [1]. The analysis was focused rather on products of primary crystallization at lower annealing temperatures with less interest on the secondary crystallization.

In this work mainly secondary crystallization at higher temperatures and its correlation to magnetization phenomena of $Fe_{73.5-x}La_{x=0,3,5,7}Si_{13.5}B\$_9Nb_3Cu_1$, (a Finemet with Fe substituted for La), was analysed by means of scanning calorimetry (DSC) and, performed at the same time, thermomagnetic measurements (TM).

Identification of structures and magnetic properties of the present alloys, was based on our previous DSC, XRD and Mossbauer spectroscopy study [2] of the alloys with dopants other than La.

[1] R.Brzozowski, M.Wasiak, H.Piekarski, P.Sovak, P.Uznański and M.Moneta, Journal of Alloys and Com65pounds 470 (2009) 5-11

[2] M.Antoszewska, M.Wasiak, T.Gwizdałła, P.Sovak, M.Moneta, Journal of Thermal Analysis and Calorimetry 115 (2014) 1381-6

Influence of carbon and basalt fillers on thermal, mechanical and fire hazard of EPDM rubber composites

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Recent years have witnessed a great interest in polymeric materials with special properties, resistant to the action of considerably lowered or increased temperature, flame-retardant and showing appropriate mechanical strength. It is the flammability of polymers that is of paramount importance, which results first of all from health and life protection as well as economic reasons.

An increase in the resistance of polymeric materials to the action of fire can be obtained by using carbon nanofillers, such as carbon nanotubes or graphene that more and more often constitute an alternative to conventional flame-retardant substances.

Graphene is a two-dimensional allotropic variety of carbon, in which each carbon atom is connected with the next bond with hybridization sp^2 having a length of 0.141 nm. Its close-packed carbon atoms form a honeycomb crystallographic structure. The thickness of 2D graphene layer ranges at the average from 1 to 1.6 nm.

Graphene as 2D carbon nanofiller with a large specific surface and excellent electric, thermal and mechanical properties is also more and more often used to prepare polymeric nanocomposites.

Basalt fibers (BFs) with basic chemical components of SiO_2, Al_2O_3, CaO, MgO, K_2O, Na_2O, Fe_2O_3 and FeO are produced from common volcanic rock. BFs are biologically inert as well as environmentally friendly and can be used in composites and other materials for some aggressive environments. With high mechanical performance, outstanding heat resistance to chemical attack and low water absorption as well as lower cost, BFs have attracted more and more attentions as a potential reinforcing agent for fire-resistant polymer composites.

In the current work, we proposed a new flame-retardant system. The system consisted from graphene in the form of graphene nanoplatelets with an average thickness of approximately 6 nanometers and surface area of 150 m^2/g and basalt filler in the form of both flakes and fibers. The performed studies indicated that synergistic action of graphene and BFs decreased flammability of EPDM rubber composites and improve their mechanical and thermal properties. The effectiveness of graphene-BFs system for reducing the flammability of the studied composites was assessed by means of cone and microcalorimetry.

Compositional effects on the interactions between structural elements in sulfur-bearing silicate-phosphate glasses

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The aim of this study was to explain the interactions between structural elements in sulfur-bearing silicate-phosphate glasses with varying content of glass formers (SiO_2, P_2O_5) as well as their sulfur free counterparts. All glasses were synthesized by traditional melting raw materials mixture but sulfur containing glasses obtained under reducing conditions. Such glasses could find application as glassy carriers of sulfur for soil environments which is essential element for plants. Thus, we can try to solve the problem of sulfur deficiency in soil.

Sulfur is a poorly glass-compatible element. Sulfur can be incorporated into silicate and borosilicate glass structures at up to 1 wt.% of SO_3 equivalent. More than 1 wt. % SO_3 causes the formation of a separate water-soluble (yellow) phase that contains alkali sulfates [1]. According to the literature [2], the solubility of sulfur in the structure of phosphate glasses is higher than that in silicate or borosilicate glasses. The volatilization of SO_2 gas due to the synthesis of sulfate glasses is the largest problem.

The amorphous nature of the samples was verified using X-ray diffraction (XRF). The bulk composition of glasses was confirmed with X-ray fluorescence spectroscopy. The homogeneity of the glasses was confirmed through elemental mapping at the microstructural level with scanning electron microscopy (SEM) combined with an analysis of the microregions with energy-dispersive X-ray spectroscopy (EDS). We employed differential scanning calorimetry-thermogravimetry-evolved gas analysis by mass spectrometry (DSC-TG-EGA (MS)) combination to explain the changes that occur when the glass batches containing sulfate is heated. All glasses were subjected to differential scanning calorimetry (DSC) measurements. The relationship between the parameters characterizing glass transformation effect of sulfur-free and sulfur-bearing glasses as a function of SiO_2/P_2O_5 content was discussed. The structure of the glasses was studied by using spectroscopic techniques. This work also referred to the density and molar volume of the glasses.

The addition of sulfur increased the abilities of glasses with higher amounts of P_2O_5 to form. The sulfur-doped glasses were characterized by a lower density value than that of their sulfur-free counterparts. The lower density of the sulfur-doped glasses was probably related to the presence of large sulfur-containing anions in their structure. The addition of sulfur showed changes in the silicate–phosphate networks, making them more polymerized, which was probably related to the concentration of potassium ions in the vicinity of the sulfur ions.

Acknowledgements

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[1] M.I. Ojovan, W.E. Lee, “An introduction to nuclear waste immobilization”. Elsevier. Amsterdam, The Netherlands, 2005.
[2] K. Ghosh, G.K. DasMohapatra, N. Soodbiswas, “Glass formation in K_2SO_4-CaO-P_2O_5 system”. Phys. Chem. Glas. 44 (2003) 313–318.

Stabilization of natural dyes onto vermiculite mineral – hybrid pigments with improved performance

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The applications of natural dyes and pigments in the actual production and daily life have encountered a series of bottlenecks with the technological development. In the recent years, the synthetic colorants almost completely replaced natural dyes and pigments due to their high yield, low price, high tinting strength, durability and a large range of colors [1]. However, there is now again a growing interest in dyes of natural origin due to their abundance in nature, low toxicity as well as biodegradability. An interesting strategy to overcome the problems related to the low thermo-, photo- and chemical stability of natural dyes is to design organic-inorganic pigments via the stabilization of the organic chromophores onto mineral supports [2]. To date, many studies have shown that the synergy of organic and inorganic compounds in hybrid materials may form new materials with enhanced stability and new functional properties [3, 4].

In this context, the present work intended to design new organic-inorganic pigments based on different natural dyes (such as alizarin, purpurin, lawsone, carminic acid) and vermiculite mineral. Secondary ion mass spectrometry (ToF-SIMS), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and UV-Vis spectrophotometry were employed to comparatively study the interactions, morphology and stability of different organic-inorganic hybrid pigments.

It was found that organic chromophores interacted with metal ions (Mg, Al) present in the vermiculite mineral forming stable, natural, multicolour hybrid pigments. The modification of the vermiculite with various chromophores did not cause the alterations in its morphology. Furthermore, the designed hybrid pigments showed a better thermal stability and chemical resistance than their corresponding natural dyes. This work sets a new route for designing natural, stable organic-inorganic hybrid pigments with improved physico-chemical performance and interesting color characteristic.

[1] Li, S. et al. *Dyes and Pigments* **2021**, 190, 109322.
[2] Fournier, F. et al. *Applied Clay Science* **2016**, 13, 12-17.
[3] Zhuang, G. et al. *Journal of Colloid and Interface Science* **2019**, 552, 204-217.
[4] Graycyellê, R.S et al. *Dyes and Pigments* **2021**, 190, 109306.

DSC Microscope Accessory - Visual Observation of Material Transitions Combined with the Enthalpy Data

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Hyphenation of techniques is often useful and can lead to an increased understanding of the transitions occurring within materials. The use of optical microscopy in combination with DSC has several applications that may prove insightful to better understanding materials' properties and behaviours. The technique allows the scientist to capture in-situ images of a material as it passes through transitions.

New synthesis strategy of $BiFeO_3$-$BaTiO_3$ electroceramics for high temperature applications

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BiFeO3-based ceramics have initially attracted considerable attention as promising lead-free piezoelectrics due to a high Curie temperature, large polarization, and high piezoelectric coefficient, especially for high-temperature applications. ABO_3-modified BFO ceramics, such as the (1−x)$BiFeO_3$-x$BaTiO_3$ (BFO-BT) system near the morphotropic phase boundary (MPB) have attracted extensive attention as a new generation of lead-free piezoelectric ceramics because of its promising piezoelectric performance, high Tc and reduced leakage current [6,9,10]. Dense $BiFeO_3$-$BaTiO_3$ ceramics are commonly synthesized by the conventional solid-state reaction method in two steps, including preparation and sintering. Both steps need high temperatures and long treatment times, which are high energy consuming. Under such conditions, it is difficult to prepare dense and stoichiometric $BiFeO_3$-$BaTiO_3$ ceramics due to high Bi volatilization and Fe^{3+} reduction that lead to the formation of secondary phases such as $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$.

In this work, we will present studies on $BiFeO_3$-$BaTiO_3$ compositions. The selected compositions will be prepared via different processing techniques such as the solid-state reaction method and Mechanosynthesis technique. In addition, the densification of the samples will be done via the flash sintering technique, which is a novel densification technology for ceramics, which allows a dramatic reduction of processing time and temperature. Structural, microstructural and electrical properties of the prepared materials will be also investigated.

[1] D. Wang, G. Wang, S. Murakami, Z. Fan, A. Feteira, D. Zhou, S. Sun, Q. Zhao, I.M. Reaney, J. Adv Dielectric. 8 (2018) 1830004.

Thermal behaviour of raw clay materials containing muscovite (illite/sericite), kaolinite and pyrophyllite: analysis of vitrification rate and estimation of optimum firing conditions

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Clays containing muscovite (illite/sericite), kaolinite and pyrophyllite have interesting properties as structural ceramic raw materials. The present work reviewed the previous investigations focusing on the sintering behaviour of such as clays and including new results on pyrophyllite clays, which have not been studied until now. A previous work [1] proposed an experimental method for the study of vitreous pottery bodies involving the so-called “range curves” and the determination of a “temperature of vitrification” where porosity becomes almost zero. Thus, sintering diagrams can be obtained using the results of linear firing shrinkage, water absorption capacity, bulk density and apparent porosity determined in the ceramic bodies as a function of firing temperatures. Vitrification is the result of heat treatment and fusion during which a glassy or non-crystalline phase is produced [1-3]. Consequently, a progressive reduction in the porosity of the clay materials can be achieved. The vitrification range is the temperature interval between the temperature at which a ceramic material begins to fuse and the temperature at which the ceramic begins to deform by melting. Vitrification is complete when maximum density and almost zero porosity are achieved without deformation in the ceramic bodies.

A semiempirical attempt to analyse vitrification process in ceramic raw materials constituted by common clays has been reported [2]. The method was based on experimental observations of apparent porosity and density, calculating heat treatment and optimum conditions of firing and an Arrhenius analysis involving the temperature dependence on the vitrification rate, using an approach under isothermal conditions and a first order kinetic. Using this approximation, an analysis of vitrification process involving two kaolinitic clays of residual origin, two podzolic clays, one latosol [2] and an industrial clay from Ecuador, with ~35 wt. % of a “disordered kaolin phase” [3], have been performed. A common clay (with chlorite and illite) and a muscovite (illite/sericite), kaolinite and pyrophyllite clay has been included in the present investigation. The chemical composition was determined and the RO, R_2O and the total flux content were calculated from these results for almost all these clay samples. The total flux content ranges from 4.18 to 26.76 wt. %. The sintering behaviour was investigated in the range 800-1500 ºC with 0.5-5h of soaking times under laboratory conditions. It was found some variations of bulk density values for the ceramic bodies heated in the range 1000-1150 ºC, with marked decreases of these values for samples fired at 1200 ºC and 1300 ºC. The temperature of maximum bulk density were determined and the vitrification temperatures where the apparent porosity becomes almost zero. The relative rates of vitrification or degree of vitrification attained during soaking were calculated.

In general, the discussion of the results of this analysis suggested that the contribution of vitrification due to the heating was relatively small compared to the vitrification during soaking. The vitrification rate equations, as included or deduced in this study, can be a useful tool to estimate the optimum firing conditions of all these clays. The research performed in this work will contribute to a better knowledge of the characteristics of sintering of such as clays applied as ceramic raw materials.

[1] A.W. Norris, D. Taylor, I Thorpe, Br. Ceram. Trans. J., 78 (1979) 102
[2] V.T.L. Bogahawatta, A.B. Poole, Br. Ceram. Trans. J., 90 (1991) 52
[3] S.M. Faieta-Boada, I.J. McColm, Appl. Clay Sci. 8 (1993) 215

Thermophysical study of mixtures bentonite + *Nannochloropsis sp* + sea water and distilled water for cosmetic uses

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In this work, the thermophysical properties of mixtures of a bentonite and the microalgae *Nannochloropsis sp* with seawater and distilled water are presented. These types of mixtures are called peloids [1]. The properties studied are the specific heat, the thermal conductivity, the density, and the thermal diffusivity as a function of the concentration of the water and the one used, at atmospheric pressure and a temperature of 308.15 K.

Specific heat has been determined using a CALVET microcalorimeter [2]. The density of the mixtures was carried out by a pycnometric method [3]. A Decagon KD2 Pro conductivity meter was used to measure thermal conductivity [4]. Thermal diffusivity was calculated from the data obtained on thermal conductivity, density and specific heat [5].

The properties studied will help in choosing the most suitable type of application for each mixture for the different uses in the field of cosmetics, thermalism and wellness [6].

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[1] C. Gomes, M.I. Carretero, M. Pozo, F. Maraver, P. Cantista, F. Armijo, J.L. Legido, F. Teixeira, M. Rautureau, R. Delgado. Applied Clay Science, 75–76 (2013) 28.
[2] M.M. Mato, L.M. Casás, J.L. Legido, C.P. Gómez, L.M. Mourelle, D. Bessières, F. Plantier. J. Therm. Anal. Calorim., 130, (2017) 479.
[3] N. Glavas, M.L. Mourelle, C.P. Gómez, J.L. Legido, N.R. Smuc, M. Dolenec, N. Kovac. Appl. Clay Sci., 135 (2017) 119.
[4] V. Caridad, J.M. Ortiz de Zárate, M. Khayet, J.L. Legido, Appl. Clay Sci., 93-94 (2014) 23.
[5] L.M. Casás, M. Pozo, C.P. Gómez, E. Pozo, D. Bessières, F. Plantier, J. L. Legido. Appl. Clay Sci., 72 (2013) 18.
[6] L. Mourelle, C.P. Gómez, J.L. Legido, Cosmetics, 4 (2017) 46.

Structural characterization of sol-gel TiO_2 and CeO_2 coated ceramics membranes

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Wastewater reuse is considered as the most suitable and reliable alternative for sustainable water management and agricultural development [1] and membrane separation technology emerged as one of the tools to tackle the water stress problem. Ceramic membranes (CMs) offer durability and high integrity during filtration [2]. The most commonly used CMs for water treatment are alumina (Al_2O_3), titania (TiO_2), zirconia (ZrO_2), silicon carbide (SiC) and silica (SiO_2) based. The structure and morphology of ceramic membranes have substantial effects on their performance. Based on their pore size, CMs could be classified into microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) with pore size ranging from > 50 nm, 2–50 nm and < 2 nm, respectively.

In this study, four commercial CMs with different composition and pore size were used: three UF ceramic membranes of TiO_2/ZrO_2 composition with 50 kDa, 150 kDa and 300 kDa molecular weight cut-off (MWCO) respectively, and a MF ceramic membrane of TiO_2/ZrO_2+TiO_2 composition with a pore size of 200 nm. The membranes were modified by sol-gel deposition of TiO_2 [3] or CeO_2 [4] film. One, two or three layers of each film were deposited on the each of the four membranes using the vacuum impregnation method to derive catalysts for application in hybrid ozonisation-filtration system. The composites were dried and subsequently thermally treated. Both the unmodified and surface-modified ceramics membranes were characterized in order to evaluate their chemical composition, phase composition, morphologic parameters, using scanning electron microscopy with energy dispersive X-ray spectroscopy, atomic force microscopy, nitrogen adsorption/desorption isotherms, X-ray diffraction analysis and Fourier transformed infrared spectroscopy.

[1] M. Fernanda Jaramillo, I. Restrepo, Sustainability, 9(10) (2017) 1734.
[2] S. Lee, J. Cho, Desalination, 160(3) (2004) 223-232.
[3] L. Ćurković, D. Ljubas, S. Šegota, I. Bačić, J. Alloys and Compd., 604 (2014) 309-316.
[4] L. Wen Jie, B. Yueping, H. Xiao, L. Teik-Thye, Chem. Eng. J., 378 (2019) 121670.

Thermal and rheological properties of dietary fiber from mushroom *Flammulina velutipes* via autoclaving associated with enzyme treatment

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Abstract Edible mushroom consists of a mass edible fiber that provides the potential to develop dietary fiber source based on a long edible history and renewability [1-2]. *Flammulina velutipes* (Enoki) is an extensively cultivated and commercially available material in the world because of its desirable flavor and high nutritional value. Actually, in the enoki composition, its non-digestible carbohydrate is predominant, which is > 90% [3-5]. However, the most of the enoki fiber is insoluble dietary fiber (IDF), which is not favorable for its development. Conversion of insoluble dietary fiber (IDF) to soluble dietary fiber (SDF) is the regular method for the better application of dietary fiber in the food industry. Therefore, various methods have been reported to improve the yield of SDF for the potential application as fiber enrichment foods, such as blasting extrusion, steam explosion and enzymolysis (1-3) [6-8]. Autoclaving, as a useful hydrothermal method, has several advantages, such as simple, economical, environmentally friendly and without corrosion [9]. According to after autoclaving for 10 minutes and adjusting the solid-liquid ratio to 20%, the extraction rate of *F. velutipes* SDF (FVSDF) increased from 10.33±0.19% to 11.48±0.45%, which is the best conversion ratio. After treatment, the glucose was to be the dominating monosaccharide of all these FVSDF and *F. velutipes* IDF (FVSDF). The DSC curves of FVSDF and FVIDF revealed a broad endothermic peak in the range of 30–170 °C. The results of microscopic structure revealed by SEM displayed that the FVSDF has smaller particles. It can be concluded that autoclaving is effective for increasing FVSDF content. The experimental results will provide effective use of *F. velutipes'* dietary fiber in the functional food industry.

[1] P.C.Cheung. Food Sci. Hum. Wellness., 2(3-4) (2013) 162
[2] H.Yasin, M. Zahoor, Z. Yousaf, A. Aftab, N. Saleh, N. Riaz, B. Shamsheer. Phytomedicine., 54 (2019) 43
[3] K. He, X. Zhang, Y. Li, B. Li, S. Liu. Food Hydrocoll. 101, (2020).105519
[4] H. Cai, X. Liu, Z. Chen, S. Liao, Y. Zou. Food Chem., 141 (2013) 2873
[5] X. Xin, K. Zheng, Y. Niu, M. Song, W. Kang. Open Chem. 16 (2018) 155
[6] Y. Wen, M. Niu, B. Zhang, S. Zhao, S. Xiong. LWT 75 (2017) 344.
[7] Z. Xue, Y. Chen, Y. Jia, Y. Wang, Y. Lu, H. Chen, M. Zhang. Food Hydrocoll. 95 (2019) 10
[8] Z. Xue, Q. Ma, Y. Chen, Y. Lu, Y. Wang, Y. Jia, ... H. Chen.Food Res Int. 129 (2020) 108870
[9] B. Ahmad, A. Gani, I. Ahmed, A. Shah, F. Ahmad, D. Chandra, Food Hydrocoll. 56 (2016) 108

Antioxidant effects of peanut skin extracts for button mushrooms and sacha inchi oil via isothermal calorimetry

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Abstract Peanut skins are primarily an industry byproduct with only small quantities utilized in animal feed or dropped directly. Due to the peanut skins being a rich source of phenolic compounds with antioxidant activity and low cost, they have a great potential utility as food preservatives [1-5]. The selection of efficient methods for extracting antioxidant compounds from peanut skins is needed to increase commercial appeal. Furthermore, the chemical composition and antioxidant activity of extracts obtained from peanut skins prepared with 95% ethanol by ultrasound extraction also need to be established. The crude peanut skin extracts of extraction yield, total phenols and flavonoids, DPPH scavenging activity, ferrous-ion chelating activity, reducing power, trolox equivalent antioxidant capacity (TEAC) and accelerated oxidation of button mushroom and sacha inchi oil were evaluated [6]. Meanwhile, in order to understand the actual antioxidant effects of peanut skin extracts, the button mushroom and sacha inchi oil were added in various doses of peanut skin extracts under air and pure oxygen ambient with the isothermal temperature of 30 and 60.5 °C by conducting isothermal calorimeter (TAM Air) analyses, respectively. Therefore, we obtained that under pure oxygen ambient, the mushroom and oil stability was destroyed more than in air atmosphere. Overall, the peanut skin extracts displayed beneficial antioxidant properties in button mushrooms and sacha inchi oil, which could be used as a natural antioxidant in food products.

[1] JM Lorenzo, PE Munekata, AS Sant'Ana, ... MA Trindade. Trends Food. Sci. Technol. 77 (2018) 1
[2] FM Yılmaz, AZ Bastıoğlu. LWT (2020) 109036
[3] YE Rossi, LP Boh, NLV Braber, MB Ballatore, FM Escobar, MA Montenegro. J. Funct. Foods 67 (2020) 103862
[4] KE Constanza, BL White, JP Davis, TH Sanders, LL Dean. J. Agric Food Chem. 60 (2012) 10776
[5] M Larrauri, MP Zunino, JA Zygadlo, NR Grosso, V Nepote. Ind. Crops. Prod. 94. (2016) 964
[6] SY Tsai, YC Hsu, HY Lin, FK Huang, CP Lin. J. Therm. Anal. Calorim., 130(3) (2017) 1281

Thermogravimetric analysis of the high-temperature oxidation behaviour of three hot-work tool steels

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The high-temperature oxidation behaviour of three hot-work tool steels H11, Dievar and W600, was investigated by thermogravimetric analysis. Since the steels studied are typically used in the heat-treated condition, the high-temperature oxidation was studied in two conditions, the soft-annealed condition, and the hardened and tempered condition. Thermogravimetry was used to investigate the effect of temperature, chemical composition, and thermal condition of the steels on the high-temperature oxidation kinetics.

The samples were oxidised in the STA instrument for 100 h in air atmosphere, the temperature range studied was between 400 °C and 700 °C. Equations describing the high-temperature oxidation kinetics were derived from the thermogravimetric results. The kinetics can be described by three mathematical functions, namely: exponential, parabolic and cubic. However, which function best describes the kinetics depends on the oxidation temperature, chemical composition, and thermal condition of the steel. Hardened and tempered samples have been shown to oxidise less, resulting in a slower oxidation rate. In addition, steels containing chromium (H11 and Dievar) generally oxidise less compared to a steel without chromium (W600).

Enthalpy balance of process path of the sheet production from EN AW 5182 aluminium alloy

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Industrial production of products, such as strips, plates, and sheet from aluminium alloys starts with semi-finished product in a form of slabs. Slabs are made with direct chilled continuous casting process, which is very fast and does not allow solidification at equilibrium conditions. Negative effects of DC casting are eliminated with the process of homogenization annealing. Homogenized slabs are then hot rolled into strips with thickness of about 10 mm. Strips are then cold rolled to final thickness with possible intermediate annealing, which softens the strips and enables easier formation of the final product.

In this research enthalpy balance analysis of the EN AW 5182 aluminium alloys during entire process path of sheet production was made, whereas samples after every step of sheet production process path were obtained. Using Thermo-Calc computer program thermodynamic simulation of equilibrium and nonequilibrium solidification was made. Differential scanning calorimetry (DSC) was made on every sample, whereas the melting characteristic temperatures and the melting enthalpies from the results were obtained. Optical microscopy and scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDS) were used to analyse microstructure and microstructural components.

It was concluded that each step of the process, which includes different processing temperatures and deformation, has a significant effect on the reaction/melting enthalpy and cannot be unambiguously described.

Key words: Aluminium alloy EN AW 5182, heat treatment, rolling, thermodynamic equilibrium, microstructure, intermetallic phases, DSC.

Study on the antibacterial effect of silver nitrate on the growth of *Pseudomonas aeruginosa*

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In the pharmacopoeia of many countries, silver nitrate, together with silver itself, is used as an antiseptic and disinfectant applied topically [1]. It is also used as a cauterizer in superficial hemorrhages or to refresh sore ulcers, and It has been proposed as a coating material for endoprotheses and other implants in the surgical practice [2, 3]. This metal is an attractive material to be used as a component of fixation devices and joint prostheses in orthopaedic surgery [4, 5], in order to decrease the postoperative infection rates. In the field of orthopaedic surgery, the formation of the biofilm around metallic implants have been a field of great interest in research due to high postoperative infection rates, and the important consequences to the health and life of patients [6].

Using a Calvet microcalorimeter designed by Professor Paz Andrade [7], the heat output produced by one of the most common bacteria in hospital infections, Pseudomonas aeruginosa, was determined when it is exposed to certain concentrations of silver nitrate from 0 to 3 mM and a saturated solution. The physiological temperature of the human body was maintained (309.65 K) in the outer chamber of the calorimeter, and the data was collected by a data acquisition and processing system, at intervals of 22.2 seconds for 48 hours.

Among the thermograms obtained, the highest voltage peak was obtained using the bacterial suspension in the culture medium. Then, when metallic dissolutions were added, the voltage signal decreased gradually and no signal was detected when the saturated dissolution of silver nitrate was used. The total amount of heat exchanged showed the same pattern.

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[1] M. Ip , S.L. Lui , V.K. M. Poon, I. Lung, A. Burd, J. Med. Microbiol., 55 (2006) 59.

[2] A. Ewald, S. Glückermann, R. Thull, U. Gbureck. BioMed Eng Online. 5 (2006) 22.

[3] G. Gosheger, J. Hardes, H. Ahrens, A. Streitburger, H. Buerger, M. Erren, A. Gunsel, F. H Kemper, W. Winkelmann, C. Von Eiff , Biomaterials. 25 (2004) 5547.

[4] W. H. Song, H. S. Ryu, S. H. Hong, SH. J Biomed Mater Res A. 88 (2009) 246.

[5] J. J. Blaker, S. N. Nazhat, A. R. Boccaccini, Biomaterials. 25 (2004) 1319.

[6] O. Herbert, M. Andrew, C. Jason, Acta Orthop. 86 (2015) 147

[7] Paz Andrade MI. Les Dévelopements Récents de la Microcalorimétrie et de la Thermogenese. 1st ed. Paris: CRNS; 1967.

Thermal, structural and superconducting properties of YBCO-123 & Ag (small percentage) system

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Abstract: The superconductor $YBa_2Cu_3O_{7-x}$ (YBCO-123) samples were prepared by a solid state reaction of suitable quantities of well-mixed metal oxides of 99.99% purity. Ag_2O of 99.99% purity was added to YBCO-123 powder, in order to attain different Ag percentages (0%, 5%, 10%, and 20%), and then, to get a homogeneous blend, an ultrasonic cleaner (with isopropanol) was used. After powder pressing into the pellets, the sintering was made at 960°C for 233 h, followed by special cooling programs, in oxygen atmosphere. The X-ray analysis and SEM microscopy showed a preferential orientation of crystallites simultaneously with the increase of their dimensions, depending of Ag percentage. In the framework of XRD diffractometry, we determined the crystallite dimensions and the unit cell parameters of the orthorhombic YBCO-123 crystalline system: a=0.38128 nm; b=0.38814 nm; c=1.16753 nm.

The thermogravimetry (TG) procedure operated during the heating process, in air atmosphere (with a rate of 10 K min^{-1}), from room temperature (RT) to 1100 °C, evidenced different values for total mass loss (the oxygen loss), depending on Ag doping: 5.85% for 0% Ag; 5.32% for 5% Ag; 15.97% for 10% Ag; 18.32 for 20% Ag. The cooling in air atmosphere, from 1100 °C to RT, endows with optimal oxygen accumulation only in the case of 5% Ag doping (m_f=100.99%), and of 0% Ag (m_f=98.67%). Although, for higher Ag doping, the final masses were rather smaller: 87.9 % for 10% Ag, and 87.47% for 20% Ag, respectively. The DSC, and DTA curves (through the heating process in air) made known that the maximum temperature of the peritectic melting point of $YBa_2Cu_3O_{7-\delta}$ is dependent on Ag percentage: 1018.2 °C for 0% Ag, 1030.5 °C for 5% Ag, 1023.3 °C for 10% Ag, and 1014.5 °C for 20% Ag, respectively.

The behaviour of the quasi Almeida-Thouless line in the range from 0.4 A/m to 800 A/m of the magnetic field amplitudes, and temperatures from 77 K to room temperature, is also investigated. The results were explained in the framework of the Müller's approach [1], based on Kim-Anderson critical state model [2] concerning the dissipation of energy in the weak links, created by the grain boundaries. The experimental data are well described by a power law: $1-\frac{T_{ir}}{T_c}=H^q$. It is observed from the log-log plots, a crossover between $q \simeq 1/4$ and $q \simeq 2/3$ curves, which corresponds to 96.351 A/m (the magnetic field amplitude). For the range of the fields, and temperatures under discussion, the penetration depth is much higher than the radius of grains, hence flux creep mechanism dominates. For higher fields and lower temperatures a linear dependence of the Almeida-Thouless line is expected.

[1] K. H. Müller, A. J. Pauza, Physica C 161 (1989), 319
[2] P. W. Anderson, Z.Zou, Phys.Rev.Lett. 60, (1988) 132

Irreversibility line of bulk $Bi_{1.8}Pb_{0.3}Sr_2Ca_2 (Cu_{1-x}Ni_x)_{3.3}O_y$ system for x=0.000, 0.002, and 0.005. Thermal and structural properties

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Abstract: For the $Bi_{1.8}Pb_{0.3}Sr_2Ca_2 (Cu_{1-x}Ni_x)_{3.3}O_y$ bulk system, where x=0.00, 0.002, and 0.005, respectively, the X-ray diffraction (XRD), EDAX, AFM, AC susceptibility and resistivity measurements have been used, as characterisation methods. All the pure pellets (x=0.000) obtained either by unidirectional (20 MPa, 50 MPa) pressing or by isostatic (100 MPa, 150 MPa, 170 MPa, and 200 MPa, respectively) pressed, possess only single phase of (Bi, Pb) 2223. The substitution of Cu with Ni, in very small percentages, leads to the presence of two phases ((Bi, Pb) 2223, and (Bi, Pb)-2212), having a volume fraction that depends on Ni concentration.

For x=0.000, during the heating process with a rate of 10 K min^{-1} in nitrogen atmosphere, two endothermic processes were evidenced on DSC, DTA, and DTG curves: the first in the range of 862–920 °C (melting and slow decomposition), and another after 944 °C (decomposition).

For samples with Ni (x=0.002, 0.005), when heating is made in air atmosphere, with a rate of 10 K min^{-1}, we evidenced a relative good thermal stability until about 869 °C, an equilibrium being established between the two principal superconducting phases: 2223, and 2212, respectively. The decomposition of 2223 phase into (2201), Cu_2O, and $(Ca,Sr)_2CuO_3$, begins at about 869 °C for the doped samples, the maximum temperature of the effect being attained at around 887 °C. This is followed by the decomposition of 2212 phase into (2201), Cu_2O and $(Ca,Sr)_2CuO_3$ as we recorded at around 890 °C a second peak on DSC curve.

All the experimental data related to irreversibility lines could be well described by power laws, with different crossover fields for the pure and Ni doped samples. In the case x=0.002, there exist three distinct regions corresponding to three different power laws: q=0.088 (I), q=0.308 (II), q=0.602 (III), the crossing fields being H_{I-II} =15.5 A/m and H_{II-III}=327 A/m, respectively. As the Ni percentage is increasing, the crossover magnetic field (amplitude) between different regions shifts to higher values. For pure samples (x=0.000), the crossover magnetic field (amplitude) is slightly depressed when the pressure is modified from 170 MPa to 100 MPa, for example. The additional crossover in Ni doped sample could be explained in the framework of Kim-Anderson critical state model.

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Kinetics of thermal decomposition of some 4-phenyldiazenyl-4’-[(4-chlorobenzyl)oxy]biphenyls

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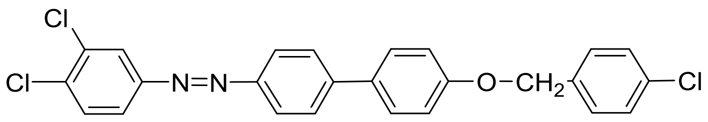
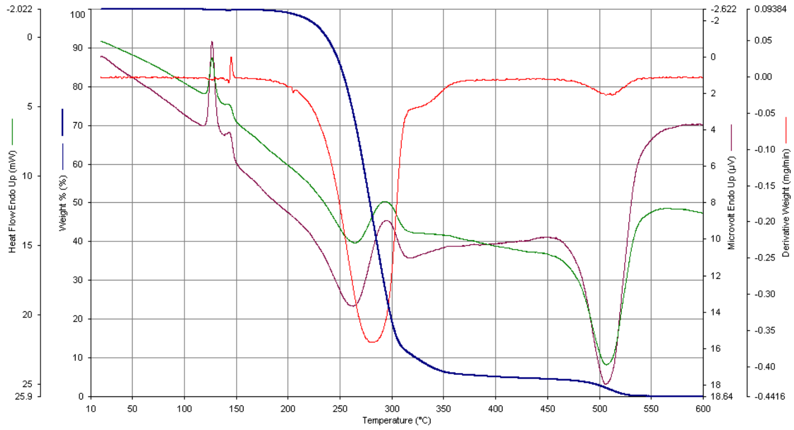
A series of five 4-phenyldiazenyl-4’-[(4-chlorobenzyl)oxy]biphenyls have been synthesized by condensing sodium salts of some 4’-phenyldiazenylbiphenyl-4-ols with 1-chloro-4-(chloromethyl) benzene [1].

The formation of azomonoethers was confirmed by the disappearance of the signal at 3019 - 3030 cm^{-1} in IR spectra which is typical for hydroxyl group of azophenols and by the appearance of an intens absorption band at 1260 - 1280 cm^{-1} which can be assigned to the antisymmetrical valence vibrations of the C-O-C group and a moderate absorption band due to the symmetrical valence vibrations of the C-O-C group at 1013 - 1014 cm^{-1}.

The paper determines the kinetics of oxidative thermal decomposition of these compounds in a dynamic air atmosphere using a PerkinElmer DIAMOND TG/DTA thermobalance. Measurements were performed at heating rates of 2, 4, 6, 8 and 10 K min^{-1}.

As an example we present the structural formula and the thermal decomposition diagram of 1-(4’-((4-chlorobenzyl)oxy)-[1,1’-biphenyl]-4-yl)-2-(3,4-dichlorophenyl)diazene, at the linear heating rate of 6 K min^{-1}.





[1] A. Moanta, J. Chil. Chem. Soc., 58 (2014) 1986-1989.

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