# CEEC-TAC7

# BOOK OF ABSTRACTS

Editors:
Jiří Kučerík
Pavel Šiler
Andrei Rotaru

CEEC-TAC7

7th Central and Eastern European Conference
on Thermal Analysis and Calorimetry

28-31 August 2023
Brno, Czech Republic

*Dedicated to the 85th Birthday Anniversary of Prof. Jaroslav Šesták*

**Publishing House**
*SITECH, Romania*

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**Book of abstracts of the 7$^{th}$ Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC7).**

7$^{th}$ Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC76).
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***28-31 August 2023 – Brno, Czech Republic***

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## Dear Participants at CEEC-TAC7 Conference,

Let us express our great pleasure to welcome you here in Brno – Czech Republic, for attending the joint 7th Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC7) and between 28th and 31st of August 2023; we thank very much to all of you for joining us! You were invited in Brno, which is the second largest city of Czech Republic. It is a city in the South Moravian Region of the Czech Republic. The Brno basin has been inhabited since prehistoric times, but the town's direct predecessor was a fortified settlement of the Great Moravian Empire known as Stare Zamky, which was inhabited from the Neolithic Age until the early 11th century. Located at the confluence of the Svitava and Svratka rivers, Brno metropolitan area has almost 700,000 inhabitants, making it the second-largest city in the Czech Republic after the capital, Prague, and one of the 100 largest cities of the EU. Brno is also an important centre of higher education, with 33 faculties belonging to 13 institutes of higher education and about 89,000 students.

This conference is dedicated to Prof. Jaroslav Šesták, the famous Czech thermal & kinetics scientist, on the occasion of his 85th birthday anniversary. Prof. Šesták is not only a great researcher, but also a great lecturer, a writer of marvellous scientific books and a fervent photographer; last but not least, he was always a great friend. Happy Birthday Jaroslav! We are all wishing you and your beloved wife Věra a good and long life!

The CEEC-TAC7 conference gathers now 202 registered participants from 28 countries, presenting a total number of 247 scientific works. Of those, 1 is Honorary Lecture (HL), 3 are Award Plenary Lectures (APL), 3 are Plenary Lectures (PL), 6 are Invited Lectures (IL), 4 Parallel Sessions of Oral Presentations – 84 contributions (OP) & 3 Sessions of Poster Presentation – 150 contributions (PS). Each session of oral presentations is comprised of 21 works, while each of the three poster presentations includes 50 works.

At this edition, Awards will be offered to exceptional scientists: *i*) Prof. Sergey Verevkin from Germany (Honorary Member of CEEC-TAC), *ii*), Prof. Kinga Pielichowska from Poland (Distinguished TA&C Researcher in Central & Eastern Europe); *iii*) Dr. Branislav Stankovic from Serbia (Outstanding Young TA&C Researcher in Central & Eastern Europe); *iv*) two “Andrzej Malecki” 2023 Grants for Best Young Researcher from Central & Eastern Europe in the field of Thermal Analysis and Calorimetry; *v*) two “Jaroslav Sestak” 2023 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, Executive Organizing Committee, Central and Eastern European Committee for Thermal Analysis and Calorimetry, Brno University of Technology, Faculty of Chemistry of the Brno University of Technology, Babeş-Bolyai University, Czech Group for Thermal Analysis and Czech Academy of Sciences. We acknowledge the great support of our Sponsors: NETZSCH (Bronze Sponsor), Rigaku (Bronze Sponsor), Setaram (Bronze Sponsor), Elsevier (Exclusive Sponsor) and ChromSpec SPOL. S.R.O. (Partner). A special acknowledgement has to be addressed to the *Journal of Thermal Analysis and Calorimetry*, *Ceramics International, Surfaces and Interfaces* and *Applied Surface Science Advances*, where special issues will be dedicated to research papers of our conference.

The 4-day meeting is hosted at the Faculty of Chemistry of the Brno University of Technology. The official language of the conference is English.

We hope that you will enjoy the city during your stay at the CEEC-TAC7 conference, and that you will leave Brno 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 2025 for CEEC-TAC8!

***Jiří Kučerík & Andrei Rotaru***
***Chairpersons of CEEC-TAC7***

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# General Information

The "7th Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC7)" has gathered **202 registered participants** from **28 countries**, presenting a total number of **247 scientific works**. Of those, 1 is Honorary Lecture (**HL**), 3 are Award Plenary Lectures (**APL**), 3 are Plenary Lectures (**PL**), 6 are Invited Lectures (**IL**), 4 Parallel Sessions of Oral Presentations – 84 contributions (**OP**) & 3 Sessions of Poster Presentation – 150 contributions (**PS**). Each session of oral presentations is comprised of 21 works, while each poster presentations includes 50 works.

# List of Honorary, Award Plenary, Plenary and Invited Lecturers

## Honorary Lecture

- ***Jaroslav Sestak*** (Czech Technical University in Prague, Czech Republic)

## Award Plenary Lectures

- ***Kinga Pielichowska*** (AGH University of Science and Technology, Poland)
- ***Branislav Stankovic*** (University of Belgrade)
- ***Sergey Verevkin*** (University of Rostock, Germany)

## Plenary Lectures

- ***Ignazio Blanco*** (University of Catania, Italy)
- ***Atsumi Miyake*** (Yokohama National University, Japan)
- ***Crisan Popescu*** (KAO European Research Laboratories, KAO Germany GmbH, Germany)

## Invited Lectures

- ***Nieves Barros*** (University of Santiago de Compostela, Spain)
- ***Laurent Delbreilh*** (University of Rouen Normandy, France)
- ***Nobuyoshi Koga*** (Hiroshima University, Japan)
- ***Nicolas Sbirrazzuoli*** (University of Cote d'Azur, France)
- ***Joan-Josep Sunol*** (University of Girona, Spain)
- ***Athanasios Tiliakos*** (ICSI-National Institute for Cryogenic and Isotopic Technologies, Romania)

| *Monday, 28th of August* | | *Tuesday, 29st of August* | | | | | *Wednesday, 30th of August* | | | | | *Thursday, 31st of August* | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $8^{30}$-$13^{00}$ | *Short Summer School on TA&C* | $9^{00}$-$9^{40}$ | Atsumi Miyake, PL1 | | | | $9^{00}$-$9^{40}$ | Ignazio Blanco, PL2 | | | | $9^{00}$-$9^{40}$ | Crisan Popescu, PL3 | | | |
| | | $9^{40}$-$10^{10}$ | Nicolas Sbirrazzuoli, IL1 | | | | $9^{40}$-$10^{10}$ | Athanasios Tiliakos, IL3 | | | | $9^{40}$-$10^{10}$ | Joan-Josep Sunol, IL5 | | | |
| | | $10^{10}$-$11^{40}$ | **Poster session 1**<br>*Coffee break* | | | | $10^{10}$-$11^{40}$ | **Poster session 2**<br>*Coffee break* | | | | $10^{10}$-$11^{40}$ | **Poster session 3**<br>*Coffee break* | | | |
| | | $11^{40}$-$12^{00}$ | OP1.01 | OP2.01 | OP3.01 | OP4.01 | $11^{40}$-$12^{00}$ | OP1.11 | OP2.11 | OP3.11 | OP4.11 | $11^{40}$-$12^{00}$ | OP1.18 | OP2.18 | OP3.18 | OP4.18 |
| | | $12^{00}$-$12^{20}$ | OP1.02 | OP2.02 | OP3.02 | OP4.02 | $12^{00}$-$12^{20}$ | OP1.12 | OP2.12 | OP3.12 | OP4.12 | $12^{00}$-$12^{20}$ | OP1.19 | OP2.19 | OP3.19 | OP4.19 |
| | | $12^{20}$-$12^{40}$ | OP1.03 | OP2.03 | OP3.03 | OP4.03 | $12^{20}$-$12^{40}$ | OP1.13 | OP2.13 | OP3.13 | OP4.13 | $12^{20}$-$12^{40}$ | OP1.20 | OP2.20 | OP3.20 | OP4.20 |
| | | $12^{40}$-$13^{00}$ | OP1.04 | OP2.04 | OP3.04 | OP4.04 | $12^{40}$-$13^{00}$ | OP1.14 | OP2.14 | OP3.14 | OP4.14 | $12^{40}$-$13^{00}$ | OP1.21 | OP2.21 | OP3.21 | OP4.21 |
| $13^{00}$-$14^{30}$ | *Lunch* | $13^{00}$-$14^{30}$ | *Lunch* | | | | $13^{00}$-$14^{30}$ | *Lunch* | | | | $13^{00}$-$14^{30}$ | *Lunch* | | | |
| $14^{30}$-$16^{30}$ | *Short Summer School on TA&C* | $14^{30}$-$14^{40}$ | CEEC-TAC7 Info | | | | $14^{30}$-$14^{40}$ | CEEC-TAC7 Info | | | | $14^{30}$-$14^{40}$ | CEEC-TAC8 Info | | | |
| | | $14^{40}$-$15^{20}$ | Sergey Verevkin, APL1 | | | | $14^{40}$-$15^{20}$ | Kinga Pielichowska, APL2 | | | | $14^{40}$-$15^{20}$ | Branislav Stankovic, APL3 | | | |
| | | $15^{20}$-$15^{50}$ | Nieves Barros, IL2 | | | | $15^{20}$-$15^{50}$ | Nobuyoshi Koga, IL4 | | | | $15^{20}$-$15^{50}$ | Laurent Delbreilh, IL6 | | | |
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| | | $16^{20}$-$16^{40}$ | OP1.06 | OP2.06 | OP3.06 | OP4.06 | $16^{20}$-$16^{40}$ | OP1.16 | OP2.16 | OP3.16 | OP4.16 | $16^{00}$ | *Farewell* | | | |
| | | $16^{40}$-$17^{00}$ | OP1.07 | OP2.07 | OP3.07 | OP4.07 | $16^{40}$-$17^{00}$ | OP1.17 | OP2.17 | OP3.17 | OP4.17 | | | | | |
| $16^{30}$-$18^{00}$ | *Afternoon break* | $17^{00}$-$17^{30}$ | *Coffee break* | | | | $17^{00}$-$17^{45}$ | *ICTAC Standards & Nomenclature* | | | | | | | | |
| $18^{00}$-$19^{00}$ | Opening Ceremony | $17^{30}$-$17^{50}$ | OP1.08 | OP2.08 | OP3.08 | OP4.08 | $17^{45}$-$20^{00}$ | *Afternoon break* | | | | | | | | |
| | | $17^{50}$-$18^{10}$ | OP1.09 | OP2.09 | OP3.09 | OP4.09 | | | | | | | | | | |
| $19^{00}$-$19^{40}$ | Jaroslav Sestak, HL | $18^{10}$-$18^{30}$ | OP1.10 | OP2.010 | OP3.10 | OP4.10 | | | | | | | | | | |
| | | $18^{30}$-$19^{15}$ | *ICTAC Kinetics* | | | | | | | | | | | | | |
| $19^{40}$-$22^{00}$ | *Welcome Cocktail* | | *ICTAC Life & Environmental Sci.* | | | | | | | | | | | | | |
| | | $19^{15}$-$20^{00}$ | *CEEC-TAC General Assembly* | | | | $20^{00}$-$24^{00}$ | *Conference Dinner* | | | | | | | | |

- 1. Room A at BUT-FCH (P1)
- 2. Room B at BUT-FCH (P16)
- 3. Room C at BUT-FCH (P17)
- 4. Room D at BUT-FCH (P4)
- *1-4: Brno University of Technology, Faculty of Chemistry, Purkynova 464/118, Brno*
- 5. Room E at BUT-Rectorate
- *5: Brno University of Technology, Rectorate, Antoninska 548/1, Brno*
- 6. Poster and Coffee break area at BUT-FCH
- *6: Brno University of Technology, Faculty of Chemistry, Purkynova 464/118, Brno*
- 7. Kanas Restaurant
- *7: Kolejní 14, Brno*
- 8. Pivovarský dům Poupě Restaurant
- *8: Dominikánská 342/15, Brno*

# Program of CEEC-TAC7

**28-31 August 2023**

***Brno, Czech Republic***

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# Honorary Lecture

# Former personalities of the Czech-Slovak thermal analysis community and their inventive contributions

**Jaroslav ŠESTÁK**
Department of Materials Engineering and Chemistry Faculty of Civil Engineering, Czech Technical University in Prague, Thákurova 7, 166 29 Prague 6, Czech Republic
sestak@fzu.cz

The development of thermal analysis has its roots in the Czecho-Slovak region The deepest ancestries go back to the beginning of the eighteenth century when the Bohemian Jan Amos Comenius (1592-1670) published the book "Distiquisiones caloris at frigoris natura" first discussing heat as a describable substance. He considered, "to observe clearly the effect of heat and cold, a visible object should be subjected to heating and subsequent cooling, the sensible changes made by heat and cold will then be visible to the eye". The greats of the middle Ages followed, such as Hájek Tadeáš (from Hájků) (1526 - 1600), Agricola Georgius (Georg Bauer) (1494 - 1555). Marcus Marci Jan (from Kronland), (1595 - 1667) and Diviš Prokop (Procopius) (1696 - 1765). Followed by Václav Šimerka (1819 – 1887), Friedrich Reinitzer (1857 – 1927) and Ernest Mach (1838 – 1916). Čeněk Strouhal (1850 – 1922) became the first thermodynamist, while Stanislav Škramovský (1901-1983) and Rudolf Bárta (1907-1985) mutually promoted thermogravimetry and the DTA practice. Modern ´thermography´ become thermal analysis and was commenced by I. Proks (Periodic TA), J. Brandštetr (Enthalpiometry), J. Komrska (Permeability TA), A. Bergstein (Dielectric TA), S. Chromý (Photometric TA), V. Šatava (Hydrothermal TA), V. Balek (Emanation TA), V. Jesenák (Radioactive TA) and M. Vaniš (Accelerated TA). World development was then signposted by pioneers of thermal methods theory and application such as M. Malinovský, V. Jesenák, P. Holba, V. Balek. In the concept of glasses become important A. Hrubý, J. Tauc., B. Hlaváček, M. Frumar, and in calorimetry J. Brandšter, J. Velíšek , M. Smíšek or V. Pekárek, etc.. The contribution of each of the cited persons is sufficiently documented and evaluated. Supported by the ČVUT institutional research program No. RVO: 1100.

[1] P. Holba, J. Šesták: *Czechoslovak footprints in the development of the methods of thermometry, calorimetry and thermal analysis* Ceramics – Silikáty 2012; 56 159-167 (2012)

[2] J. Šestak: *Thermal science and analysis: history, terminology, development and the role of personalities*, J. Therm. Anal. Calor. 2013; 113 1049–1054.

[3] J. Šesták: *Thermal analysis and thermodynamic properties of solids*, book by Elsevier 2021

# Award Plenary Lectures

# The Gibbs-Helmholtz equation in modern thermochemistry: combining calorimetric and quantum chemical methods

**Sergey P. VEREVKIN**
University of Rostock, A. Einsteinstr.27, Rostock, Germany

The thermodynamic feasibility of a chemical process is determined by the sign of the Gibbs reaction energy. The Gibbs-Helmholtz equation applied to thermochemistry is clearly represented by the enthalpic and entropic contributions to the Gibbs energy. The thermochemical methods useful to derive these contributions from experiment and theory are collected and analyzed. The concept of the in-silico" based Gibbs-Helmholtz equation was proposed. The application of the "in-silico" procedure to modern areas of chemistry such as hydrogen storage and ionic liquids was demonstrated.

Various areas of application will be presented in which the Gibbs-Helmholtz equation can help to optimize chemical-engineering problems. This includes the synthesis of the platform chemicals, the utilization of the renewable sources (glycerol, lignin, etc.), and hydrogen storage. A useful combination of quantum chemistry with experimental methods has been developed and applied to the determination of liquid-phase equilibrium constants, which are essential for chemical technology.

In the context of hydrogen storage, Gibbs energies have proven important to calculate the equilibrium temperatures specific to the reversibility of hydrogenation of liquid organic hydrogen carriers. Thereby, nitrogen-containing heterocycles, furfuryl alcohol and diphenyl ether derivatives were screened using the equilibrium temperature for the selection of the most promising LOHC systems.

The combination of combustion experiments with diamonds and graphite with high-precision calorimetry and quantum-chemistry has disproved the superior stability of diamonds at extremely low temperatures, which theorists suspected. Thereby, the textbook paradigm was re-enforced that graphite is the most stable modification of carbon at atmospheric pressure at all temperatures below 400 K, even very close to absolute zero.

# Thermal analysis of advanced phase change materials for thermal energy storage

**Kinga PIELICHOWSKA**
AGH University of Krakow, Faculty of Materials Science and Ceramics, Department of Biomaterials and Composites, al. Mickiewicza 30, 30-059 Kraków, Poland

Rapidly growing energy consumption is today a crucial issue. The exhaustion of fossil fuels requires further development of renewable energy sources, such as the sun, wind, and biomass. The main challenges for further research include the design and manufacture of new advanced materials for efficient energy technologies, such as batteries, solar cells, fuel cells and phase change materials (PCMs) for thermal energy storage and conversion. New advanced materials need to be fully characterized; especially thermal properties, like the temperature range of the phase transition, heat capacity, and heat of the phase transition, supercooling, thermal stability, and thermal reliability after multiple heating-cooling cycling should be carefully investigated [1,2]. For this purpose, thermal analysis methods are an indispensable tool and allow for extended characterization of PCMs. In this work, applications of thermal analysis methods, in particular differential scanning calorimetry (DSC), temperature modulated DSC, thermogravimetry (TG), TG with evolved gas analysis (TG-FTIR, TG-MS), and dynamic mechanical analysis (DMA), for characterization of organic and polymeric phase change materials for thermal energy storage will be presented and discussed. PCMs based on fatty acids and poly(ethylene glycol) with different molar masses, modified with selected nanoadditives and shape stabilized in polyurethane systems or by using polysaccharides have been prepared and investigated using thermal analysis methods. DSC and crystallisation kinetic studies revealed that the incorporation of selected nanoadditives in small amounts can significant improve the heat storage capability of novel PCMs because of the nucleation effect. On the other hand, increasing the content of additives hinders PCM crystallization and leads to decreased heat of phase transition.

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# Modelling of the kinetics of dehydration of poly(acrylic acid) hydrogel – 15 years after

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Hydrogels are crosslinked hydrophilic polymer materials which can quickly absorb large amounts of water, solutions, and biological liquids. Due to their hydrophilicity, biocompatibility, high swellability, low toxicity, and capability to respond to even small stimuli, hydrogels are applied in various fields, such as medicine, pharmacy, and agriculture [1]. Understanding the mechanism and kinetics of dehydration of poly(acrylic acid) or hereinafter PAA hydrogel is important from both fundamental and practical aspects since the majority of applications are based on periodical absorption and desorption.

PAA hydrogel is the first hydrogel for which dehydration kinetics (both, isothermal and non-isothermal) was investigated, back in the mid-2000s. [2] In this research, we describe original thermogravimetric data by various state-of-the-art kinetics models with the nucleation-limited step and discuss to which extent our perception of hydrogel dehydration kinetics, as well as modeling the kinetics of reaction and processes in solid state in general, changed over the years. We evaluate differences in values of kinetics parameters obtained within the framework of applied models and how to select the most suitable model. Both isothermal and non-isothermal thermogravimetric curves of PAA hydrogel dehydration can be successfully described by the Gompertz function [3]. Changes in PAA hydrogel structure with dehydration are analyzed from the point of view of the selected kinetics model. The dependencies of apparent activation energy on the dehydration degree are determined by isoconversional methods for both isothermal and non-isothermal conditions and compared with dependencies calculated from the model equations corresponding to the Gompertz function. Limitations of isoconversional methods are discussed.

During dehydration, the state of absorbed water within the hydrogel is changed continuously. Relaxation processes within the hydrogel become faster and thus, dehydration nuclei with a bigger critical radius are formed, resulting in an increase of rate constant, i.e. in a decrease of the activation energy. The obtained results are confirmed by dielectric spectroscopy measurements and quantum chemistry calculations. Both methodologies indicate a decrease in the strength of hydrogen bonds in the system which can explain the observed decrease in activation energy for dehydration. Bond decomposition analysis is done to further shed light on changes in the hydrogel structure.

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# Plenary Lectures

# Thermal risk analysis of lithium-ion batteries under overheating in waste treatment systems

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Lithium-ion batteries (LIBs) are the dominant power source for various portable electronic devices due to their high operating voltage, low memory effect, and high energy density [1]. As the use of LIBs increased, so did the number of discarded LIBs [2]. Some LIBs are not properly collected and are intentionally or unintentionally mixed into municipal waste. Because various flammable organic solvents with low flash points are used as electrolytes in LIBs, LIBs are highly flammable and cause thermal runaway due to exponential temperature rise [3]. LIB has a thermal risk and extensive research has been done to ensure its safe use [4]. Accidental entry of LIBs into waste treatment facilities has increased the number of fires [5], causing serious damage to the facilities. It is important to analyse the thermal risk of LIBs in waste treatment systems from the perspective of life cycle safety management.

In order to analyse the thermal risks and thermal runaway mechanisms of LIBs leading to fires in waste treatment facilities thermal analysis and evolved gas analysis were performed. Thermal risk of LIBs was obtained by performing a thermal analysis of the LIB components. In analysing the ignition and the fire mechanism, we conducted overheating experiments based on the risk scenario for waste LIBs in the facility. To elucidate the mechanism of ignition and fire, we measured the temperature change and the gas evolution of overheating LIBs by the real-time temperature monitoring combining an infrared camera, a high-speed camera, and a gas detector. This experiment was conducted with a focus on the difference in behaviour depending on the state of charge (SOC) of LIBs. As a result, it was revealed that the SOC is an important parameter for fire risk management in waste treatment facilities.

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# The Role of Thermal Methods in Additive Manufacturing

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Polymer was the defining material of the twentieth century whilst, both for the considerable increase in articles published in literature and for the growth of applications over the last fifteen years the defining material platform of the twenty-first century could very well be the hybrid material. The design of an hybrid material is related with the combination of two or more components in a single material to give new and previously unattainable combinations of useful properties [1].

Among the different techniques available, thermal analysis offers, in addition to high accuracy in the measurement, smartness of execution, allowing to obtain with a very limited quantity of material precious information regarding the property–structure correlation, essential not only in the production process, but overall, in the design one. Thus, techniques such as differential scanning calorimetry (DSC), differential thermal analysis (DTA), dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) can be used in the design, preparation and characterization of these materials.

Furthermore, since the public pressure about the problems derived from the environmental issues increasingly pushes the research areas, of both industrial and academic sectors, to design material architectures with more and more foundations and reinforcements derived from renewable sources. In these efforts, researchers make extensive and profound use of thermal analysis to this transition from fossil feedstock to renewable ones, and in the development on new manufacturing processes such as those of additive manufacturing (AM).

AM is increasingly in industry with a worldwide market, for AM products and services, estimated to grow to over $5 billion by 2020 [2]. AM is accepted not for prototyping only but for functional parts too [3], and the filament based technology referred as the Fused Deposition Modelling (FDM) is one the most widely used. Thermal analysis can be used to study the behavior of polymer melts, and not only, during FDM processing to rationalize its effect on printing quality.

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# Stories of hair told by Thermal Analysis

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The talk aims at showing how the use of thermal analysis concepts and methods helps the understanding of hair structure, assists the hair care industry, and hints towards new applications.

Fibrous proteins, particularly keratin fibres, were among the first systems undergoing the exploration with thermal analysis means, when first instruments became commercially available. The investigations focused initially on discerning structural details and evaluating thermodynamic quantities. After decades of revealing incrementally the keratin intricate structure, the thermal analysis methods begin being increasingly used to substantiate product claims, to assist the development of hair care treatments and to assess the damage incurred by the action of various treatments. Recently developed thermal analysis techniques opened new fields of application for hair, like for medical diagnosis, for the trace analysis, or for the developing of new materials, with unexpected economic impact.

Surveying various examples, the talk points out to hurdles in applying TA methods and underlines some of the problems of data interpretation, which may hinder the meaningful exploitation of the results.

# Invited Lectures

# Advanced isoconversional kinetic analysis: Insights in polymerization mechanisms

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Advanced isoconversional kinetic analysis combined with model-fitting may provide new mechanistic interpretations, opening the door to new applications. Polymerizations are complex chemical reactions during which long macromolecular chains are produced from small monomer molecules, complicated by physical transformations such as gelation or vitrification. As consequence, during the later stages of the reaction, there is an interplay between the contributions of chemical reaction and diffusion step to the overall reaction rate, followed by a shift of the reaction from chemical to diffusion control. This is the result of the high increase of the molecular weight and viscosity due to crosslinking. Thus, extracting the kinetic parameters of each individual step for such complex processes is not straightforward. The present work describes the polymerization kinetics and chemo-rheology of various systems, by coupling real-time ATR-FTIR, DSC, TMDSC, rheometry, and DMA, with isothermal and nonisothermal kinetics. It is shown how new insights into the mechanisms of crosslinked network formation can be provided [1-10].

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# Beginning to calculate thermodynamic state functions for soils: the role of thermal analysis and calorimetry

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Soil is one of the few systems that continue to be thermodynamically opaque. It is an open system interchanging matter and energy with the environment, thus evolving under thermodynamic laws. The theoretical role of thermodynamics on soil biological evolution is a matter of debate since the beginning of the last century. Numerous theories and hypotheses report mechanisms of soil evolution because of the direct impact on human lives. Some of them refer to thermodynamic state functions like entropy, as key factors to understand biological evolution [1].

Now, it is a realistic option to go beyond Odum´s and Schrödinger's theories about the development of biological ecosystems [2,3], and to assess the evolution of soils by experimental thermodynamic data to go further than the existing theoretical hypothesis. That is possible due to advances in the fields of thermal analysis and calorimetry.

Recent research shows the possibility to quantify the heat of combustion and enthalpy of combustion of the soil organic matter by formulation of the organic matter and by direct measurements with simultaneous thermogravimetry and differential scanning calorimetry, yielding data that were not significantly different. It allows us to complete the soil thermodynamic characterization by different enthalpic and entropy models.

The first approaches to the molar entropy of the soil organic matter indicated a trend of entropy to increase with an increased degree of reduction of the organic substrates. Soil molar entropy increased with soil depth; therefore, the organic matter evolves from a lower to a higher degree of decomposition and mineralization. By assuming that a higher degree of organic matter mineralization would correspond to a higher maturity state, the result would support that soil organic matter evolves following the second law of thermodynamics.

Calorespirometry connects the soil thermodynamic properties with the organic matter biodegradability and demonstrated that an increased degree of reduction of organic substrates slows down the bio decomposition rates. That is a way to parametrize the concept of soil recalcitrance. All these results provide models explaining the evolutionary mechanisms of soil survival.

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# Ion transport mechanisms in superionic ceramic conductors

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Less constrained by bandwidth limitations and sampling scarcity, broadband profiling in a wide temperature range, starting at the cryogenic threshold at -150 °C and extending to 200 °C, can be used to derive parameters of minimal variance for the Jonscher power law for ionic conductivity; these are employed to model the superionic regime over elevated temperatures and frequencies beyond the limits accessed by contemporary electrochemical impedance spectroscopy (EIS) equipment [1–3]. We apply this technique to non-stoichiometric NaSICON based on the canonical NZSP formula with 5% excess sodium, synthesized by an augmented solid-state reaction (SSR) method. We thoroughly analyze broadband conductivity, dielectric permittivity, and electric modulus data over the extended temperature range. Activation energy anomalies and scaling distortions inherent to the Arrhenius approximation are investigated, and an alternative formulation based on linearized difference equations is proposed to remedy these issues. With Cole-Cole analysis establishing non-Debye relaxation behavior, dissipation analysis is employed to identify relaxation bands, used for extracting initial condition parameters for the Jonscher power law. Finally, simulations of the AC dispersion region at high temperatures and frequencies suggest the dominance of polaron tunneling mechanisms instead of the classical ion hopping mechanism assumed for NaSICON, in line with the latest insights on superionic conduction.

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# Exploring physico-geometrical kinetic features of the thermal decomposition of solids using thermal analysis

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Thermal decomposition of solids has been treated as typical examples of thermoanalytical measurement for revealing kinetic behavior. Many named calculation methods of formal kinetic analysis were proposed using the thermal decomposition as an example [1]. However, the reaction is complex heterogeneous process constrained geometrically [2] and controlled bimodal parameters of temperature and partial pressure of evolved gas [3]. In addition, temperature and partial pressure gradients in reacting particles and system are inevitable during the reaction due to the enthalpy change and gaseous evolution by the reaction [4]. The formal kinetic analysis of the thermoanalytical data successfully describes the physico-geometrical reaction feature for some reactions [5]. However, in many cases, the resulting kinetic parameters have mere empirical significance to reproduce the measured thermoanalytical curves, exhibiting a linear correlation between the kinetic parameters [6] and causing the difficulty to interpret the physical meaning of the kinetic exponents in the empirical kinetic model function [7]. The major issues of the formal kinetic analysis are due to the gaps between the idealized kinetic modelling and the actual reaction process, which can be related to the intrinsic physico-geometrical kinetic features of the reaction including sample characteristics such as particle size distribution [8], multistep reaction features [9], effect of evolved gas [3], and contribution of physical events [10]. Revealing of the targeted physico-geometrical feature of the reaction is not formal kinetic approach, but requires a strategical design for the inquiry [11]. In this presentation, such a kinetic study for exploring physico-geometrical features of the thermal decomposition of solids is demonstrated as exemplified by the thermal dehydration of sodium carbonate hydrates [12-14].

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# Thermal analysis of magnetic materials

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Thermal analysis techniques make it possible to determine the transformation temperatures of magnetic and structural transitions of magnetic materials. It is known that the Curie temperature limits its applicability. The magnetic materials can be classified as a function of the coercivity, $H_c$: very soft ($H_c$ from 10 to <100 A/m), soft ($H_c$ from 100 to <1000 A/m), semi-hard ($H_c$ from 1000 to <2000 A/m) and hard ($H_c$ is 2000 A/m and greater). Optimized One option for soft composites is the production by adding soft magnetic powders to a polymer matrix. Other option (hard composite) is to mix soft and hard magnetic materials to develop spring magnets.

In this work, results of magnetic shape memory alloys (MSMA) and amorphous and nanocrystalline soft magnetic alloys will be presented. MSMA are characterized by having the transition from ferromagnetism to paramagnetism. Some, such as the Heusler, also have a structural transformation of hysteretic and reversible behaviour (between a stable austenitic phase at high temperature and a stable martensitic phase at low temperature). Thermal analysis allows to determine both the characteristic temperatures and the thermodynamic parameters (entropy, enthalpy) [1-2]. The thermal response depends largely on the composition and microstructure of the material. In amorphous and nanocrystalline alloys the main thermal process analysed is the crystallization of the amorphous phase (or the crystalline growth of the nanocrystalline phase) [3]. Linear or isoconversional methods are commonly applied to determine the apparent activation energy [4]. Production technology and processing conditions (including thermal annealing) greatly influence the microstructure and thermal and functional responses.

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# Investigating the physical aging of epoxy resins for civil engineering applications

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The use of epoxy resin in the field of civil engineering has made it possible since many years to protect concrete structures against water infiltration, which leads several civil engineering constructions to target century-old applications. Nevertheless, there is no definitive way to predict the behaviour of an epoxy resin over such a long-time scale, and more complicated, the possible interactions between the different aging processes.

Physical aging by structural relaxation occurs in glass stored below its glass transition temperature. It consists of minimizing its thermodynamic quantities, such as enthalpy and specific volume, to approach equilibrium. In glassy polymers, this phenomenon can negatively affect dimensional stability during storage, leading to degradation of mechanical and barrier properties, for example. It is often neglected because it is a process with an extremely long-time scale, which also makes its study very difficult; however, it becomes a concern for all applications targeting sustainability.

New experimental calorimetric techniques like fast scanning calorimetry (FSC) provide new possibilities for experimentally studies of physical aging. During an FSC experiment, a low-mass sample (about tens to hundreds of nanograms) is heated and cooled at rates on the order of a thousand Kelvins per second. FSC can generate glassy polymers with a high level of enthalpy or specific volume [1]. Additionally, since the glass transition is shifted to higher temperatures with increasing cooling rate, physical aging can also be studied at higher temperatures than in standard differential scanning calorimetry. Furthermore, structural relaxation can be studied under accelerated conditions since the surface-to-volume ratio is significantly increased [2]. All these advantages favour the monitoring of physical aging in its entirety by simulating accelerated aging at higher temperature.

In this study, the relaxation dynamics of two epoxy resins differing in their crosslinking density are compared. The study of physical aging is carried out from the FSC at different distances from the glass transition. The Tool-Narayanaswamy-Moynihan (TNM) model is used to analyse the relaxation data. Finally, the impact of combined thermo-oxidation on relaxation kinetics is evaluated.

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# Oral Presentations 1

## Theory & Methods, Kinetics & Structural Changes, Fuels & Biofuels, Energetics and Applied Thermal Engineering

# Effect of S, Cu and Li doping on $C_3A$ hydration kinetics

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The ordinary Portland cement clinker contains 4 main components that contribute to the hydration phenomena. One of the least abundant - calcium aluminate ($Ca_3Al_2O_6$ - $C_3A$) has a significant effect on early heat release during the setting initialization and strongly influences further workability (i.e. flash set) [1]. The $C_3A$ rapidly reacts with the added water to form solid hydration products. The nature of the precipitates depends on the water content and humidity. Typically, in OP the AFm or AFt phases are precipitated. In absence of Sulphur the $C_4AH_{13}$ and $C_2AH_8$ are formed. Therefore, Sulphur-containing compounds are commonly added to retard these undesirable phenomena [2]. Added Sulphur-containing could also play a role as mineralizers during the clinker burning process. CuO and $LiO_2$ can act as mineralizers too and influence the melt formation temperature. Cu and Li ions can be introduced from standard raw materials (fly ash, iron ore, waste from battery production, etc.) [3]. This means that they can be found in standard clinkers.

The paper deals with the influence of combined dopants such as S, Cu and Li in different concentrations on the crystal structure and the hydration mechanism of $C_3A$. Doped calcium aluminates were prepared by high temperature solid state reaction from carbonate and oxide precursors. The synthetized and hydration products were characterized by means of phase composition (XRD, Raman) and morphology (SEM, particle size distribution and BET). The expected cation doping and crystal symmetry of the solid solutions were observed by Raman and FT-IR spectroscopy. Hydration kinetics at different temperatures (15, 25, 35 °C) was evaluated from isothermal calorimetry analyses.

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# Thermokinetic analysis and characterization of polyethylene terephthalate (PET) nanoparticles biodepolimerization via isothermal titration calorimetry

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The ever-growing plastic production has been a concern for the last decades, reaching a production of 390.7 million metric tons in 2021, excluding polymers that are not used in the conversion of plastic parts and products (i.e. for paints, cosmetics, textiles, adhesives, etc.). This has put in the spotlight the current plastic waste management system, as according to the OECD only 9% of the plastic waste is being recycled. Consequently, a large fraction of the plastic enters the environment, which afterwards will most likely be fragmented and turned into microplastics (<5 mm) and nanoplastics (NP, <100 nm). In addition, NP are of higher concern as they can permeate into animal and human tissues.

Polyethylene therephtalate (PET) is of particular interest, since it is mainly used for packaging and disposable items and tehrefore more often ends up in the environment instead of beeing recycled. It has been reported that PET-NP can be degraded by different microorganisms or enzymes (e.g. *Ideonella sakaiensis*, TfCut2 from *Thermobifida fusca.*) to obtain some oligomers or the original monomers, i.e. terephtalic acid and ethylen glycol [1-3]. The technical exploitation of these potentails would open up options for efficient recycling and approaching to a circular economy. This requires mechanistic knowledge, kinetic and thermodynamic parameters of the depolymerization that are difficult available with conventional analytical methods.

Based on titration calorimetric data, a thermokinetic model was developed that can well describe the depolymerization process. The model was successfully tested at the depolymerization of PET-NP with an average diameter of 100 and 180 nm using two cutinases (plant-metagenome-derived - LCC ICCG, thermophilic from *Thermobifida fusca* - TfCut2). For the first time, calorimetry provides a real-time insight into the kinetic of cleavage of ester bonds [3]. A great advantage is that calorimetry has the potential to be applied at technical scale for process monitoring.

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# New NETZSCH Software for Thermal Simulation of Chemical Reactions in Big Volumes

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Kinetic analysis is usually done for the small samples without significant temperature gradient inside. The kinetic software can simulate the rate of chemical reactions for two limiting cases. The first case has two conditions: the sample without temperature gradient because of infinite heat transfer in the sample; and controlled sample temperature because infinite heat loss to surrounding. The second limiting case is the pure adiabatic heating without any heat loss to surrounding media.

However, in the chemical industry, as well as in storage and transport of highly energetic materials the heat transport and heat loss are between these two cases, and for safe conditions we need to make the simulation for non-constant temperature in reacting volume. The areas with higher temperature have the faster reaction and more intensive heat production in the case of exothermal reaction. The increasing of the temperature leads to the further heating of these local areas, and they can serve as the hot spots for thermal explosion. It is important to know them for the solving the problem of thermal safety in chemical industrial processes like production, storage, and transportation. For the heat transfer simulation, a lot of different CAD systems exist, with the possibility to calculate the heat transfer and temperature distribution for given volume. But the using of these systems is extremely difficult for solving heat transfer equation together with kinetic equations, especially for complex multi-step reactions.

Our target is to create the thermal simulation software, which is completely compatible with NETZSCH Kinetics Neo Software and can use any existing kinetic solutions from Kinetics Neo project. It should work for both model free and model based kinetic approaches, also for both single step and multi-step kinetic models of any complexity, which are described in [1]. Now we have this new Thermal Simulation software, which has the input data in the form of the chemical parameters (e.g., kinetic model from Kinetics Neo software) and the physical parameters like temperature dependent heat capacity, density, and thermal conductivity of reacting material. The additional input parameters also include container material which can be different for each plane of reactor geometry, and different surrounding media like air on the top, water on the side and ground on the bottom. The surrounding temperatures can be also different for different geometry planes.

The simulation results are the time-dependent and coordinate-dependent properties like temperature, concentrations of all reactants, conversion, reaction rate. The software can also calculate the optimized values like Self-Accelerating Decomposition Temperature (SADT) for safe material storage.

The life presentation of the software with the example of simulation for exothermal material will be done.

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# Applicability of the methods based on the general rate equation

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Mechanisms of the processes in condensed state are very often unknown or too complicated to be characterised by a simple kinetic model since they tend to occur in multiple elementary steps with different rates. For the description of the kinetics of such complex processes, the methods based on the general rate equation (GRE) are often used.

Within the framework of GRE, the rate of the complex process is expressed as [1-3]

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

where $\alpha$ is the conversion, $t$ is time, $k(T)$ is the temperature function depending solely on temperature $T$ and $f(\alpha)$ is the conversion function, depending solely on the conversion of the process [1-3].

It will be demonstrated that the kinetics cannot be in general expressed in the form of Eq. (1) for a complex process. Hence, Eq. (1) represents just an approximation of the experimental data, and it is just a mathematical tool for the description of the kinetic data. There can exist a number of couples of $k(T)$ and $f(\alpha)$ so that the both functions may not have any physical meaning and neither the parameters occurring in the both functions. Eq.(1) can be directly applied only for the simple processes, i.e., the elementary processes or the processes the rate of which is governed by a single elementary step.

Thus, $k(T)$ in GRE is not the rate constant in general and the conversion function, $f(\alpha)$, does not reflect the mechanism of the complex process. No mechanistic conclusions should be drawn from the values of an individual kinetic parameter; particularly, just from the values of activation energy. The conclusions can be drawn from the quantities with clear physical meaning, i.e. from the values of isoconversional times, isoconversional temperatures, conversion, reaction rate, etc., i.e. the quantities that can be accessed experimentally.

Interpretation of GRE as a mathematical tool for the description of thermoanalytical kinetic data is in sharp contradiction with the concept of variable activation energy. Since Eq. (1) describes the kinetics of simple processes and the thermoanalytical processes are mostly complex, the methods based on the constancy of parameters in $k(T)$ should be omitted. Such methods are the Kissinger method or the integral isoconversional methods.

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# Application of isoconversional methods for predicting the cure of epoxy composites under arbitrary thermal histories

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Epoxy resins are among the most widely used thermostable polymeric matrices in the aerospace industry because of their good mechanical strength and corrosion resistance [1]. However, mass manufacturing of fibre-reinforced composite is stuck by long curing times. Therefore, there is a need for reliable methods to analyse the kinetics and to predict the curing evolution in view to design shorter curing cycles while maintaining material properties. Besides, the cure reaction involves two stages of chain extension with primary amine reaction and crosslinking with secondary amine reaction. In addition, as the reaction proceeds the molecular mobility decreases and eventually the kinetics becomes diffusion-controlled. As a result, the kinetics is usually complex so it cannot be reduced to a relatively simple model [2].

Conversely, isoconversional methods are easy to implement, capable of dealing with complex processes and have been successfully applied to analyse the cure kinetics [3,4]. However, predictions are usually limited to isothermal or constant heating programs. In this work, we apply isoconversional methods to analyse the cure kinetics of two different commercial aero-grade epoxy resins. We use two different methods to perform predictions for complex temperature programs. These predictions are validated experimentally. Finally, two optimized cure cycles are proposed that allow a significant reduction of the curing time (up to 72% shorter) with respect to that recommended by the resin manufacturer. Despite such a reduction of the curing time, the specimens manufactured with these two cycles showed mechanical and physical properties still within the range accepted by a sector as restrictive as the aeronautical one.

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# Determination of Biomass Composition by Kinetic Analysis of Thermogravimetric Data

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Biomass-derived materials are increasingly being used to produce, convert and store energy [1]. The biomass composition is among the most important factors affecting the quality and the quantity of the end product. Cellulose, xylan and lignin are three primary lignocellulosic biomass components [2]. For many biomasses, the distinct decomposition zones of these components can be identified via thermogravimetric analysis (TGA). Furthermore, the DTG curve can be used to deconstruct and determine the kinetic parameters and/or composition of each component [3–5]. This approach can be used as a quick method to determine the composition of a biomass via a single TGA.

In this study, instead of deconstructing a biomass thermogram, a predetermined set of kinetic data for cellulose, xylan and lignin is used to find out the composition of pine dust. The thermal decomposition kinetics of cellulose, xylan and lignin were studied via Friedman, Kissinger-Akahira-Sunose (KAS) and Ozawa-Flynn-Wall (OFW) methods as well as Kissinger and Invariant Kinetic Parameters (IKP) methods. Studies were carried out over a wide range of heating rates (10 heating rates between 2K/min and 40K/min). The kinetic parameters obtained from pure components are used to determine the composition of pine dust from TG curves at various heating rates.

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# Application of isothermal and non-isothermal TG to acrylate coatings on optical fibers: experimental verification of isoconversion principle

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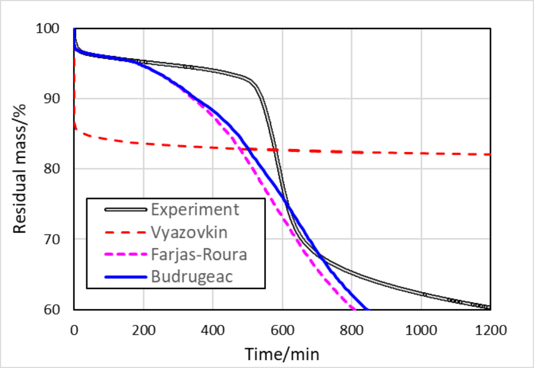
Thermal decomposition in nitrogen, air and oxygen of two optical fibers with different dual acrylate coatings was studied via isothermal and non-isothermal thermogravimetry (TG). For one of the coatings, the isothermal mass loss behaviour resembles an *n*-th order kinetics function. For the other coating, the TG curves exhibit a more complex behavior, suggesting presence of an antioxidant in the chemical composition. From the non-isothermal TG data, using isoconversional Flynn-Wall-Ozawa, Kissinger-Akahira-Sunose and advanced Vyazovkin [1], Farjas-Roura [2] and Budrugeac [3] approaches, the activation energies were determined, and the isothermal mass loss functions were simulated. For several fiber/gas combinations a significant discrepancy was observed between the experimentally obtained isothermal TG curves and those simulated from the non-isothermal data. As an example, the figure below shows isothermal TG results obtained for one of the fibers in oxygen environment at 180 °C. Following our previous study [4], the noted disagreement was analysed in a view of miscellaneous assumptions of the advanced simulation methods, including the basic isoconversion principle. It is concluded that in general, the isoconversion principle is an invalid assumption for TG data processing.



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# On the comment to ISO 11358-2 obtaining activation energy of thermal degradation of linear low density polyethylene

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The estimation of the life time of the polymer being used under the long period of the thermal degradation requires the short time test. Activation energy of the thermal degradation of polymer is of importance to decide the condition of the short time test. Thermogravimetric analysis (TGA) is able to obtain the value of the activation energy by the experiment in a short time.

The sample used in this experiment was linear low density polyethylene (LLDPE). The thickness of the samples was about 0.15 mm. TG curve was obtained using TG 8120 (Rigaku Co.) with supplying air. The sample was thermally aged under the rising temperature with the constant rate to obtain TG curves. The TG curves obtained under the different heating rate were analysed with reference to ISO 11358-2 [1].

The analysis was compliant with ISO 11358-2. This standard says that the analysed result shown in the figure (logarithm of heating rate vs 1/T) has to be the straight line. Also, each line has to be parallel each other. Figure 1 shows the analysed result of LLDPE in which very small amount of the antioxidant reagent was added in the production process. The straight line was obtained and was parallel each other. The activation energy was from 97.1 kJ/mol to 112 kJ/mol, which depended on the weight retained.

LLDPE which was added 0.0625 phr of antioxidant reagent showed the straight line, but the lines were not parallel as shown in Figure 2. This brought about the broadening of the range of the activation energy. But the degree of the range did not broaden even if the concentration of the antioxidant reagent was increased [2]. The averaged activation energy of LLDPE which was compliant with ISO 11358-2 was considered to be 90.8 kJ/mol [2].

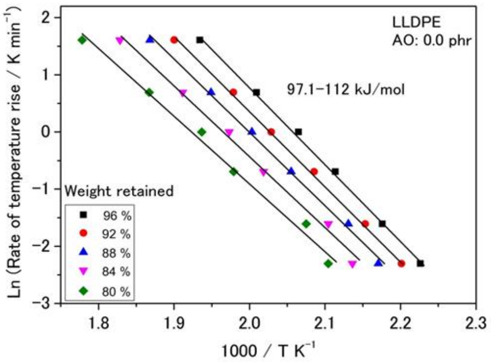

Fig.1 Result of LLDPE analysed with ISO 11358-2
Antioxidant reagent was not added

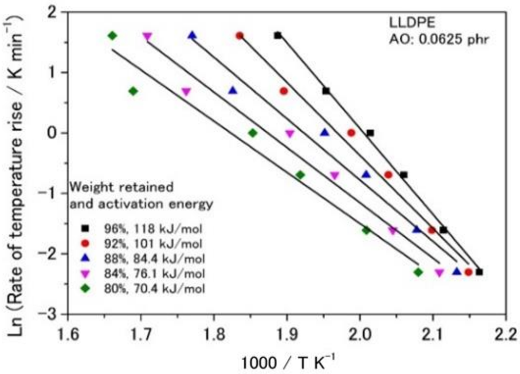

Fig.2 Result of LLDPE analysed with ISO 11358-2
Conc. of antioxidant reagent is 0.0625 phr

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# Thermodynamic prediction and experimental verification of phase transformation kinetics in 3Mn steel with Ti and V microadditions

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The most promising alloys to be used for automotive forging steels are multiphase Advanced High Stength Steels (AHSS) containing retained austenite (RA). The RA is a crucial microstructural constituent, which allows to prevent the formation of microcracks by providing local plasticity, while the martensitic transformation of RA during in-use plastic deformation contributes to blocking the propagation of possible microcracks [1]. The high mechanical properties and fatigue resistance can be provided by the microstructure composed of bainitic ferrite and retained austenite [2, 3]. The thermomechanical processing of such steel requires the detailed knowledge on the critical temperatures of steel and the kinetics of phase transformation during cooling from the austenite region.

The aim of the study was to determine the phase transformation kinetics and precipitation processes in 0.17C-3Mn-1Si-0.5Al-0.2Mo-0.03Ti-0.07V multiphase steel. The thermodynamic calculations using Thermo-Calc and JMatPro softwares were performed for designing the chemical composition of investigated steels and the range of phase transformations upon cooling from the austenite region. The continuous cooling transformation (CCT) and temperature–time–transformation (TTT) diagrams were calculated and experimentally compared using dilatometry. The microstructure details were revealed using light and scanning electron microscopy techniques. The obtained data will be used for the further design of thermomechanical processing parameters of investigated steel.

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# Effect of nucleation on crystallization of chalcogenide glasses

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Chalcogenide glasses are very interesting materials used as optical fibres, lenses, sensors, phase change materials and glass ceramic. It is important to know the crystallisation process to prepare and use them. The crystallization can be studied by differential scanning calorimetry (DSC) and microscopy. Unlike a microscope that observes directly the formation of crystals and their development, DSC records overall crystallisation indirectly through an evolved heating which is subsequently described by appropriate kinetic models.

There are two subsequent steps, nucleation and crystal growth, in the crystallization process. Whereas the heat is released from crystal growth, DSC does not detect nucleation. However, the nucleation has a significant impact on the overall crystallization process. This has a significant influence on the shape of DSC peak and crystallization kinetics. It is still hard to identify nucleation and transition mechanisms, due to a complex nature of the whole process.

For that contribution, the shape analysis of DSC peak is applied to reveal the crystallization mechanism. Analyses and simulation of different types of nucleation are carried out with a view to their influence on the overall DSC curve. Crystallization of selected chalcogenide glasses [1-7] is demonstrated. Improved experimental and analytical procedures are suggested to describe better the crystallization mechanism.

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# Overall evaluation of structural relaxation of selected chalcogenide glasses based on DSC data

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Chalcogenide materials are frequently used because of their optics and optoelectronic properties. Their applications based both on amorphous and crystalline state or changes between these two arrangements. The particular structure of the glass affects its properties, which is why we observe even small changes in the structure in the region close to the glass transition temperature, which is called structural relaxation (or physical ageing) [1].

Structural relaxation of glasses is often measured using differential scanning calorimetry (DSC), where the relaxation is reflected in the position of the peak of the glass transition, its size and shape. To analyse the relaxation behaviour, both isothermal and non-isothermal conditions can be used to define the temperature history of the material, but the glass transition is only visible by DSC under non-isothermal conditions (where the entire temperature history becomes apparent).

The structural relaxation can be described by a 4-parameter TNM model [2,3], where one of the parameters can be related to the viscosity behaviour of the glass and its melt. Thus, when determining the parameters of TNM model, it is advantageous to know also the temperature dependence of the viscosity at least in the region around the glass transition.

In this paper, the study of structural relaxation of selected compositions of binary chalcogenide glasses is presented. Structural relaxation was measured using DSC and isothermal and non-isothermal conditions. The results of all methods of estimation of individual parameters of the TNM model are summarized and compared with the final values obtained by fitting all data. The relationship between the viscosity behaviour, the description of structural relaxation by the TNM model and the structure of the observed materials is discussed.

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# Viscosity of chalcogenide glass-formers

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Chalcogenide glass-formers are interesting materials with unique properties that determine them as suitable candidates for many potential applications beyond the field of optics, optoelectronics, electronics, and data storage [1]. One of the most important property of these materials is viscosity. Knowledge of this property and an understanding of the processes underlying viscous flow are very important, not only for the preparation of glassy products with specific shapes like fibers but also generally for the improvement of glass physics cognition. Viscosity influences the cold crystallization process, which is crucial for both the thermal stability of amorphous materials and the process of structural relaxation determining the long-term stability of these materials. Although there is an unrelenting desire to formulate a generally valid viscosity theory containing parameters with clear physical meaning, the final solution has not yet been achieved.

Naturally, there are several approaches and theories which were formulated during the decades of research. The well-known and long-established Vogel–Fulcher–Tammann–Hesse empirical equation [2-4] has been widely used in glass science and industry. The novel viscosity theories introduced by Mauro et al. [5], Aniya [6], and Ojovan et al. [7] are nowadays intensively applied and tested for different systems. Meanwhile, several other models were also introduced. One of them, which is also well-known, was introduced by Adam and Gibbs [8] in the 1960s. This model and its modifications have been mainly used to describe structural relaxation processes and to solve changes related to this important feature observed in amorphous materials. Nevertheless, it was shown that this model has the potential also to describe viscosity behavior. In our previous work [9], we used this model combined with heat capacity data to describe selenium viscosity in broad temperature interval. A similar procedure can also be used to describe the viscosity of arsenic triselenide.

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# $CO_2$-induced crystallization of poly(L-lactic acid): enhanced cold crystallization with growth of α'-crystals

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Crystal polymorphism of poly(L-lactic acid) (PLLA) induced by $CO_2$ was investigated by differential scanning calorimetry and temperature-resolved X-ray scattering.

A PLLA thin disk (0.5 mm thick) was exposed to low $CO_2$ pressure (3.0 MPa) for short time (5 min) at 25 °C. This led to only partial diffusion of the gas into the polymer: in surface-near regions of the disks, a $CO_2$-induced mesophase (α''-form) developed [1], whereas the core of the samples was not reached by the gas and remained amorphous. This allowed comparing cold crystallization of mesophase-containing PLLA, with cold crystallization of fully amorphous PLLA, both coexisting within a single sample.

Cold crystallization of $CO_2$-treated PLLA was analyzed after full desorption of the gas, in a 2-decade range of heating rates. Slow heating allowed identifying two cold crystallization events: a low temperature cold crystallization in the outer parts of the sample treated with $CO_2$, promoted by prior formation of the mesophase, and a high temperature one, occurring at similar temperatures as in case of non-$CO_2$ treated amorphous PLLA. In both cases, formation of conformationally disordered α'-crystals was observed, as disclosed by temperature-resolved wide-angle X-ray scattering.

While growth of α'-crystals was expected for the initially amorphous parts, development of α'-crystals by heating PLLA containing $CO_2$-induced mesophase had not been reported yet, with this transition route only hypothesized to date [2].

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# The Ice and Salt Crystallization Patterns of the $MgSO_4 \cdot nH_2O$ System within the Sandstone Under Temperature Fluctuations

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Salt weathering is a common phenomenon which threatens the structural durability of cultural heritage and contemporary building materials. The origin of salt weathering is coming from the fact that building materials like sandstone, clay brick, limestone, cementitious composites, etc. possess a porous microstructure which allows the intrusion of the external saline sources. Once absorbed, saline solutions are liable to precipitate various forms of salts within the interconnected pores of the building materials after reaching their saturation degree. The excessive formation of such salts imposes an expansive crystallization pressure within the porous skeleton of the materials, which eventually causes their internal cracking and failure [1]. Among the possible threatening salts, the salts of the $MgSO_4.nH_2O$ system have been frequently found within the weathered structures [2]. The forms of the crystal salts of the $MgSO_4.nH_2O$ system strongly depend on the temperature [3]. Thus, common seasonal temperature fluctuations can easily lead to the subflorescence of Epsomite ($MgSO_4.7H_2O$), Meridianiite ($MgSO_4.11H_2O$). etc. within the contaminated porous mediums.

During the past decade, the complex phase diagram of the $MgSO_4.nH_2O$ system received a developed formulation [3]. Yet, the crystallization pattern of this system within the porous building materials under the freezing temperatures is not well explored yet. Under freezing temperatures, the precipitation of the $MgSO_4.nH_2O$ salts plus ice occur, which is common in the saturated materials during the cold seasons. Considering the importance of the problem, the present research explored the ice and salt crystallization pattern of the $MgSO_4.nH_2O$ system within the cultural heritage sandstones under positive & freezing temperature cycles. Differential scanning calorimetry was used to identify the nature and order of the crystallized salts and ice under the temperature fluctuations. In addition, mercury intrusion porosimetry was employed to detect the possible location of the crystallized $MgSO_4.nH_2O$ salts and their adverse microstructural aftermaths within the sandstone.

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# Influence of additives on the thermal and combustion behaviors of gas generators based on guanidine nitrate and basic copper nitrate

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A mixture of guanidine nitrate (GN) and basic copper nitrate (BCN) is used as a gas generator for automotive airbags, along with various additives. Generally, the combustion rate ($r$) of the gas generator increases with an increase in ambient pressure ($P$), following Vieille's equation ($r = aP^n$), where $a$ and $n$ represent the constant and the pressure exponent, respectively. A gas generator with a lower pressure exponent is more suitable for this purpose as it ensures stable combustion regardless of pressure changes inside the inflator. A previous study has shown that the addition of a mixture of synthetic hydrotalcite (HTS), iron oxide ($Fe_2O_3$), and carboxymethylcellulose sodium (CMCNa) reduces the pressure exponent in the GN/BCN-based gas generator. In this study, we investigated the thermal and combustion behaviors of the GN/BCN gas generator containing HTS, $Fe_2O_3$, and CMCNa to gain insights into the action of these additives.

The results of the combustion tests using a chimney-type strand burner revealed that GN/BCN/HTS demonstrated a lower pressure exponent (n = 0.2–0.3) compared to additive-free GN/BCN (n = 0.3–0.5), GN/BCN/$Fe_2O_3$ (n = 0.5–0.7), and GN/BCN/CMCNa (n = 0.5), and it roughly corresponds to GN/BCN with all three additives (n = 0.2–0.3). Therefore, HTS is believed to primarily influence the reduction in pressure exponent. Video observations of the combustion process revealed that gas generators containing HTS exhibited significant growth in the size of the condensed layer (red-hot decomposition product). Additionally, the results of TG/DTA/MS measurements suggest that HTS reacts with GN and suppresses the self-decomposition reaction of GN. Based on these observations, it becomes evident that gas generators containing HTS alter the thermal decomposition behavior during the early stages of combustion, possibly contributing to the decrease in pressure exponent.

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# Gas generation behaviour in the decomposition of ammonium dinitramide and hydrazide mixtures

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Ammonium dinitramide (ADN)-based energetic ionic liquids (EILs) are promising new liquid rocket propellants for small satellites due to their high energy content and ease of preparation [1]. This study focused on mixtures of ADN and hydrazide compounds. Our previous study [2] showed that simply mixing two solids, ADN (melting point = 92°C) and formic acid hydrazide (FH) (melting point = 56°C) in a 50:50 (mass ratio) ratio, could make them liquid at room temperature. We also report that the droplets have relatively high ignition properties among ADN-based EILs.

In order to better understand the mechanism of the condensed phase reaction of the mixture of ADN and hydrazide, the thermal behaviour and gases evolved during heating were analysed by thermogravimetric-differential thermal analysis (TG-DTA) and pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS). TG-DTA of ADN/FH at a heating rate of 5 K $min^{-1}$ revealed that ADN and FH react markedly exothermically in the condensed phase at about 180 °C. Py-GC/MS showed that the gases generated from the condensed phase reaction of ADN/FH included $N_2$ ($m/z = 28$), NO (30), $CO_2$ (44, 28), $N_2O$ (44, 30, 28), $NH_3$ (17), $H_2O$ (18, 17), $HN_3$ (43), $HCONH_2$ (45), $C_2H_3N_3$ (69). $HN_3$ is known to be a highly reactive substance. The heat generated by the oxidation of FH and the formation of highly reactive $HN_3$ may contribute to the ignitability of ADN/FH.

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# Thermal analysis as a tool to assess safety of ammonium nitrate and its mixtures

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Ammonium nitrate (AN), mostly known for its use in agriculture as a fertilizer component, has caused multiple disasters that occurred in the past. It can also be used as a novel, chloride-free propellant and an explosives component for mining purposes. The thermal stability of ammonium nitrate can be majorly impacted by a set of various factors, such as contamination with impurities, mechanical shock, pressure or temperature. Even though it is studied by research groups around the world and produced by multiple fertilizer or explosives companies, its regulations are still extremely underdeveloped in both USA and EU. Thermal analysis is a method that gained a significant role in the safety and thermal stability assessment of samples containing ammonium nitrate. However, there are no recommendations or guidelines defined in the literature and, as a result, there are inconsistent experiments and conclusions in many studies [1-3].

This work presents an in-depth discussion on suggested TA methodology and its various aspects in relation to systems containing AN. Various parameters of the methodology are mentioned and discussed. The presented research has been conducted with the use of differential thermal analysis/differential scanning calorimetry coupled with thermogravimetry and mass spectrometry (DTA/DSC-TG-MS). Samples containing AN in various proportions with selected additives are used to highlight the importance of appropriate methodology choice. Conclusions and proposed methodology are supported by both presented experiments and literature references. Multiple meaningful differences between obtained results for the same systems are discussed [4,5]. The study is based on many years of experience with TA and AN systems and is constantly being improved with additional examples and suggestions of the scientific community. It underlines the importance of safety assessment of ammonium nitrate systems and should provide useful guidelines for scientists at every stage of their careers on how to design an appropriate research plan and interpret obtained results.

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# Unique setups for unique applications

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SETARAM has been manufacturing thermal analyzers and calorimeters for decades. Its products range includes instruments that operate with “standard experimental conditions”.

But what differentiates SETARAM from other suppliers is the capability to provide instruments/accessories that allow customer operating in “exotic conditions”. Example of such instruments/accessories will be given in this presentation and will include:

- A TGA allowing to test up to 5 samples simultaneously for a huge gain of time when it comes to applications involving several days experiments such as cyclic oxidation.
- A Large Volume Calorimeter to measure activity of nuclear waste in drums as large 380 L
- A calorimeter to measure phase changes at pressure up 2000 bars.

# The effect of temperature on gradual degradation of structural components in biomass residues

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Biomass residue such as agriculture or forestry ones are renewable forms of energy and materials whose valorisation has increased due to the interest in replacing exhaustible and environmentally unfriendly fossil resources. Thermal methods are largely used for conversion of biomass resources into value added products. Thorough knowledge on gradual degradation of chemical and structural components of biomass is still needed to allow selection of best procedures and conditions that lead to desired properties according to target applications. Thermogravimetry (TG) is a highly used technique for the study of thermal degradation of materials. It offers valuable information on thermal stability range, degradation steps and associated mass loss, as well as on kinetics of the process. Thermogravimetry alone cannot offer information on the nature of the volatile compounds formed during thermal degradation but this information can be obtained from pyrolysis followed by gas chromatography.

Torrefaction (To) and pyrolysis (Py) were tested as standalone or combined (PyTo) methods for valorisation of biomass residues. Thermogravimetry was used to determine the thermal behaviour of biomass residues before and after thermal treatment. This allowed us to observe the gradual degradation of structural components in biomass. Hemicelluloses started to degrade around 250 °C into furans, acids and linear ketones. Part of volatile terpenes remained embedded in the unaffected lignin and cellulose. Degradation of lignin became significant around 270 °C, producing phenol derivatives, especially at higher temperatures. Cellulose was apparently not affected by torrefaction but was degraded by pyrolysis.

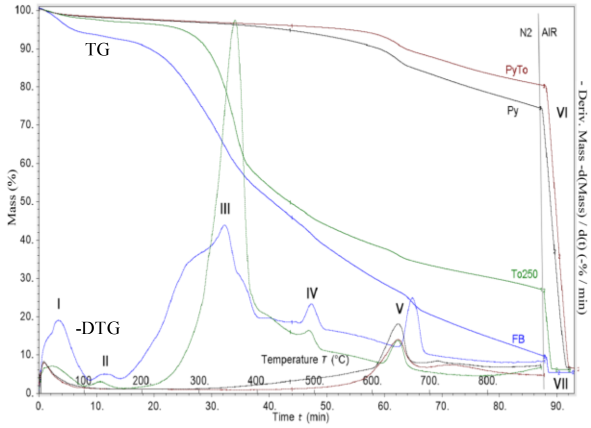

Fig. 1. The TG/DTG curves of a biomass residue (FB) before and after standalone or combined torrefaction and pyrolysis.

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# Thermogravimetric analysis of bioadsorbents from coffee residue for $CO_2$ capture

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The article explores the feasibility of using used coffee grounds as effective adsorbents for $CO_2$ capture. Thermogravimetry is used to evaluate the adsorption behaviour of coffee grounds under different temperature conditions. Bioadsorbents produced from biomass possesses high surface area and good thermal stability which makes them a highly attractive for $CO_2$ capture by adsorption methods [1-4]. In order to evaluate the possibility of using biocarbon for $CO_2$ adsorption in large-scale VPSA units, in$_2$vestigations of these compounds in laboratory are necessary. The main parameter of the evaluation of the potential of adsorbents to be used in VPSA plants still remains to be the sorption capacity, as expressed by the amount of adsorbed $CO_2$ per unit adsorbent mass. The paper presents the potential of biocarbon for $CO_2$ capture. The examination of the $CO_2$ sorption capacity and regeneration performance of biocarbon was carried out using a Mettler TGA/SDTA 851e thermobalance and TG-Vacuum system.

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# Changes in the thermal behaviour of phosphorite sample from Toolse deposit (Estonia) along the drill-core

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The changes in the thermal behaviour of shelly phosphorite ore from Toolse deposit along the drill-core PH014B (depth 21.1 – 26.7 m) cut into sub-samples with the length of 0.1 m has been studied. The primary phosphorus bearing mineral in Estonian phosphates is fluorcarbonate apatite (francolite) originated from lingual brachiopod shells which during the following millions of years of deposition has partially transformed into fluorhydroxyl apatite.

The experiments on a Setaram Labsys Evo 1600 thermoanalyzer coupled with Pfeiffer Omnistar Mass Spectrometer were carried out under non-isothermal conditions at the heating rate of 10°C $\mathrm{min}^{-1}$ up to 1200°C in an oxidizing atmosphere containing 79% of Ar and 21% of $O_2$. XRD, FTIR and XRF methods were used to estimate the mineralogical and chemical composition of the sub-samples.

In all studied sub-samples prevailed two minerals—apatite and quartz. The content of apatite decreased moving upwards and, in contrary, the content of quartz increased—both minerals with certain fluctuations depending on changes in the geological scale of formation of these sediments. Pyrite was also presented in all sub-samples, clay minerals almost in all, but K-feldspar, mostly, in the upper layers. Carbonates were presented in many sub-samples along the drill-core, at that, the content of dolomite was especially high in the deepest sub-samples—between 26.3 and 26.7 m. Organic carbon was concentrated into the upper layers (21.1–23.0 m) of the drill-core.

Thermooxidation of organic matter contained in the samples starts at 200-230°C and continues up to 500–550°C with the emission of water, carbon dioxide and sulphur dioxide in the case of all studied sub-samples, but more intensively from upper layers—between 21.1 m and 23.0 m—where the content of organic matter was much higher than in the lower layers. The emission of $SO_2$ into gas phase with the maximum at around 460-480°C that is characteristic to the first step of thermooxidation of pyrite, was more intensive for the sub-layers 21.1-21.2 m, 22.3-22.4 m, etc. having higher content of pyrite.

At 500°C the decomposition of dolomite starts with the peak value at around 550°C and then the calcite part of it—depending on its content—with the peak maximum between 650–745°C. It can be especially well seen in $CO_2$-emission profiles of the sub-samples between 26.2–26.7 m which contain much more dolomite than other sub-samples.

Between 700–1100°C the changes in the crystal structure of apatite continue with the emission of $CO_2$. The emission of $SO_2$ from the apatite structure started at around 1100°C and did not end at heating of the samples up to 1200°C.

Analysis of the results showed a good correlation between the thermal behaviour of sub-samples (emission of hygroscopic water, thermooxidation of organic matter and pyrite, dehydroxylation of clay minerals, etc.) and the changes in their mineralogical and chemical composition along the drill-core.

# Oral Presentations 2

## Thermodynamics & Calorimetry of Solids, Thin Films, Nanostructures & Nanomaterials

# Characterization of unknown animal glues from artwork samples by thermal, rheological and structural analysis

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Animal glues have been widely used as adhesives and binders in various fields [1]. The earliest uses date back to ancient Egypt, where animal glues were used to fix wood inlays with ebony and ivory, to anchor faience to pyramid walls, or as a binder in pigments [1]. Animal glues are produced by hydrolysing animal tissues such as bone, skin, cartilage, and connective tissue at high temperatures (60-80 °C). During the production process, collagen, the main protein component of animal tissues, is partially hydrolysed [2,3].

In this study, animal glue samples derived from artworks and provided by the Museo Nacional del Prado (Madrid) and restoration workshop of the University Suor Orsola Benincasa (Naples) were characterized from a thermal, rheological, and structural point of view to determine possible correlations between macroscopic properties and collagen molecular structure.

Thermal analysis was carried out to study the thermal degradation and the degree of denaturation of collagen by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively.

Modulated-DSC was used to study for the first time the physical aging of fibrous protein, namely collagen, in animal glue samples by determining the enthalpy relaxation value.

The findings obtained through thermal analysis together with results from IR spectroscopic and rheological analysis related to collagen secondary structure and glue strength, respectively, allowed the identification of two main glues groups, namely strong glues and weak glues, characterized by different degrees of hydrolysis of collagen and consequently different viscoelastic properties, temperature range of thermal decomposition and decomposition rates.

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# Thermal behaviour of lead and mercury carboxylates as paintings' degradation products

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Painted artworks are subjected to degradation over time due to various environmental factors such as light exposure, humidity or temperature fluctuations as well as conservation treatment. A conservation technique involving heat treatment is for example relining[1]. This restoration process is used for reinforcement of degraded canvas and often consists of application of a new canvas on the reverse of a painting by ironing. Formation of metal soaps (i.e., long chain metal carboxylates resulting from interaction of some metal-based pigments and fatty binders) represents a serious problem for stability and appearance of paintings. Consisting of complex chemical processes, mechanism of saponification and role of individual factors has not been fully understood yet and the thermal behaviour of neo-formed soaps in paint layers is unknown.

Lead[2], mercury[3,4] and mixed lead-mercury carboxylates (palmitate and/or stearate), found in degraded areas of paintings, were synthesized and investigated by x-ray powder diffraction (XRPD), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) coupled with mass spectrometry (MS) and differential scanning calorimetry (DSC) to characterise their structural features and to determine their thermal properties. Furthermore, thermal behaviour of studied metal carboxylates in an oil medium was also examined.

Besides others, we found that temperature around 100°C led to volatilization of mercury from mercury-containing carboxylates and the release of metallic mercury was significantly higher in the systems containing oil than in pure carboxylates. Moreover, the release of mercury in oil-based mixtures was accompanied by formation of crystalline free carboxylic acid, which in turn, can facilitate formation of carboxylates with other metals present in a paint.

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# Fe spinel-based materials for biomass combustion applications

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Chemical looping combustion technology where oxygen required for fuel combustion is provided by an oxygen carrier seems to be promising. In this power generation process the carbon dioxide sequestration is simplified and also emission of nitrogen oxides is reduced significantly. Nowadays, plant biomass is considered an important renewable energy source worldwide.

In the paper, selected oxygen carriers (OCs) with a spinel structure are used for the selected plant biomass (wood chips) combustion. Evaluation of the OCs' redox reactivity toward fuel was completed with application of thermogravimetric analyser coupled with a quadrupole mass spectrometer (TG-QMS).

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# Controlling the reaction path of Ni/Al reactive multilayer on substrates

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Ni/Al reactive multilayer are known for producing extremely rapid gasless reactions. It’s widely used in micro joining application due to have sufficient Joule heat for joining. Here we considered the exothermic reaction of Ni/Al reactive multilayer nanofoils as a local heat source for micro resistance welding, designing to increase the heat accumulation and improve the joints strength. In this paper, tried to monitor the reaction front path of Ni/Al multilayers which will be useful in controlled micro joining applications. In this paper, we prepared structured obstacles with different sizes on the path of 5 µm Al/Ni multilayers. Obstacles were fabricated from different methods: lithography and etching of the substrates. Obstacle are created in systematic order with different spaces between them on the path of Ni/Al multilayers over substrates. The self-propagating reaction was initiated by an electrical spark on the surface of the Ni/Al multilayers. The reaction front was recorded with a high-speed camera. The maximum temperature of the self-propagating reaction was observed by time-resolved pyrometer measurements. X-ray diffraction results showed the phase formation of NiAl phase. SEM analysis showed the morphological changes that occurred after the reaction on Al/Ni multilayers and quenching zone as well, where reaction front stopped at different spaces between obstacles. Finally, it is predicted that: (I) The minimum spaces between obstacles can quench the reaction front; (II) The influence of different substrates through the effect of the heat loss on the reaction front; (III) The reaction front can be guided between obstacle rows with a specific dimension.

**Keywords:** reactive multilayers; self-sustained reaction; nickel; aluminum; propagation velocity; phase transformation; Lithography.

# Defect engineering of titanium oxide thin films printed via one-step reactive spark plasma discharge coupled with aerosol direct writing

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Nowadays, the need for clean energy solutions is rapidly growing. Systems of high interest include versatile nanomaterials capable of energy conversions and storage, whether as photocatalysts, battery materials or transport layers in photovoltaic devices. Such materials need to satisfy multiple criteria, depending on their application, while the method of their synthesis needs to be reproducible, low-cost, green and scalable.

In this study, we investigate the potential of reactive spark ablation coupled with direct aerosol writing for one-step synthesis of titanium oxide thin films. The samples were printed onto silicon wafers for characterization with varying oxygen partial pressure in a nitrogen atmosphere.

Morphology was analysed by TEM, SEM and AFM, while structural characterization was performed by grazing incidence X-ray diffraction and XPS. Optical properties were determined by UV-Vis spectrometry. Morphology analysis points out to highly porous self-assembled aerogels while structural characterization points out to highly oxygen defective titanium oxides ranging from amorphous to semicrystalline which have significantly lowered bandgaps, increasing their photoactivity in visible light.

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# Surface mobility and crystal growth study in chalcogenide thin films

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Chalcogenide thin films are promising materials widely used in practical applications (e.g., memory storage devices, optical switches and filters, diffractive optical elements, planar waveguides, solar cells, etc.) due to their diverse optical, electrical, and thermal properties.

Physical properties (viscosity, diffusion, hardness, elasticity, surface tension) are essential for amorphous materials processing (e.g., hot-embossing) as well as for the description of kinetic processes taking place in glass-forming materials (such as structural relaxation or crystallization). [1-3]

The contribution is focused on measurements of near-surface mobility (near-surface viscosity and surface diffusion) in amorphous chalcogenide thin films. The surface mobility is studied using nanoindentation and following the smoothing process of the surface structures embossed in the samples using atomic force microscopy and light scattering. The obtained data are compared with the data found for bulk materials using other thermo-analytical techniques. The knowledge of mobility in amorphous materials is also essential to describe and predict crystal growth behavior in these materials in a wide temperature range, which is crucial for amorphous films preparation, storage (long-term stability), processing, and possible utilization of the prepared materials. Therefore, the obtained mobility data are combined with the crystal growth data measured directly by optical microscopy techniques. The data are described within the current crystal growth models. [2, 4]

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# Two types of crystal growth in Se–Te thin films

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Generally speaking, chalcogenide glasses have interesting optical and electrical properties and thus technological applications [1]. The perfect, stable, and crystallization-resistant glasses are used as infrared-transmitting optical elements. Contrary, the applications such as phase-change memories and glass ceramics call for fast or controlled crystallization. The promising utilization of chalcogenide glasses is also in solar cells as photovoltaic devices [2]. To evaluate the suitability of the material and its tunability for specific applications, one needs information about thermodynamics, the kinetics of the nucleation and crystal growth processes, the temperature dependence of viscosity, etc. of various forms of the material.

The study of crystal growth in $Se_{90}Te_{10}$ thin films was performed under isothermal conditions using an optical microscope. Thin films were deposited on soda-lime and PVC substrates. The crystals formed at the thin film-substrate interface were followed quantitatively and the results were compared with our previously published data relating to the crystal growth at the thin film free surface [3]. These two types of crystals were described by Stephens [4] and others in the past, but their data were qualitative. The crystal growth below $T_g$ was discussed with the known behavior from the organic molecular glasses [5]. A brief study of the influence of illumination and aging of thin films on crystal growth was performed. The found experimental crystal growth data in $Se_{90}Te_{10}$ thin films were described using a theoretical crystal growth model with the considered relationship of viscous flow and diffusion. The thin film crystal growth data were compared with the crystal growth data from the $Se_{90}Te_{10}$ bulk surface and bulk volume [6] so a complex view of the crystal growth process was obtained.

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# Tuning properties and behaviour of W-Zr thin-film metallic glasses

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Metastable solid materials such as amorphous or nanocrystalline alloys, supersaturated solid solutions, high-temperature or high-pressure phases persisting at normal conditions, have been of great interest due to a possibility to explore novel structures with unknown properties. These materials are kinetically determined and can be therefore synthesized only by non-equilibrium processes. Magnetron sputtering, which is one of the plasma technologies, is a suitable technique for their preparation as thin films. Recently, we have shown that using magnetron sputter deposition, we were able to prepare W–Zr thin-film alloys with several metastable structures in respect to the equilibrium phase diagram [1,2,3].

The present study focuses on systematic investigation of the evolution of properties of W–Zr thin-film metallic glasses with three different Zr contents (32 at.%, 48 at.% and 61 at.%) after annealing in synthetic air. The films were annealed to temperatures in the range 300°C – 600°C and after cooling down to room temperature the evolution of their structure, elemental composition, hardness, electrical resistivity and optical properties was studied. Attention was also paid to their oxidation behavior investigated using a symmetrical high-resolution Setaram TAG 2400 thermogravimetric system during dynamical heating to 600 °C in synthetic air.

The results obtained show a very interesting thermal behavior during annealing in air. No protective surface oxide layer grows on the surface of the films up to 550°C, but oxidation leads to the formation of very compact, homogeneously oxidized substoichiometric W–Zr–O films with an amorphous structure. The mass gain increases smoothly for all three films as oxygen penetrates the entire volume of the amorphous films. The lowest final mass gain and the latest onset of oxidation (~350°C) is observed for the lowest Zr content (32 at.%) investigated. Controlled oxidation of these films to selected temperatures leads to a significant enhancement of mechanical properties and tuning of their optical and electrical properties. All evolution trends will be thoroughly presented.

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# $Li_2O$-$Al_2O_3$ and $Li_2O$-$SiO_2$ systems: experimental investigations and thermodynamic modelling

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The importance to recycle and recover valuable transition metals (such Co, Ni) and Li increased in the recent years because of wide usage of Lithium-ion Batteries. Several metallurgical methods have been studied to obtain transition metals from their respective oxides after slag separation and crystallization processes. In this context, $Li_2O$ reacts with slag forming $LiAlO_2$ or spinel solid solution [1-2]. Thus, the development of thermodynamic database for the $Li_2O$-$MnO_x$-$SiO_2$-$Al_2O_3$ is an important tool to optimize conditions, aiming to obtain maximal separation of $Li_2O$ from the slag [3]. Using the CALPHAD method, investigations of pseudo-ternary and pseudo-binary systems among these oxides have been performed by our research group. The $Li_2O$-$Al_2O_3$ and $Li_2O$-$SiO_2$ systems were investigated in the present study. Crucial experiments were performed using samples produced by solid state reaction for the $Li_2O$-$Al_2O_3$ system (initial chemicals were $Li_2CO_3$ and $Al_2O_3$) and sol-gel reaction for the $Li_2O$-$SiO_2$ system (using LiNO3, tetraethoxysilane and $HNO_3$ as precursors). Microstructural investigations were carried out via microstructural characterization using Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD). Furthermore, Differential Thermal Analysis (DTA) was used to measure the temperature of invariant reactions followed by microstructure investigation to determine nature of these reactions. Heat capacities of $LiAlO_2$ and $LiAl_5O_8$ phases were experimentally obtained by Differential Scanning Calorimetry (DSC). Both phase diagrams were optimized using Compounds Energy and Formalism (CEF) for solid phases. Two-sublattice partially model was adopted for liquid description. The spinel phase $(Al^{+3},Li^{+1})_1^{T}:(Al^{+3},Li^{+1},Va)_2^{O}:O_4$ was modeled using two cationic sublattices to describe the high degree of inversion and its extension in $Al_2O_3$ composition region assuming presence of the vacancies in octahedral sites. The derived thermodynamic databases reproduce the $Li_2O$-$Al_2O_3$ and $Li_2O$-$SiO_2$ phase diagrams and thermodynamic values satisfactory.

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# Isothermal Calorimetry for Investigation of Heat Signatures of Batteries During Charging and Discharging

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Accelerating Rate Calorimetry (ARC) is a method to study worst-case scenarios and thermal runaway reactions. In contrast to other caloric techniques such as reaction calorimetry, combustion calorimetry or Differential Scanning Calorimetry (DSC), ARC-type equipment allow for an adiabatic sample environment. Adiabaticity is essential in order to observe the most tremendous reaction progress possible. Decomposition reactions, which are of particular interest in this context, produce heat and pressure, since the reactions are usually strongly exothermic and are forming decomposition gases. The adiabatic sample environment is realized inside the ARC-type calorimeter via a set of heaters surrounding the sample compartment and via a smart temperature control regime. The first objective is to detect the temperature at which the self-decomposition of a sample or a sample mixture starts. The second objective is to avoid any exchange of heat between the sample and the surroundings once the exothermic decomposition reaction has started.

This setup can also be used for isothermal cycling of batteries to measure the heat signature of 18650-cells (ARC 305) or coin cells (MMC 274) for instance. The heat dissipated by the battery is independently quantified during charging and discharging. Together with the applied power, the quantified heat can be used to calculate the efficiency of the cycling process. Special attention was turned on the influence of temperature as well as the charge and discharge rate. This information is helpful for the further development and optimization of battery components.

# Development of thermodynamic database for $ZrO_2$-$Y_2O_3$-$HfO_2$-$Ta_2O_5$ system

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The materials within the $ZrO_2$-$HfO_2$-$Y_2O_3$-$Ta_2O_5$ system have gained significant interest for their potential application as new thermal barrier coatings [1,2]. Understanding of the thermodynamics of this system is crucial for future practical implementations. Investigations of the pseudobinary systems are important for thermodynamic database development. Recently, we investigated phase relations in the $ZrO_2$-$Ta_2O_5$ system and measured heat capacity of $Ta_2Zr_6O_{17}$ compound. The experimental data obtained in our work, enthalpy of formation $Ta_2Zr_6O_{17}$ obtained by drop-solution calorimetry in rature (Voskanyan et al. 2021) were used to derive thermodynamic database for the $ZrO_2$-$Ta_2O_5$ system by CALPHAD approach.

Building upon the insights gained from the $ZrO_2$-$Ta_2O_5$ system, we extended our research to the $HfO_2$-$Ta_2O_5$ system. Of particular interest in our investigation was the intermediate compound $Hf_6Ta_2O_{17}$ (McCormack and Kriven 2019), which melts by peritectic reaction. To determine its heat capacity, we conducted differential scanning calorimetry (DSC) measurements. The enthalpy of formation of this compound is available from literature (Voskanyan et al. 2021). Phase equilibria in the $HfO_2$-$Ta_2O_5$ system were studied within the temperature range of 1573 K to 1873 K using the equilibration technique and up to 2473 K using differential thermal analysis (DTA). The samples were characterized using X-ray diffraction and scanning electron microscopy with energy-dispersive X-ray spectroscopy. The melting relations, reactions, and phase transformations were investigated using DTA, followed by microstructure analysis with SEM/EDX. The preliminary thermodynamic database of the $HfO_2$-$Ta_2O_5$ system was derived.

Another significant side system is $Y_2O_3$-$Ta_2O_5$. In this system, our focus was directed towards the region surrounding the P phase ($YTa_3O_9$) (Fernandez et al. 2018). Like the approach used in the $HfO_2$-$Ta_2O_5$ system, we studied the phase equilibria and characterized the samples. Based on our findings, we will discuss the nature of the melting reaction of the P phase at high temperature.

Furthermore, we will provide an outlook on utilizing the obtained database and phase diagram modelling for pseudobinary and pseudoternary systems.

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# Regeneration and reuse properties of the highly effective electrochemically-derived nanostructured ordered titania photocatalyst

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Immobilised photocatalyst systems based on titania nanotube arrays proved efficient based on inherent favourability of titanium oxide, further enhanced by the advanced morphology that the nanotube array configuration can offer. Previously we observed the possibility to modify the titania nanotube anodization process to yield highly effective photocatalysts with reduced level of order, i.e. increased microstructural inhomogeneity at horizontal level and chemical inhomogeneity at vertical scale. Briefly, we recognised the defects induced on behalf of such modification favour high photocatalytic activity.

Here we investigate the durability and reusability of the as-prepared photocatalyst samples. The photodegradation tests of acetylsalicylic acid were done in triplicates using the same selected samples. Results were modelled and photocatalyst lifetime was discussed. Vibration spectroscopies and depth sensitive diffraction techniques were used to monitor the samples before and after the extensive use in order to evaluate the contribution of the as-formed different areas in the final photocatalytic efficiency. Samples retain their photocatalytic properties for reasonably long time.

Here we test a novel concept of photocatalyst regeneration where the used samples were electrochemically re-synthesized in order to enable new activation in degradation efficiency. The reactivated photocatalyst was subjected to degradation tests to show remarkable photocatalytic activity regeneration. The cross-section high-resolution electron microscopy of cycled and then regenerated samples offered an insight in the complex microstructural and chemical evolution on behalf of photodegradation and anodic re-growth. This novel concept may be considered as ground breaking in terms of facile, cheap and environmental photocatalytic micro-pollutants removal.

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# γ-$Al_2O_3$ supported $MnO_x$ catalysts for VOCs oxidation

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Manganese oxides are well-known for their high catalytic activity and durability in various catalytic processes, due to the ability of manganese atoms to switch between different oxidation states and to form structural defects which results in high oxygen mobility and storage. [1] On the other hand, γ-alumina is the most commonly used catalyst support, due to its high surface area, wear resistance, good adsorption capacity and catalytic activity. [2] The aim of this work was to develop manganese oxides catalysts on γ-alumina support with high activity in the oxidation of harmful volatile organic compounds (VOCs).

Alumina supported catalysts with 0, 2, 4 and 8 at. % of Mn were prepared using the spray drying technique. The samples were thermally treated at 700, 800 and 900 °C for 2 hours, as well as characterized using X-ray diffraction analysis (XRD), simultaneous differential thermal and thermogravimetric analysis (DTA-TGA), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and $N_2$ physisorption analysis. The samples thermally treated at 700 °C were amorphous, while the manganese rich samples treated at 900 °C showed the presence of corundum alongside the dominant γ-alumina phase. The XRD patterns of samples calcined at 800 °C for 2 hours consisted solely of γ-$Al_2O_3$ diffraction peaks, thus these samples were selected for catalytic activity tests in the toluene oxidation process.

The EDS mapping analysis showed that manganese is evenly distributed on the surface of the samples. According to the physisorption results, all samples exhibit type IV isotherms characteristic for mesoporous materials, with average pore sizes in the range between 5 and 8.5 nm. All samples are highly active in the toluene oxidation process showing a decrease of temperatures necessary for achieving 10, 50 and 90 % of conversion with the increase of manganese atomic ratio in the samples.

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# Study of the Hf-Mn system by thermal and phase analysis and calorimetry

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The Hf-Mn system is of a serious interest due to the existence of the intermetallic $HfMn_2$ Laves phase C14 and the HfMn phase, candidates for hydrogen storage materials. This system has been experimentally studied by several groups of authors, e.g. [1,2], and experimentally and theoretically assessed, e.g. [3-5], but there is still a lack of reliable information on the respective phase diagram, particularly as the HfMn phase, described sometimes as $Hf_2Mn$ or $Hf_3Mn_2$ phase, is suspected to be oxygen stabilized.

To clarify the situation in controversial parts of the Hf-Mn phase diagram and to exactly characterize the intermetallic phases, a series of experimental alloys was studied by X-ray single crystal and powder diffraction, thermal and phase analysis and a low and high temperature calorimetric investigation of the Laves phase C14 was performed. The HfMn phase was characterized as $Hf_3Mn_3O_x$ (defect $W_3Fe_3C$-type). The new information together with literature data will create the basis for thermodynamic reassessment of the Hf-Mn system.

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# In-situ TEM annealing of Al-Cu-Al heterogeneous nanostructures

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Aqueous aluminum ion batteries are a promising candidate for substituting commonly used lithium-ion batteries [1]. The main drawbacks hindering their practical application are the formation of an aluminum oxide layer and hydrogen evolution side reactions [2]. An improvement of reversibility can be achieved by using lamellar Al-$Al_2Cu$ nanostructures, where $Al_2Cu$ lamellas serve as nanopatterns to guide dendrite-free Al plating [3]. Magnetron sputtering and subsequent annealing offer a convenient way to produce dendritic structures of α-Al and $Al_2Cu$ intermetallic phases.

Heterogeneous Al-Cu-Al structures were prepared by DC magnetron sputtering and gas aggregation source [4]. Cu nanoparticles (diameter ~15 nm) were sputtered on a thin Al-film and subsequently covered with another Al-layer. The microstructure evolution of the heterogeneous structures was analyzed during in situ annealing in a transmission electron microscope (TEM) using conventional TEM with selected area diffraction and scanning electron microscopy (STEM) with bright field, high angle annular dark field, and secondary electron detectors combined with energy dispersive X-ray spectroscopy. The dissolution of Cu nanoparticles and formation of new Cu-rich phases was observed during the annealing at temperatures below 600 ˚C. The observations in TEM were compared with the results of computer simulations.

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# Thermodynamic simulation and experimental verification of phase transitions in medium-Mn alloy

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The intercritical annealing of medium-Mn steels is an effective way to stabilize a high fraction of retained austenite (20-40 vol.%) in the microstructure. This type of steels usually contains from 3 to 12% of manganese [1]. The steels with a microstructure composed of ferrite and retained austenite (RA) show moderate tensile strengths at the level of 800–1000 MPa and high total elongation of 20–40%. The high fraction of ductile RA is possible to obtain by carbon and manganese partitioning into austenite during the intercritical annealing [2, 3]. The stabilization of high fraction of RA requires the detailed monitoring the kinetics of phase transformation of steel.

The present work aims at analysing the phase transformation kinetics in an iron alloy containing 5% Mn using thermodynamical calculations and dilatometry. The investigated steel was subjected to the intercritical annealing at temperatures from 660°C to 740°C for different holding times from 5 min to 120 min. The obtained results showed the influence of temperature on the thermal stability of retained austenite. The structural constituents and phase composition of the investigated alloy for particular heat treatment variants were revealed using light and scanning electron microscopy techniques. The quantitative analysis of the fraction of RA in the microstructure was carried out using X-ray diffraction.

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# Electron microscopy and molecular dynamics study of Ni nanoparticles at elevated temperatures

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The properties of metallic nanoparticles are often controlled by their characteristic dimension [1]. For example, in ferromagnetic materials such as nickel, it might be the size of a single domain. However, their significant sintering could occur at elevated temperatures resulting in the growth of the diameter of nanoparticles and a modification of their properties. Ni nanoparticles with a diameter close to 10 nm were prepared by a gas aggregation source [2]. Their thermal stability was studied by in-situ transmission electron microscopy (TEM) during heating at elevated temperatures. Their susceptibility to sintering was observed already at 100 °C, and significant coagulation occurred at temperatures above 300 °C. Details of sintering processes were studied by TEM, high-resolution TEM, and scanning electron microscopy. Observed processes were compared with molecular dynamics simulations. Enhanced surface diffusion, dislocation activity, and viscous flow were identified as the main processes controlling the coagulation of Ni nanoparticles.

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# Fitting theoretical models to viscosity of Graphene Nanofluids as a function of temperature

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Understanding the thermal-physical properties of fluids is an important factor in the design and development of thermal energy transfer equipment to operate more efficiently. These properties determine how much energy a fluid can effectively transfer, and its performance in thermal energy exchange processes. Fluid viscosity is an essential physicochemical property that plays a vital role in mass and heat transfer. Its understanding and control are fundamental to designing more efficient processes and maximising the performance of related systems.

The present study aims to correlate the theoretical models existing in the bibliography with the experimental values obtained. The nanofluid used in the present work was prepared by the two-step method [1], using as base fluid the ethylene glycol, with the CAS number 107-21-1 and graphene platelets with the CAS number 7782-42-5, of 11-15 nm and the surface area between 50 and 80 $m^2 \cdot g^{-1}$. Several nanofluids with different volume concentrations (0.1, 0.2, 0.3, 0.5, 0.7, 1%) of graphene in ethylene glycol were prepared and their viscosity measured with a Cannon-Fenske viscometer for different temperatures. Several mathematical fits to the experimental values were performed to correlate the geometric shape of the nanoparticle with the viscosity for different temperatures in the range of 293.15-318.15 K. The models used are shown in Table 1.

Table 1 - Theoretical viscosity models studied [2-3].

| *Model* | *Mathematical equation* |
|---|---|
| *Brinkman* | $\eta_{nf} = \eta_{fb}(1-\phi)^{-2.5}$ |
| *Wang* | $\eta_{nf} = \eta_{fb}(1+7.23\phi+123\phi^2)$ |
| *Batchelor* | $\eta_{nf} = \eta_{fb}(1+2.5\phi+6.2\phi^2)$ |
| *De Bruijin* | $\eta_{nf} = \eta_{fb}(\frac{1}{1-2.5\phi+1.552\phi^2})$ |
| *Vand* | $\eta_{nf} = \eta_{fb}(1+2.5\phi+7.349\phi^2)$ |

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# Natural hybrid pigments as durable multifunctional coloring agents for polymer composites

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Recently, natural colorants have attracted renewed attention in different areas of industry such as textile, building, packaging and polymer technology. Unlike synthetic ones, they are generally environmentally friendly and non-toxic, as well as plentifully available from various plants, invertebrates, insects etc. [1]. However, natural colorants are known to suffer from high instability and rapid degradation due to external factors (such temperature or light) [2]. Therefore, researchers have investigated different strategies to prevent color fading of natural colorants. The stabilization and immobilization of organic dyes on inorganic or organic substrates result in the production of high-performance hybrid pigments with improved resistance to environmental factors [1-3].

In turn, this study presents a comprehensive investigation on the designing of new functional organic-inorganic (natural dye/clay mineral) and organic-organic (natural dye/biopolymer) hybrid pigments. This study analyzes and discusses the structure-property relationships in the obtained hybrids based on a series of complementary techniques starting from basic research (NMR and TOF-SIMS spectroscopic studies), through physical-chemical investigations (morphology (XRD, SEM), thermal stability (TGA), color characteristic (UV-Vis)), to application in polymeric materials (dispersion, mechanical, barrier, combustion, UV stability, migration tendency).

Owing to the combined qualities of high coloring ability, improved thermal and chemical stability, UV protection, barrier performance, reduced migration, and pH sensitivity developed hybrid pigments represent a promising breakthrough in the technology of smart colorants for polymer materials.

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# Thermal and Structural Properties of PVDF@Zn-MOF Nanocomposites

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The thermal and structural properties of PVDF (Polyvinylidene fluoride) @Zn-MOF (Metal Oxide Framework) nanocomposites have been investigated by applying differential scanning calorimetery (DSC), scanning electron microscopy (SEM) and X-ray diffraction (XRD). SEM images indicate the homogeneous dispersion of ZnMOFthroughout PVDF matrix. DSC shows that crystallinity is influenced by the presence of Zn MOF in the PVDF matrix because the filler acts as efficient nucleating agent to facilitate PVDF crystallization. DSC results indicated the enhancement of the glass transition temperature ($T_g$), melting temperature (Tm) and crystallization temperature ($T_c$) of nanocomposites as compared to pristine PVDF. The new DSC peak in PVDF@Zn-MOF (i.e. 12wt.%) is exclusively due to uniform dispersion of Zn-MOF in polymer matrix. DSC analysis of the MOF is confirming that the thermal decomposition of the molecules could be divided into different well-separated regions. The first peak that appeared at (109ºC) could be attributed to the sample moisture. The middle peak (147ºC) could be attributed to the sample decomposition, and last peak (197ºC) may be due to stability of PVDF@ Zn-MOF nanocomposites. It is well observed in case of PVDF@Zn-MOF (*i.e.*, 12wt.%) strongly. XRD shows that the full-width at half maximum decreases with increasing Zn-MOF content, which is attributed to the improvement in crystallinity.

# Modified plant fillers of polymer composites

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The main aspect of the work was the characterization of elastomer biocomposites filled with modified fillers of plant origin. Such materials are not only "environmentally friendly", but also allow to partially solve the problem of agricultural waste management. However, the use of natural fillers as polymer reinforcement is limited mainly by the poor thermal resistance of the lignocellulosic material, which makes it difficult to process composites. Another important problem related to the use of plant fibres in polymer composites is its polar structure, which hinders good mixing and dispersion of the filler and interaction with the non-polar matrix. Poor compatibility between composite components may result in ineffective stress transfer from the matrix to the filler and, consequently, low mechanical strength of the materials. One of the solutions that improve both the thermal stability of natural additives and their adhesion to non-polar polymers are various types of chemical modifications of their surface.

The main objective of the research was to determine the impact of various methods of plant waste modification in order to obtain active ingredients for the production of elastomeric composites.

The study examined the effect of mechanical and chemical treatment of the biofiller on its properties and chemical structure. Detailed studies of the effect of modified fillers on the properties of the produced natural rubber vulcanizates were also carried out.

Analysis of filler properties including thermogravimetric analysis (TGA) and analysis of their surface, taking into account the measurements of the contact angle (CA) and scanning electron microscopy (SEM). Characteristics of the properties of rubber mixtures was based on the measurement of rheometric properties, crosslinking kinetics using differential scanning calorimetry (DSC). The vulcanizates, in turn, were tested for mechanical, barrier and thermal properties, as well as crosslinking density.

The applied modifications significantly affected the structure and properties of the fillers. The treatment removed a significant part of the non-cellulosic substances and exposed the surface of the fibrils, ensuring better wettability and reactivity of the fibres. It also resulted in greater thermal stability of the tested materials. The increase in the filler-polymer interactions resulted in an increase in the density of the elastomer spatial network, which in turn enabled more effective stress transfer between the polymer matrix and the additive, and consequently improved tensile strength.

# Oral Presentations 3

## Calorimetry of Polymers, Bio(macro)molecules, Life science and Organic Functional Systems & Compounds

# Use of thermal analysis for the study of the adsorption of pharmaceuticals from water

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The contamination of water with pharmaceuticals is one of the serious problems in the modern world. Their occurrence in surface- and groundwater brings a risk to the environment as well as human health [1]. Therefore many methods are studied in order of their removal. Adsorption on activated carbon belongs to the most popular ones [2].

Adsorption processes are conventionally studied by determining the equilibrium concentration in the solution, usually with liquid chromatography or UV-visible spectrophotometry. Thermal analysis is usually applied for the investigation of the thermal regeneration of activated carbon. Nonetheless, these methods could be used for the basic research study of adsorbents with different amounts of adsorbed contaminants.

This contribution is aimed at using thermal analysis to study the adsorption of analgesic paracetamol (acetaminophen) on activated carbon. Two different samples of commercial activated carbon (one powder activated carbon and one granulated activated carbon) and different initial concentrations of paracetamol were used. The granular activated carbon had to be homogenized by short-time milling in a vibration mill. Equilibrium concentrations were determined with the aid of UV-visible spectrophotometry and compared with thermogravimetric curves.

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# Phase transition in polymer hydrogels investigated by swelling, DSC, FTIR and NMR

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Polymer hydrogels are crosslinked polymers (polymer networks) swollen in water. Amount of the water absorbed by this kind of hydrogels is controlled by a delicate balance between stretching of the polymer network chains and thermodynamic interaction of the chains with water. Consequently, polymer hydrogels respond very sensitively to changes of external parameters (temperature, pressure, etc.) by adaptation of their structure to new situation. When certain conditions are satisfied, a discontinuous drop of hydrogel volume (hydrogel collapse – 1st order phase transition) accompanied by water release and heat absorption are observed [1].

Hydrogels based on single polymer network - single network (SN) hydrogels - are usually too fragile for many applications. Their strength can be significantly improved by filling their interior with a second less crosslinked polymer network. Resulting hydrogels are referred to as double network (DN) hydrogels [2].

In this study, SN hydrogel was prepared by crosslinking copolymerization of a thermosensitive polymer – poly(*N*, *N*-diethylacrylamide) (PNNDEAAm) in aqueous solution. Two series of DN hydrogels were prepared by swelling of this hydrogel in aqueous solutions of polyacrylamide or PNNDEAAm and subsequent crosslinking polymerization using UV-irradiation.

In this communication, effect of the presence of the second polymer network on the phase transition in the prepared DN hydrogels will be discussed. Information about the phase transition on macroscopic level was obtained by swelling and differential scanning calorimetric (DSC) measurements. Changes of the hydrogel structure on microscopic level accompanying the phase transition were monitored by spectroscopic techniques.

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# The step-wise dissolution method: An efficient DSC-based protocol for API–polymer solubility determination

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The development of an amorphous solid dispersion (ASD) is a promising strategy for stabilizing the amorphous form of poorly water-soluble active pharmaceutical ingredients (APIs), which may offer enhanced bioavailability concerning oral administration. An API–polymer temperature–composition (T–C) phase diagram can facilitate a measured approach to successful ASD formulation design, thereby reducing costly and timely experimental efforts. Since it is typically challenging to accurately measure the API solubility in a polymer under ambient conditions, differential scanning calorimetry (DSC) is employed to measure it at elevated temperatures. The experimental dataset is subsequently extrapolated to lower temperatures of interest using a solid-liquid equilibrium (SLE) curve modeling approach (e.g., the PC-SAFT equation of state (EOS)). However, the currently followed DSC-based protocols (e.g., the melting point depression method) are inefficient and cannot provide reliable data points close to the API–polymer glass-transition temperature line. Hence, we recently developed the "step-wise dissolution" (S-WD) method [1], which is a new DSC-based protocol that is both cost- and time-effective. A precursor to the S-WD method is the innovative "annealing time investigation" experiment, whereby an appropriate time of annealing is established that ensures the equilibrium solubility conditions are attained at each temperature of annealing. In the current study, the S-WD method was used to check the veracity of the purely-predicted PC-SAFT EOS-based SLE curve for more than fifteen API–polymer binary systems. Overall, the PC-SAFT EOS provided satisfactory qualitative descriptions, but not necessarily accurate quantitative predictions. The identification of different API–polymer case types based on the pure component physicochemical properties was an important finding in the creation of a decision tree for rational DSC-based API–polymer T–C phase diagram construction. The quantum chemistry-based COSMO-RS model was trialed as an alternative to the PC-SAFT EOS, and the pure predictions were in close agreement with the experimental values. Therefore, the application of the COSMO-RS model in conjunction with the S-WD method may represent an invaluable strategy regarding the reliable and expeditious screening of polymeric candidates for APIs; especially in the case of expensive anticancer compounds.

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# Sandwich Fibrous Paraffin Wax Encapsulations for Selected Applications

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Phase change materials (PCMs) textiles have applied in various fields. Although there has a significant progress in PCM textiles, there are some problems (e.g., limited PCM loading amount, poor mechanical property of PCM capsules etc.) [1-2]. In our previous work, a sandwich fibrous encapsulation was successfully developed to store PCMs which was a result of weak interfacial adhesion between melting PW and PU nanofibrous membrane [3]. The sandwich fibrous PW encapsulation consisted of PU nanofibrous membrane as barrier layers and PW-coated viscose fabric as PCM-loaded layer. However, the working temperatures of the sandwich fibrous PW encapsulation was not adjusted. Besides, PU nanofibrous membranes are no suitable as outer layer due to their poor mechanical properties and protection layers covering barrier layers and PCM-loaded layers are necessary.

In this work, the sandwich fibrous PW encapsulations were prepared, consisting of common cotton fabric as protection layer, PU nanofibrous membranes as barrier layers and PW-coated viscose fabrics as PCM-loaded layer. Seven different PWs were used, including n-tetradecane (TC), n-pentadecane (PC), n-heptadecane (HC), n-octadecane (OC), n-nonadecane (NC), n-eicosane (EC) and n-docosane (DC). The phase transition behaviour and thermal energy storage of different sandwich fibrous PW encapsulations were investigated. After obtaining working temperature ranges of various sandwich fibrous PW encapsulations, the visual-temperature property was then enriched by making a coating of thermochromic pigments on cotton fabric. We believe that the work not only contributes to fields related to thermal energy storage but also initiates the applications of nanofibrous membrane.

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# Combining calorespirometry and simultaneous thermal analysis (TGA-DSC) to assess energy fluxes of soil organic matter

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The main components of soil are minerals and soil organic matter (SOM). The latter plays a vital role in maintaining soil fertility and addressing climate change challenges. An important and significant portion of the SOM is constituted of microbial residues, accounting for approximately 50%. The dynamics of SOM involve carbon fluxes in the form of plant residues (influx) as well as mineralization and leaching processes (outflux) [1]. These matter fluxes are intrinsically linked to energy fluxes and are governed by the laws of thermodynamics. Although investigations into the thermodynamics of biological systems, including microbial metabolisms and growth, have been conducted since the late 1900s [2], the interactions between soil and microorganisms remain relatively understudied, despite recent attempts [3]. Thermal analysis is one of the techniques employed to study the thermodynamics of SOM fluxes. In our specific case, we aim to combine energy and matter fluxes; therefore, we use simultaneous thermal analysis (TGA-DSC) in conjunction with a gas analyzer (MS) to assess the soil energy content, and the calorespirometric analyses to obtain thermokinetic information about microbial metabolism. In this study, we present a method for TGA-DSC-MS analyses, building upon previous research [4]. This method was applied to German agriculture soil characterized by low organic matter (OM) content. Additionally, we conducted substrate-induced measurements on the same soil using an early-engineered isothermal macrocalorespirometer. This approach overcomes the limitations of the current calorespirometric techniques and enables undisturbed and simultaneous monitoring of heat and $CO_2$ production, higher sample throughput and sample size, and minimal oxygen limitations. Both types of analyses provide valuable kinetic and thermodynamic information, respectively, mass loss and energy content during combustion at a controlled rate (TGA-DSC-MS) and, on the other hand, time-resolved $CO_2$ production and heat release caused by microbial processes in soil (isothermal macrocalorespirometer). By integrating the findings from these thermal measurements with other analytical approaches, we aim to gain a deeper understanding of the dynamics of soil fluxes and the role of microbial reactions in the carbon-energy system.

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# Temperature dependence of the enthalpy of formation of oligomeric DNA duplexes: Implications for the thermodynamics of DNA

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DNA is a biopolymer that is increasingly being considered for applications in nanotechnology, ranging from novel nanostructures to functional nanomachines capable of operating in vivo. The field is based on the stability and kinetics of hybridization between complementary DNA sequences. The DNA thermodynamics and nearest neighbour model have been successfully developed to predict the sequence-dependent melting temperature of small oligos [1], and they have been essential in the advancement of large-scale sequencing. DNA nanostructures, such as DNA origami, self-assemble through interactions involving hundreds of DNA strands. The thermodynamics and kinetics of these interactions are likely to play a crucial role in guiding the system towards its configuration of minimal free energy.

We propose to investigate the main assumption made in [2], which assumes temperature-independent enthalpy $\Delta H$ and entropy $\Delta S$ during hybridization. To do this, we conducted DSC and ITC on 3 DNA duplexes with lengths of 14 bp, 16 bp, and 32 bp. We analysed the excess specific heat of hybridisation using a two-state binding model, from which we extracted the enthalpy and entropy of the duplex. Van 't Hoff analysis yielded consistent values for these parameters. Additionally, isothermal titration calorimetry performed at different temperatures with a fixed salt concentration 300 mM, allowed us to extract the enthalpy and entropy of hybridization. In contrast to the standard models, our results revealed that these values are temperature-dependent. Specifically, the enthalpy value decreases linearly with increasing temperature (20-50 °C). The slope, *i.e* the heat capacity, was found to be (-5.76 kJ/K), (-6.47 kJ/K) and (-21.48 kJ/K) for the 14 bp, 16 bp and 32 bp duplexes respectively. Consequently, there appears to be a heat capacity jump that is sequence-length dependent during the hybridisation of a DNA duplex. Our findings are in line with results obtained for similar sequences [3] and underscore the importance of directly measuring the thermodynamics of DNA hybridisation. These findings may have significant implications in the understanding and the better control of the assembly of complex DNA nanostructures.

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# Biocalorimetry as a tool to analyse fungal lignocellulose utilization strategies

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Fungi are important primary destructors of lignocelluloses of plant biomasses and thus play a key role in the global carbon cycle [1]. At the same time, they are also considered as promising biocatalysts with considerable potential for various (environmental) biotechnological applications. These include, for example, the conversion of lignocellulosic by-products from agriculture and forestry into valuable materials using bio-refineries, as well as the potential treatment and detoxification of various wastes and environmental pollutants [2-4]. This raises the question of whether non-invasive metabolic heat flux analysis can be used to determine functional traits in free-living saprotrophic decomposer fungi and to predict fungal influences on ecosystems processes. To answer such questions, the growth of seven fungal species, including ascomycetes, basidiomycetes, and zygomycetes, was studied in a standardized laboratory environment on wheat straw as a globally relevant lignocellulosic substrate. Our study demonstrates that biocalorimetry can provide various growth-related parameters of fungal activity. These include apparent maximum growth rates (*AMGR*), cultivation times until the observable onset of fungal growth at AMGR ($t_{AMGR}$), and heat yield coefficients ($Y_{Q/X}$); the latter indicating the degree of resource investment in fungal biomass relative to other functional properties. Particularly exciting is the quotient obtained from *AMGR* and $t_{AMGR}$, which we refer to as competitive growth potential (*CGP*). All these parameters seem to be suitable to link the fungal potential for biomass production with the corresponding ecological strategy in resource utilization. Therefore, they may be considered as fungal life history traits. A close relationship observed between *CGP* and $Y_{Q/X}$ values suggests an interpretation in terms of fungal life history strategies [5].

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# Accuracy of Simultaneous Calorespirometric Measurement and its Importance for Thermodynamic Modelling in Soil Systems

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Soil is recognized as the largest carbon storage sink in terrestrial ecosystems, making it crucial to understand its dynamic processes. The microbial activities involving in metabolic degradation and stabilization of soil organic matter adhere to thermodynamic principles. In soil systems, the interplay between heat flux (*P*) and carbon dioxide respiration rate (*CER*) plays a significant role in linking thermodynamics and respiration dynamics. The calorespirometric ratio (*P/CER*) is considered as an important indicator of carbon use efficiency (*CUE*) through stoichiometric relationships. This ratio is vital for connecting heat and mass flux in soil systems.

However, accurate thermodynamic approaches to link carbon and energy flux in soil are still lacking due to the complexity and heterogeneity of soil. To further validate the thermodynamic approach in soil systems, we conducted simultaneous measurements of heat flux and respiration using $CO_2$ traps (NaOH solution). The respiration rate was calculated by measuring the absorption enthalpy between NaOH and $CO_2$.

It is important to note that oxygen limitation in the airspace and the typically low amount of soil and the related small heat signal in isothermal microcalorimeter may pose limitations on obtaining reliable calorimetric-derived respiration results, which have not been previously tested [1]. To address the first concern, we employed regular open and fully closed ampoules as experimental setups to investigate the influence of aeration on heat flow signals and the reliability of $CO_2$ measurements derived from heat data. To address the second concern we used three devices with different sensitivities (TAM Air, TAM III, and Mc-Cal/100P) and varying sample sizes (20 mL and 4 mL).

The *CR* ratio may vary depending on the level of anaerobicity and biomass formation. In this study, we employ theoretical expectations to explore the effects of anaerobic conditions and biomass elemental compositions on *CR* ratio, building upon previous studies [2]. We will present preliminary results on the accuracy requirements of the CR ratio for delivering information on CUE from a theoretical perspective

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# Cellulose II highly porous materials as sound absorbers

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Many health effects of loud environments ranging from psychological issues due to the sleep disturbances, even to different cardiovascular diseases. Therefore, it could be said that noise reduction is an important priority in the modern society, especially for urban areas, buildings, and transport systems [1]. Commonly, commercially available foams and fibrous materials are the materials for mitigating applications used nowadays. The optimal choice for materials used is depending on the proposed sound frequency range, as the absorption mechanism highly depends on the frequency range [2].

In this work, special emphasis is given to a bio-aerogels which are biomass-based, i.e. cellulose II-based. This type of aerogels is very attractive as due to the renewability, availability, non-toxicity, and chemical stability. Specifically, different porosity in the samples were investigated. The ones prepared using aqueous sodium hydroxide solution with different microcrystalline cellulose (MCC) concentration, and the ones prepared by adding foaming agents (i.e. sodium sulphate dodecahydrate) in order to gain different pore size distribution. Continuous porous bodies were enabled by supercritical $CO_2$ drying. Thus, morphology of the samples, as well as the specific surface area were analysed by SEM and BET. Sound absorption coefficients of the samples were tested in the impedance tube. Frequency sweeps were performed, and data were recorded from 500 to 6000 Hz.

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# Synthesis and performance comparison of methacrylic pour point depressants with commercial additives

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For diesel fuel to be used in cars, it must meet quality standards. [1] Since diesel fuel cannot be completely adjusted by refinery processes to meet all the prescribed properties, the addition of additives to diesel fuel is necessary. Some of the most important types of diesel fuel additives are pour point depressants and cold flow improvers. These additives influence the crystal structure of the paraffin wax crystals in diesel fuel to prevent fuel line blockages and filter clogging. [2]

In this study, we compared the influence of a methacrylic polymer additive synthesized in our laboratory with a commercial additive used in industry on the low-temperature properties of diesel fuel. The thermal properties of fuel formulations with additives were observed using differential scanning calorimetry, while the influence of additives on crystal morphology during cooling was studied using an optical microscope with polarization equipped with a cooling stage. The standard ASTM D5950 test for pour point (PP) was used to measure the PP of the formulations, where an equally good and in some concentrations even greater improvement of the PP value was observed for formulations with newly synthesized additive compared to the commercially available additives.

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# Thermal reliability of n-eicosane – loaded phase change fibers

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The increasing demand for energy has led to the exploration of efficient, environmentally friendly, and renewable technologies utilizing smart materials. Phase change materials (PCMs) have gained significant attention in passive thermal energy storage, and various organic PCMs, including hydrocarbons, fatty acids, and poly(ethylene glycol) (PEG), have been extensively studied. Encapsulation of PCMs is crucial to prevent leakage and protect them from the environment [1]. Electrospinning has emerged as a versatile method for generating PCM-containing fibers in the nano- and micrometer range. These fibers have potential applications in thermoregulating coatings, smart fabrics, and energy-saving buildings.

This study focuses on the fabrication of form-stable phase change fibrous membranes using a blend of poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA), and n-eicosane as the PCM. PMMA enhances the structural integrity, while PEO improves the hydrophobicity of the fibers. The intermixing of these polymers effectively entraps the n-eicosane within the fibrous mat, preventing leaching during thermal cycles. The thermal properties of the resulting fibers were extensively characterized, and the effect of n-eicosane content was investigated. The thermal reliability of the fibers was evaluated through thermal cycling tests, and the kinetic analysis provided insights into the thermal degradation process [2].

The melting and crystallization enthalpy of the PEO/PMMA/n-eicosane samples remained unchanged during the initial and subsequent cycles. The PCF with 7.5 and 10 wt% n-eicosane content showed no significant temperature or enthalpy changes. The system with 10 wt% n-eicosane content was particularly promising, as it displayed a higher crystallization enthalpy (184 J/g) and maintained stable melting and crystallization peaks throughout all cycles. The degradation kinetics of n-eicosane, pristine PEO/PMMA fibers, and PEO/PMMA/n-eicosane fibers with a 10 wt% n-eicosane content were investigated. Furthermore, the Activation Energy (Ea) and pre-exponential factor (A) were calculated using the Friedman and Vyazovkin methods, and the reaction mechanisms were studied using model fitting methods. Overall, most of the PCF showed good thermal reliability making them suitable materials for thermal energy storage applications.

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# Prediction of tensile modulus in semicrystalline polymers based on their melting characteristics recorded by calorimetry

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The properties of the semicrystalline materials are depending on their complex crystalline structure. Isotactic polypropylene (iPP) polyamide-6 (PA6), poly(lactic acid) (PLA) as well as polyethelene-terephthalate (PET) is studied in this work. The tesnile modulus is one of the most important properties from the point of view of several applications. Although the key parameters of the crystalline structure, which determine the aforementioned properties are known in the literature, but the quantitative modeling is difficult and time-consuming procedure if possible at all. In fact, the number of models, which link the crystalline structure to the properties, is limited in the open literature. Accordingly, prediction of upper limit of stiffness is an open question in general.

In the present work we introduce a versatile technique for the prediction of modulus in semicrystalline polymers, based on a simple DSC measurement. An empirical equation was developed to calculate tensile modulus [1-5], from parameters of crystalline structure like crystallinity and average melting temperature. We have used to predict tenslie modulus of iPP, PA6, PLA and PET, and it worked with reasonalby good accuracy for all of these polymers. The results indicate clearly that stiffness can be predicted reliably, and this approach can be adopted for other polymers as well.

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# Innovative biocomposites based on PLA and beer bagasse used in two different additive manufacturing techniques

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Beer bagasse is a residue waste produced in great amounts, nevertheless, it is still underestimated in the industry. Its composition, characterized by a content of protein and polysaccharide allowed it to be used to produce biopolymers. The aim of this paper is to develop an innovative and efficient methodology to recycle the beer bagasse, by producing bio-composite PLA-based materials, in the forms of pellets and filaments to be used in additive manufacturing processes. To assess the suitability of beer bagasse for 3D printing techniques, it was, firstly, physicochemically characterized. Then, 10wt. % of bagasse was added in combination with different kind of plasticizer to PLA to make biocomposites, analyzing their thermal and physical properties. The results proved the great potential of bagasse, evidencing its suitability and printability. Both composites' pellets and filaments were used in two different 3D printing machines and the mechanical properties of the 3D printed models were evaluated as a function of the composition and the kind of technology used. With the addition of bagasse, embrittlement was observed. The different plasticizers considered improved processability and the polymer-bagasse interface. compared to neat PLA, the thermal properties did not change significantly in the mixtures, but a lowering of the mechanical properties was observed. Finally, a comparison was made between the two printing techniques.

# Isothermal thermogravimetry to fingerprint the oxidative behaviour of lipids

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Lipids, when exposed to atmospheric oxygen, are subject to a complex series of reactions which may evolve toward two main competitive pathways: oxidative degradation - resulting in the formation of polar species, including volatile compounds (such as short chain carboxylic acids, aldehydes and ketones), and cross-linking – resulting in the formation of higher molecular weight species. [1]

Several methods are routinely used to assess if an oil can be considered oxidized or not, and to rank the degree of stability toward oxidation among different oils. Induction time, peroxide value, presence of free fatty acids and conjugated dienes and trienes, are commonly tested by means of automated methods, such as Rancimat and Oxitest, spectroscopy, and gas chromatography .

Alternatively, mass changes upon oxidation, "oxygen uptake" curve, are also recorded using isothermal thermogravimetry (TG) under air flow. In the literature, the oxidative stability of a lipid, the presence of antioxidants, and the effect of pretreatments are associated exclusively to the induction period of oxygen uptake, and the latter is related to the onset time and the oxygen uptake curves have frequently been acquired until the start of mass gain only.

Here we present a method based on isothermal TG with two innovative aspects:

1. a prolonged "oxygen uptake" curve (4000-10000 minutes) is collected,
2. experimental data are fitted with a semi-empirical equation.

With this approach, an increased set of information becomes available. Beside the induction time, the parameters of the fitting equation give information on:

- the apparent time constants for the oxygen uptake process and for the main mass loss phenomena
- the overall mass loss and the mass of oxygen taken by the lipid upon time
- the trend of the curve for a time tending to infinite

The proposed approach has been successfully applied to oils with different degrees of unsaturation such as olive oil (non-drying oil), linseed oil (drying oil) and safflower oil (semi-drying oil) [2] and to model paint systems containing white lead, [3] synthetic ultramarine blue [3], carbon black, [4] and cadmioum red all historically and artistically relevant pigments with different effects on the curing of the oil.

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# Application of plastic materials by evolved gas analysis (TG-MS and TG-FTIR) equipped with optical microscope

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Simultaneous hyphenated thermal methodologies such as STA, TG-DTA coupled with an evolved gas analysis technique such as mass spectrometry (MS) or Fourier transform infrared spectroscopy (FTIR) gives us a profound understanding of the volatile products evolving from a material during heating and provides an accurate qualitative interpretation of the thermal behaviour of materials. In addition, in-situ visual observation technology, which integrates an optical microscope and thermal analysers to observe changes in materials during thermal processes, can be used to observe the shape, size, color, and other characteristics of the sample. It not only directly reveals visible changes, but also greatly aids in the interpretation of precise chemical or physical transformations [1].

The sample observation TG-MS result of ethylene-vinyl acetate, EVA resin obtained by Rigaku ThermoMassPhoto equipped with a sample observation attachment is shown in Fig.1. We can roughly see the two mass loss stages accompanying the endothermic peaks around 300-500℃. The approximately 30% mass loss component with an endothermic peak in the first stage between 300 and 400°C could be identified as acetic acid from the mass spectrum of the evolved gas. Similarly, the second mass loss component of approximately 70% with an endothermic peak between 400 and 500°C was found to be the simultaneous evolutions of several aliphatic hydrocarbons. In the thermal decomposition of EVA, below 400°C, it could be interpreted that the reaction that eliminates acetic acid while taking up a six-membered ring structure in the transition state proceeds preferentially, followed by continued cleavage of the main chain as in ethylene polymers in the subsequent high-temperature region.

In order to demonstrate the effectiveness of some unique hyphenated thermal analysis of TG-MS and TG-FTIR with sample observation function, the results of application to several plastics will be presented and discussed.

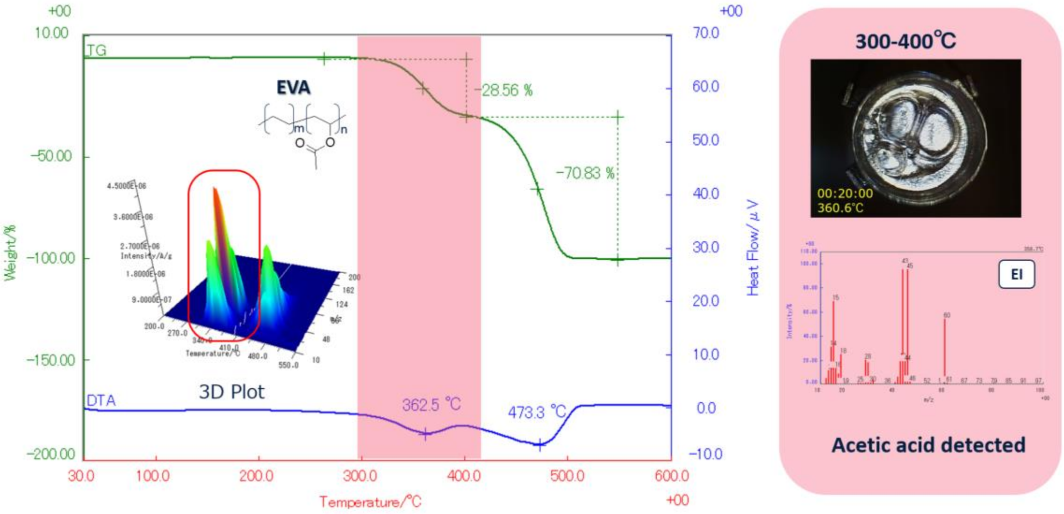

Fig. 1 Thermal decomposition of EVA by TG-MS equipping optical microscope.

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# Drying and Thermal Characterisation of Limequat Peel

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Fruit peel waste is created in vast quantities by citrus fruit processing industry and household kitchens, resulting in significant nutritional and economic losses as well as environmental issues. The processing of fruits alone produces a substantial amount of waste, approximately 50-55% of the total fruit weight [1]. Fruit peels are rich in bioactive compounds which are being used in the food industry mainly as probiotics and dietary supplements, and other industries especially pharmaceutical and fragrance industries. The use of shelf stable, high quality, nutritious and low-cost fruit peel wastes are the primary concern to create value-added products for long-term sustainability.

The citrus limequat (*Citrofortunella x Floridana*) is tiny and greenish-yellow fruit, which is a hybrid specie of lime and kumquat, has bitter-sweet taste and widely cultivated in many Mediterranean countries [2]. Because of high moisture content, the limequat peels are highly susceptible to microbial contamination and enzymatic degradation. Reduction of moisture content reduces the risk of microbial spoilage and limits enzymatic actions, and keeps the nutritional and organoleptic quality of limequat peels. Temperature is an important factor affecting the quality of fruits during drying. High drying temperatures and improper drying conditions are known to have a drastic effect on the quality of final product. [3].

In this study, four different drying methods (oven drying, vacuum oven drying, vacuum drying without ultrasound and ultrasound-assisted vacuum drying) were used to investigate drying characteristics of limequat peels and energy consumption of different drying methods. Thermal stability of dried limequat peels was evaluated using thermogravimetric analysis (TGA) [4]. Ultrasound-assisted vacuum drying yielded the shortest drying time where the drying time was shortened up to 21% by using the ultrasound-assisted vacuum drying as compared to the oven drying. Ultrasound-assisted vacuum drying also consumed the lowest energy among other drying methods. Energy savings up to 79% were achieved by employing the ultrasound-assisted vacuum drying as compared to the oven drying. TGA curves suggested that limequat peels were thermally stable below 100°C. It can be concluded that, among four drying methods, ultrasound-assisted vacuum drying offers the best drying for drying of limequat peels in terms of drying time and energy consumption.

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# Influence of mechanochemical activation on the degree of amorphisation and pozzolanic activity of kaolin

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Kaolinite belongs to the 1:1 class of clay minerals with the chemical formula $Al_2Si_2O_5(OH)_4$, and due to its high content of aluminium and silicon, and pozzolanic reactivity, it is one of the most commonly used natural occurred materials for enhancing various properties of cement-based concrete [1-2]. The activated form of kaolinite and kaolinitic clays is called metakaolin, and it is usually obtained by dehydroxylation of the kaolinite in the temperature range of 600 to 800 °C [3]. The mechanochemical approach (intense grinding) in the production of metakaolin represents a green approach due to reduced energy consumption and faster kinetics. Intensive grinding with correctly set working conditions causes structural disorder (amorphization/dehydroxylation) of kaolin to metakaolin and reduces the particle size, which increases the pozzolanic reactivity of (meta)kaolin [4]. The possibility of applying mechanochemistry in the production of metakaolin was examined by monitoring the degree of dehydroxylation, that is, the degree of amorphisation using structural (PXRD), spectroscopic (ATR-FTIR), morphological (SEM), and thermal (TGA/DTA) characterisation. Bearing in mind that pozzolanic reaction is slow (heat rate of hydration is low) and hydration in Portland cement is fast (heat rate of hydration is high), the change in the rate of heat of hydration in the cement/(meta)kaolin system was also investigated with regard to the degree of amorphisation of the kaolin sample.

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# Natural rubber biocomposites filled with chemically modified agricultural waste

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Natural fiber reinforced composites (NFRC) have been used since the beginning of human civilization. It is on these types of materials that a large part of the current research in the field of designing new polymer composites is focused. The source of natural raw materials that can act as fillers in polymer composites can be considered both a number of cultivated and herbal plants, as well as residues and waste from agricultural or forestry production. Natural fibers contained in plants, mainly lignocellulosic, have been the basis for the design and production of polymer composites for many years. Natural fillers are environmentally friendly and are an alternative to expensive synthetic additives, while increasing the technological importance of agricultural biomass. An example of such fillers is cereal straw.

The application of straw and its use as a filler for polymer composites is an extremely interesting solution, especially considering the availability of raw materials and low price. Additional advantages include a new, economically effective way of managing agricultural waste in balance with environmental issues and pro-ecological policy. Above all, however, it is a material that positively affects a number of functional properties of finished products filled with them. Despite a number of described and confirmed advantages of using lignocellulosic materials as functional fillers of polymer composites, there are several significant disadvantages that set trends and shape the directions of research on these extremely valuable bioadditives. Undoubtedly, one of them is poor adhesion between hydrophilic plant fibers and hydrophobic polymer matrices resulting from the limited mutual interaction of composite components. The second issue concerns the low thermal stability of natural fillers, leading to their degradation and the emission of volatile decay products as a result of processing processes. Undoubtedly, however, one of the most important and widely described material properties of polymer composites is the mechanical characteristics, for which interactions at the interface between the natural fiber and the polymer medium are to the greatest extent responsible. Ensuring optimal reinforcement of the composite is possible through the stresses generated and transferred between the matrix and the filler, which in turn result from the wetting of the fiber surface by the polymer. Achieving an appropriate level of filler wetting is therefore crucial from the point of view of ensuring the occurrence of intermolecular interactions. They can be obtained by chemical modifications of lignocellulosic fibers, which, due to the presence of hydroxyl groups in the structures of both lignin and cellulose, create appropriate possibilities for this. The methods of chemical treatment concern both the modification of the polymer and fillers, but they can also be based on the use of additional compatibilizing substances. Among the methods of chemical modification, the following can be distinguished: alkalization, acetylation, mercerization, esterification as well as the addition of compatibilizers or coupling agents, which is the subject of the presented research.

# Challenges of developing of a pyrolysis plant for thermal treatment of plastic wastes

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Plastic materials are are a basic pillar of the current industrial revolution being light, having a sufficient strenght for most of their aplications, are relatively easy to produce and handle, allowing the saving of resources, are electric insulators, are generally non-toxic and allow the creation of aesthetic products. However, plastics are also a major waste management problem worldwide, with only 9% of plastic waste being recycled [1]. After storage, plastic waste decomposes naturally over a long time and has a negative impact on the environment during degradation [2]. The solving of this problem requires the development of new efficient technologies for the regeneration and recovery of plastic materials, in order to integrate them into the concept of circular economy, which focuses on finding ways to eliminate waste and limit the use of natural resources through recovery, reuse and recycling.

This paper presents the authors' experience in the process of designing and developing of a thermal recycling plant for plastic waste, starting from the analysis of the composition of plastic waste, the establishment of the chemical reactions that are the basis of their recycling process, the realization of mass and thermal balances, the computer modelling of the chemical process and the plant, the design and physical realization of the plant prototype and the tests undertaken on it.

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# The influence of the ultrasound and pulsed electric field application in extraction process on thermal properties of berry seed oils

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Berry fruit seeds are considered as a by-product of fruit industry. Those seeds are usually a source of oil with unique properties [1]. In order to fulfil the rules of circular economy and to valorize the waste products, the oil extraction can be conducted [2]. However, conventional extraction methods may be harmful to environment, thus they are being replaced by novel, alternative extraction methods e.g., ultrasound (US) or pulsed electric field (PEF)-assisted.

In the following study, the oil was extracted from raspberry, blackberry, chokeberry, red currant and black currant seeds. US and PEF-assisted procedures were conducted as well as control extraction and thermal properties of obtained oils was examined. The oxidative stability was studied in pressure differential scanning calorimetry (PDSC) with kinetic parameters of oxidation reaction determination. The melting and crystallization characteristics of oils were assessed in the differential scanning calorimetry (DSC). Additionally, gas chromatography (GC) was applied to determine the fatty acid profile in berry seed oils.

Oxidative stability of oils obtained in the US-assisted extraction was significantly higher, what may suggest simultaneous antioxidants release during US-assisted process. The PEF-assisted extraction resulted in increased oil stability only in a few conditions. Generally, blackberry seed oil was described as the most resistant to oxidation. DSC study showed that differences in the courses of melting and crystallization characteristics are only slight, however the influence of extraction methods is visible. As the berry seed oils contain mainly polyunsaturated fatty acids, the endothermic transformations during oil melting occur in low temperatures- from around -50°C to -10°C. The composition of berry seed oils was confirmed in the GC study. The extraction method had some impact on the percentage share of fatty acids in triacyclglycerols, moreover, the most abundant fatty acid in every studied oil was linoleic acid belonging to omega-6 family.

Based on the results, it can be conluded that alternative extraction methods can be successfully applied to obtain oil from fruit industry by-products. Extraction methods influences the most oxidative stability of obtained product but also has some impact on other thermal properties and fatty acid profile.

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# Evaluation of biodegradability and thermal stability of edible and biodegradable disposable tableware of waste from olive oil production

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The use of olive pomace from olive oil production is still insufficient. The lingering olive pomace is harmful to the environment. On the other hand, the world is increasingly polluted with plastic or by-products from the production of biodegradable products [1,2]. Considering these two problems, the aim of this work was to develop a mixture and create biodegradable disposable tableware characterized by high thermal stability.

The disposable tableware was made by mixing olive pomace with teff flour and sorghum groats and lecithin (National patent application 437771). Baking was carried out at the temperature of 180 °C. The resulting disposable tableware were examined using: Differential Scanning Calorimetry (DSC) and Fourier-transform infrared spectroscopy (FTIR). Physical and mechanical properties were examined using: Z Test texturometer, drop test, biodegradability test. Colour parameters were measured in the CIE L*a*b* system, using a Konica MinoltaCR-40 [3].

The study found that disposable packaging such as a plates, cups or bowls can be made from olive oil by-products. The use of olive pomace allows the management and the reduction of landfills. In addition, designed disposable tableware can reduce the consumption of plastic products, or products whose manufacturing is not environmentally friendly. Disposable dishes can be used for serving cold or hot drinks, soups and for serving dry products. Importantly, the storage of the produced disposable packaging does not affect the characteristics of the product. These vessels were the toughest, with low water absorption and high thermal properties, not fragile and easy to eat [3].

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# Oral Presentations 4

## Functional Materials, Ceramics, Metals & Alloys, Cements and Engineering Materials & Composites

# Comparison of Thermogravimetry Response of Alkali-Activated Slag and Portland Cement Pastes after Stopping Their Hydration Using Solvent Exchange Method

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Sample preparation is a vital step for any subsequent instrumental analysis. In the field of cementitious binders, special attention is paid to stopping their hydration reactions. This means the removal of unbound water from their pores, which is, however, practically impossible without alteration of their chemical or microstructural properties [1]. The most common and easy-to-use technique for hydration arresting is a solvent exchange method, comprising the soak of the crushed sample in an organic solvent and its subsequent removal by drying at sufficiently low temperature (typically 40 °C) to avoid decomposition of hydrated phases. In the RILEM report [2], this technique was evaluated as the best one.

The experiences obtained on ordinary Portland cement (OPC) are commonly used for the research, development, and testing of other alternative binders, such as alkali-activated materials. However, these alternative binders have different reaction products compared to OPC. For example, portlandite is only rarely formed in alkali-activated slag (AAS) pastes. This could result in a different effect of organic solvents on the thermogravimetric analysis (TGA) outcome of AAS pastes and OPC pastes. Therefore, the objective of this study was to compare the effect of different types of organic solvents (acetone, methanol, ethanol, isopropanol, and diethylether), immersion time, drying time at 40 °C, and washing with diethylether during filtration as well, on the TGA responses of AAS and OPC paste. TGA was carried out for the temperature range of 30 to 1000 °C, with a heating ramp of 10 °C/min in an argon atmosphere (flow rate of 100 $cm^3$/min).

In general, a lower sensibility to the investigated aspects of arresting of hydration was observed for AAS compared to that for OPC. As expected, methanol exceptionally changed the response around 105 °C (dehydration of C-S-H), while acetone had the most pronounced effect in the carbonate range (500–1000 °C), especially after long-term immersion. From AAS pastes, the paste activated with $Na_2CO_3$ showed the lowest sensitivity to the type of organic solvent (except for methanol).

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# Performance of hybrid steel and aramid fibre reinforcement in ultra-high performance concrete

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The UHPC offers unprecedented mechanical properties, such as high compressive strength. Its properties can also be modified by the incorporation of steel fibres to obtain high flexural strength and ductile behaviour. One of the new approaches to further improving the properties of UHPC is the combination of steel and polymer fibres for their potential synergistic effect.

In this study, we explore the possibility of combining steel and short-cut aramid fibres for possible improvement of mechanical properties. First, the slump flow of each mix was determined. Second, the flexural and compressive strength were measured after 7 d, 14 d, 28 d and 56 d. Finally, the fracture surfaces of these composites were studied by means of scanning electron microscopy.

It was found that the addition of short-cut aramid fibres decreases slump flow significantly and that the short-cut aramid fibres tend to agglomerate in the matrix. Mechanical properties were not significantly influenced by the addition of short cut aramid fibres. However, there are some preliminary results that indicate that the overall performance of aramid fibres in UHPC could be significantly improved by their surface modification.

# Thermal stability of catalyst based on semicrystalline calcium silicate hydrate with intercalated $Co^{2+}$, $Cu^{2+}$, and $Cr^{3+}$ ions

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Volatile organic compounds (VOCs) are mainly human-made chemicals with high vapor pressure and low water solubility [1]. These compounds are toxic to humans and harm the environment. There are many methods for the removal and neutralization of VOCs; however, catalytic oxidation is one of the most attractive [2]. Unfortunately, conventional oxidation requires expensive catalysts (precious metals), which limits their application. The alternative for conventional catalysts can be calcium silicate hydrates and/or calcium silicates with intercalated transitions metal ions (Cu, Co, Fe, etc.) [3]. Thus, this work aims to synthesize catalyst based on semicrystalline calcium silicate hydrate with intercalated $Co^{2+}$, $Cu^{2+}$, and $Cr^{3+}$ ions, and to determine its thermal stability.

The hydrothermal method was employed to conduct the synthesis of the catalyst. The molar ratio of CaO/amorphous $SiO_2$ = 1.5 was used. It was subsequently mixed with Co, Cu, and Cr nitrate solution (the concentration of each metal ion was 3.33 $g/dm^3$). A suspension featuring the solution/solid ratio of 10.0:1.0 was then obtained. A 4 h- and 16 h-long sessions of hydrothermal treatment were performed in unstirred suspensions at 175 °C. The compounds (silicates containing metal ions and/or nitrate anion) with undescribed structure and composition were formed during hydrothermal treatment. The calcination of synthetic catalyst led to the formation of the mixture consisting of calcium silicates and metal oxides. It was obtained that the temperature of calcination plays a crucial role in the porosity of the sample. It was determined, that synthetic and calcined (550 °C) samples acted as catalysts for propanol oxidation reactions. 6 methods in total (AAS, STA, XRD, TEM, SEM, and BET) along with propanol oxidation experiments served to confirm the obtained results.

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# The impact of internal hydrophobization on a supplementary cementitious materials hydration

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Porous building materials are strongly prevalent among those ones applied in civil engineering. Porous structure causes that they are not sufficiently resistant to some physical and chemical external contaminations. Water is one of the main factor causes deterioration of porous building materials. It may cause a decrease in durability and thermal resistance of building materials. One way to contract these degradation phenomena is hydrophobization. It is process of implementing the hydrophobic agents into the porous structure of a material. As a result of a chemical reaction, hydrophobic compounds fill voids preventing or restricting the penetration of moisture. The key function of internal hydrophobization is to protect porous materials from adverse water effects, thereby increasing their durability by reducing the water absorption. Organosilicon compounds (e.g., silanes) have proved to be one of the best in protecting cement-based building materials from water penetration and environmental influences [1].

The influence of organosilicon compounds on the hydration of Portland cement is quite well presented in the scientific literature [2]. However, according to the best knowledge of the authors there is no available research which determine the influence of the organosilicon compounds on the hydration and properties of the supplementary cementitious materials (SCM) (e.g., microsilica or ground, granulated blast-furnace slag) and thus on the effectiveness of internal hydrophobization of those materials.

The main objective of the conducted research was to determinate the impact of triethoxyoctylsilane used as integral hydrophobic admixture on the hydration kinetics and basic properties of the SCM: microsilica and ground, granulated blast-furnace slag. The isothermal calorimetry was used to measure the heat of hydration and observe the process itself. The impact of silane on the compressive strength and capillary water absorption of SCM mortar was determined as well. The research was supplemented with the microstructure analysis of SCM paste which was monitored by mercury intrusion porosimetry (MIP).

Our research indicates that silane might interact with microsilica and ground, granulated blast-furnace slag and have influence on its hydration and thus on the properties of the final product. Our results may have particular significance during selecting a hydrophobic silicon-based compound for the hydrophobization of supplementary cementitious materials.

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# Comparison of commercial nitrate-based accelerators and their pure constituents on hydration kinetics, composition, and hydration degree of zinc oxide blended Portland cement

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The rising concentration of zinc in ordinary Portland cement (OPC) has a concerning impact on the behaviour of cement-based mortars by drastically prolonging setting time and decreasing early mechanical properties. The current theory behind the mechanism of the effect of this contaminant is the depletion of $Ca^{2+}$ ions from pore solution and formation of a semipermeable layer of $Ca(Zn(OH)_3)_2 \cdot 2\,H_2O$ on the surface of silicate cement phases, thus retarding their hydration.

The cement industry employs various additives to counteract these problems in the form of water-soluble salts of alkali metals such as sodium nitrate. The induction period, which describes the time interval before the setting of cement, can be easily determined by various calory metric methods. One of the simplest methods is Isoperibolic calorimetry, which gives information about the natural behaviour of samples in a set environment by measuring temperature changes in the sample placed in a stable ambient environment. Changes in the hydration mechanism caused by additives can be expressed by Hydration degree. This factor can be determined using differential thermal analysis(DTA), indicating the degree of retardation. X-ray diffraction (XRD) and scanning electron microscopy (SEM) can also study composition changes. These methods are commonly used to determine phase changes in materials.

Pure base components of commercial additives proved to be more effective at countering the effects of zinc, especially the retarded setting. Calcium nitrate had little effect on early mechanical properties, while commercial accelerators and sodium nitrate decreased early compressive strength.

Keywords: Thermal analysis, hydration degree, Cement, Zinc oxide, Hydration, Retardation, sodium setting accelerators

# Low Temperature DSC Characterisation of the Influence of Admixtures on the Hydration of Cement

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The hydration of cement results in a change in the capillary and gel pore structure as the hydration reactions proceed. This refinement of the porosity has been investigated using DSC by a variety of authors using the concept of thermoporosity to interpret the change in the thermal behaviour [1-4]. By freezing the water contained in the capillary and gel pores, the amount of crystallisable water present can be determined from the melting endotherm or the freezing exotherm. As the temperature at which freezing and melting is depressed with reducing pore size, the refinement in the pore structure can also be followed with time. This paper uses these phenomena to investigate the influence of admixtures (retarders and accelerators) on the hydration and pore size refinement.

Samples of general purpose (GP) Portland cement were hydrated in the presence of commercially available accelerators and retarders. The rate of hydration and the pore refinement was monitored as a function of time by measuring the temperature at which crystallisation occurred and by determining the proportion of crystallisable water present in the cement by measuring the area of the exotherm produced on freezing of the crystallisable water. The results of these experiments are reported and correlated to the development of strength in mortar prisms.

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# Effect of different hydration accelerators on the properties of zinc-doped cement

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The zinc content of cement has been constantly increasing recently, mainly due to the use of alternative fuels such as tires. The negative effect of zinc consists mainly in a considerable slowing down of hydration. One way to eliminate this effect is to use hydration accelerators. This work deals with the use of individual compounds to eliminate the negative effect of zinc. Zinc was doped in the form of ZnO. Hydration is monitored using isoperibolic and isothermal calorimetry. Properties of cement pastes are studied using differential thermal analysis (DTA), measurement of mechanical properties, X-ray diffraction (XRD) and morphology is studied using a scanning electron microscope. It was found that by using hydration accelerators it is possible to significantly shorten the hydration time of cement doped with zinc and at the same time improve the mechanical properties.

# Comparison of performance of lime- and magnesia-based hempcrete in water vapour permeability tests

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This paper presents an experimental investigation into the water vapor permeability of hemp-concrete samples using the cup method. The study aims to evaluate the performance of hemp-based construction materials in terms of their resistance to water vapor transmission and compares the advantages and disadvantages of binders based on magnesia and lime.

The water vapor permeability measurements were conducted by fixing the hemp-concrete samples to cups filled with calcium chloride, silica gel, and potassium nitride, and placing the measurement assemblies inside an environmental chamber for 40 days. Sensors within the cups and the chamber were used to measure the relative humidity during the experiment, which enabled comparisons of performance of the desiccants (calcium chloride vs silica gel) as well as hempcrete samples using different binders (magnesia vs lime).

The paper highlights the environmentally advantageous aspects of hempcrete as a bio-based construction material. Hempcrete is a sustainable alternative to traditional concrete, as it utilizes hemp fibers as a primary component. Additionally, the inherent properties of hemp fibers, such as low thermal conductivity and moisture buffering, contribute to improved energy efficiency and indoor air quality in buildings.

The study presents a comparative analysis of hemp-concrete samples utilizing magnesia and lime binders. Magnesia, though less prevalent in hempcrete applications, offers the benefits including accelerated setting time and enhanced mechanical strength of the resulting composite material.

# The influence of $ZrO_2$ addition on thermal and mechanical properties of $Y_2O_3$-$Al_2O_3$-$ZrO_2$ ceramics materials

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The four glass compositions in the system $Y_2O_3$-$Al_2O_3$-$ZrO_2$ were prepared in the form of glass microspheres by flame spraying method form precursor powders synthesized via Pechini sol-gel method. The composition of the prepared glasses was derived from the eutectic composition ofthe $Al_2O_3$-$Y_2O_3$ system (76.8 mol.% of $Al_2O_3$ and 23.2 mol.% of $Y_2O_3$), where 5 and 10 mol.% of $Al_2O_3$ in the AYZr1 and AYZr2 samples were replaced with $ZrO_2$, and 5 and 10 mol.% of $Y_2O_3$ were replaced with $ZrO_2$ in the AYZr3 and AYZr4 samples.

The prepared glass microspheres were characterized by differential scanning calorimetry (DSC; temperature interval 35 - 1200 °C), X-ray diffraction (XRD) and SEM and SEM EDX analysis. The high-temperature X-ray diffraction analysis (HT XRD; temperature interval 750 – 1450 °C) were used to study phase evolution during thermal treatment of glasses.

In DSC record of sample AYZr4 only one exothermic effect with the maximum at 939 °C was observed, while remaining DSC records of samples AYZr1-AYZr3 include three exothermic effects with maxima in interval 937 – 1142 °C. For more detailed study of phase development, HT XRD analyses were performed. A comparison of individual XRD patterns shown crystallization of mainly of YAG ($Y_3Al_5O_{12}$) and $ZrO_2$ phases (monoclinic and tetrahedral). While the onset of $ZrO_2$ phases crystallization was detected at temperatures up to 980 °C, crystallization of YAG was observed at higher temperatures, up 1080°C. However, slow crystallization of intermediate phase of aluminum oxide $\theta$-$Al_2O_3$ (~1100°C) was found upon careful examination of XRD patterns and crystallization of $\alpha$-$Al_2O_3$ was detected up to 1300°C.

Based on results of DSC and HT XRD experiments, the preliminary hot-press (HP) experiments were performed at temperature 1500°C, pressure 30 MPa and with isothermal dwell 10 min. Very fine eutectic microstructure, with a high level homogeneity (YAG and $ZrO_2$ grains embedded into $\alpha$-$Al_2O_3$ matrix) in whole volume of sintered bodies was obtained as documented by SEM and SEM EDX. The average values of Vickers hardness ($H_V$=17 GPa) and the indentation fracture toughness $K_{IC}$ =3.9 MPa.$m^{1/2}$ were obtained by Vickers indentation at a load of 10 N and dwell time 10 s.

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# Thermoporometry of carbons with large mesopores: PSD evaluation difficulties

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Thermoporometry is a relatively new, quick and simple method for porosity characterisation which is based on DSC observations of melting point depression of a liquid confined in pores. Thanks to its suitability for analysis of wet and soft materials, short measurement time, simple sample preparation, and low analysis cost, thermoporometry has a great potential to become an equal method in porosity characterisation to already well-established methods like mercury porosimetry and gas physisorption. Nevertheless, its potential has not been fulfilled yet due to several difficulties occurring during conversion of DSC signal to pore size distribution.

In thermoporometry, porosity evaluation is based on the Gibbs-Thompson equation. Pore size distribution can be calculated having in mind that pore size and volume are connected with melting point depression and melting enthalpy, respectively. However, difficulties can show up during porosity characterization of materials with large mesopores.

The first difficulty is that the liquid in large pores melts at temperatures very close to the melting temperature of the bulk liquid causing overlapping of corresponding peaks. The separation of these peaks is thus necessary. The separation can be approached by deconvolution of experimental DSC record using basic kinetic equation leading to individual records for peaks for liquid in pores and in bulk.

The second difficulty is correct determination of melting point depression. The commonly used approach for determination of melting point depression uses difference between temperatures for pore liquid melting and onset of bulk liquid melting. The newly proposed approach uses temperature difference between DSC curves for bulk and pore melting at given conversion.

In this contribution, the previously mentioned difficulties (focusing mainly on the latter) that have to be overcome when characterising material with large mesopores by thermoporometry will be discussed. Series of carbon xerogels with pore sizes covering whole mesoporous range will be used for demonstrational purposes.

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# Design and dilatometric processing of nanobainitic structures in Al-alloyed 3Mn multiphase steel

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The development of new construction designs of car bodies, especially electric cars generates some problems of increasing car mass. It results in a lower range of travel because of high electric usage [1]. This problem demands the use of high or ultra-high strength steels of relatively good formability. Such steels allow to reduce the mass of the car body, not only by the use of the complex components but also by using thin-wall elements. From the safety point of view, the steels need to have very high strength levels and moderate plasticity. This prevents the intrusion of external body into the passenger zone [2]. Up to now, mostly martensitic steels were used for such applications. However, the plasticity of such steels does not allow for complex shaping of elements. Nowadays, the medium manganese steels are developed as potential steels to be used in such applications. These steels have complex microstructures composed of ferrite, bainite, martensite and retained austenite. Depending on the demand, mechanical properties could be tailored by changing a volume fraction of each phas or by the grain refinement [3].

The purpose of the research was to determine the possibility of nanobainite formation in the hot-rolled 3Mn steel with a high aluminium content. Such microstructure design could increase the strength of the steel, keeping moderate plasticity (better than in case of martensitic steels). The main issue of such approach is that the nanobainite forms at a temperature below 300 °C. Such temperature is lower than martensite start temperature ($M_s$) of the alloy. This results in a need to use a two-step heat treatment composed of intercritical annealing and isothermal bainite holding. The first step is necessary to control the $M_s$ temperature by carbon and manganese diffusion into the austenite. The purpose of the second step is to transform the austenite into nanobainite. The presented results of the dilatometric, microstructural and hardness analyses are carried out in the intercritical annealing temperature range of 760 ÷ 870 °C, which ensures the $M_s$ temperature in the range of 200 ÷ 300 °C. The dilatometric results confirms the formation of bainite in this temperature range. The final cooling shows that the austenite remaining in the microstructure is thermodynamically stable to room temperature.

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# The interaction between Al-Li-Mg alloy and crucible coating during melting and processing

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The appropriate melting and processing of aluminum-lithium-magnesium (Al-Li-Mg) alloys require consideration of furnace atmosphere and refractory materials [1]. Lithium as an alkaline metal exhibits highest reactivity with gases present in furnace atmosphere [2,3]. Commonly utilized refractory materials have proven unsuitable to produce Al-Li alloys. Although, iron (Fe) and special grade stainless steel crucibles exhibit good resistance to Li attacks, their application is limited due to high solubility of Fe in liquid Al. On the other hand, the tantalum and carbon crucibles have good resistance to liquid Al, but their resistance to Li attacks strongly depends on the furnace atmosphere [4]. Since there is no single crucible material compatible with both Al and Li, it is necessary to adopt melting and casting procedure to avoid long holding times, reduce crucible degradation and prevent melt contamination. Otherwise, improper melting and processing will decrease the soundness of cast billets, hinder further material processing and result in a final product with poor functional properties [4].

The aim of this investigation is to estimate the impact of crucible attack on the Al-Li-Mg alloy solidification sequence and microstructure development. The crucible attack occurred during synthesis in an induction melting furnace using carbon crucible covered with Fe-based coating. The resulting melt contamination and Fe-pickup were detected using atom emission spectrometry. The thermodynamic calculations based on chemical composition indicated the occurrence of $Al_{13}Fe_4$, AlSiLi, $\beta$-$Al_5FeSi$ and $Mg_2Si$ intermetallic phases that would not normally appear in Al-Li-Mg alloys. The complexity of solidification sequence is further increased when the results of microstructure analysis are taken into consideration. Based on their morphology and localization in the microstructure, the negative effect of Fe-based intermetallic phases on mechanical properties can be expected.

Based on the results, it can be concluded that the Fe-based crucible coating is not suitable for synthesis of Li containing Al alloys despite optimal laboratory conditions concerning the furnace atmosphere, melting and alloying temperature, homogenization and melt retention time.

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# Interaction kinetics between molten aluminium alloy Al99.7 and H11 tool steel with and without a protective coating

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The tool used in die casting or hot forming is subjected to thermal and mechanical stress, resulting in damage and cracking due to thermal fatigue and melt flow. This reduces the profitability and efficiency of production, as the products may not meet the required dimensions and mechanical properties. Understanding the interaction between tool steel and molten aluminium alloy is critical to extending tool life. Protective coatings on tool surfaces can improve wear resistance.

The protective coating on the sample served its purpose and slowed down the interaction between the aluminium melt and the tool steel, as the DSC curve of the sample that had the protective coating applied flattened out faster, indicating the cessation of dissolution in the material. DSC analysis was performed at two different temperatures, 670 °C and 700 °C, respectively, for 12 hours. Measurements of the interaction layers thicknesses also confirmed these results, whereas the thickness of the composite layer was almost the same in both cases without a protective coating, and the temperature has no effect on this layer. The types of interaction layers did not differ from each other.

# Solidification of remelted $AlSi_9Cu_3$(Fe) alloy

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The potential of secondary raw material usage is enormous and becomes an imperative of recent industrial production. Aluminium alloys belong to the group of green materials in which the remelting is an important aspect in extending theirs' end of life. In the commercial application of secondary material as a charge material, it is easy to achieve chemical composition corresponding to those required by norm [1], but is not guarantee that solidification process will proceed on the same manner. Required chemical composition does not always allow replication of microstructure and therefore other functional properties development due to numerous interactions in multicomponent technical alloy and technological solidification conditions [2].

Alloys from the Al-Si-Cu group have an important role in automotive industry for various safety critical parts due to their high strength at room and elevated temperatures. In order to achieve functional properties such as mechanical, technological and corrosion resistance of cast material it is of general importance to understand the solidification process and microstructure development during solidification [3]. Beside common melt treatment processes, cooling rate and heat treatment as a post-casting process, it is mainly dependent from the chemical composition and possible interaction of present elements. An influence of silicon, copper, iron, magnesium and other alloying and trace elements on solidification process of $AlSi_9Cu_3$(Fe) alloy is widely investigated considering regular preparation of charge materials with corresponding ratio of own return material [4]. In this work, secondary return material was applied as the only charge material for $AlSi_9Cu_3$(Fe) alloy production. Modelled equilibrium and non-equilibrium phase diagrams enable solidification sequence prediction. The influence of remelting and solidification sequence is compared to the thermodynamic DSC investigation results as well as to obtained microstructure. Microstructural investigation of remelted $AlSi_9Cu_3$(Fe) alloy test samples confirms the presence of following phases: $\alpha_{Al}$ matrix, eutectic $\alpha_{Al}+\beta_{Si}$, intermetallic phase on the iron base $Al_5FeSi$ and also $Al_{15}(Fe,Mn)_3Si_2$, Mg-phases such as $Mg_2Si$ and intermetallic script $Al_8Mg_3FeSi_2$, and $Al_2Cu$ and $Al_5Mg_8Si_2Cu_2$ phases on the copper base.

Remelted $AlSi_9Cu_3$(Fe) alloy indicates good application potential due to maintenance of solidification sequence and microstructure development. Lower silicon content influences on disturbance of main eutectic phase development and distribution in microstructure.

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# Thermodynamic approach for designing processing routes of 4Mn Quenching and Partitioning steel

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Nowadays, the most developed group of steels for the automotive applications are Advanced High Strength Steels (AHSS) including three generations of steels. Currently, research efforts are focused mainly on the newest 3rd generation of AHSS, especially medium-Mn steels. These steels are characterized by high strength-ductility product UTSxTEl exceeding 20GPa% [1]. The microstructure of Quenching and Partitioning (Q&P) steels consists of fine-lath martensite and retained austenite (RA). Such microstructure is produced via a heat treatment consisting of austenitization followed by quenching to the temperature between $M_s$ and $M_f$ to produce some fraction of martensite. Then the steel is heated to a higher temperature for providing some carbon partitioning from the supersaturated martensitic laths into the RA. As a result the $M_s$ temperature is reduced and some fraction of retained austenite is stabilized to room temperature [2, 3]. The design of Q&P heat treatment routes requires the detailed thermodynamic analysis to ensure proper conditions for stabilization of 10-15 vol.% of retained austenite and limiting formation of harmful transition carbides and secondary martensite.

The study addresses the thermodynamic analysis of phase transformation kinetics and accompanying precipitation processes in 0.17C-4Mn-1Al-0.9Si-0.05Nb multiphase Quenching and Partitioning steel. The pseudo-binary Fe-C diagram of the steel was calculated using Thermo-Calc software. The evolution of individual phases as a function of temperature under thermodynamic equilibrium conditions was estimated using JMatPro software. The investigations included the determination of continuous-cooling-transformation (CCT) and the time-temperature-transformation (TTT) diagrams of the investigated steel. The calculated equilibrium diagrams were compared with the experimental diagrams determined using dilatometric tests. Microstructural features of phases were revealed using light and scanning electron microscopy techniques.

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# Splat-to-splat interface thermal conductivity determination for dual phase YSZ/zirconates thermal barrier coatings

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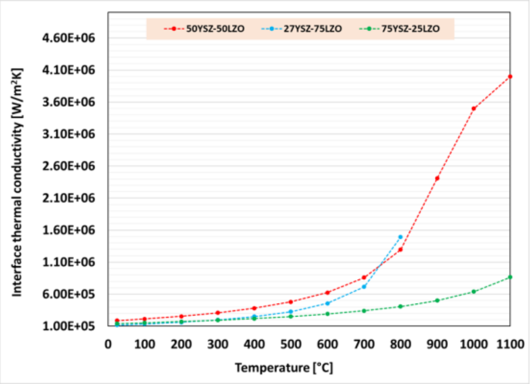
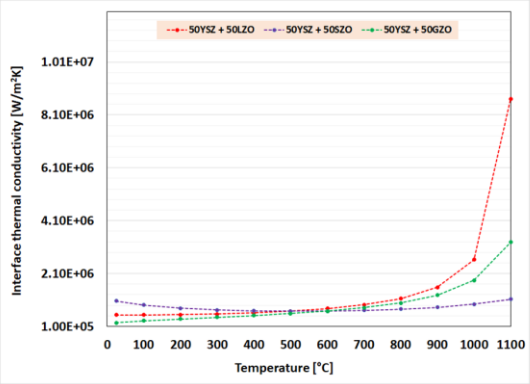
The article presents the methodology for determining the thermal conductivity coefficient of splat-to-splat interfaces, typical for plasma-sprayed ceramic layers. The value of this coefficient allows the estimation of the thermal resistance of the interfaces of plasma-sprayed coatings, including two-phase coating thermal barriers based on conventional zirconium oxide 8YSZ (8 wt% $Y_2O_3 \times ZrO_2$) and rare earth zirconates of the $RE_2Zr_2O_7$ type.

To determine the value of the thermal conductivity coefficient of the interfaces, the results of measurements using the pulsed laser LFA method (allowing to determine the value of thermal diffusivity in a wide temperature range) and the relationships described by Hasselan-Johanson, Evere and Tzou and Tavangar were used.

Based on the LFA measurements and the mentioned equations, the value of the thermal conductivity coefficient of the interfaces in the systems thermally sprayed with the APS method (atmospheric plasma spraying) in the temperature range from 25 to 1100°C was determined. The results of these measurements (for the Hasselman-Johanson and Evre and Tzou relationships) are presented below.



Hasselman-Johanson



Evry and Tzou

# Carbothermal reaction of mechanically activated ZrC powders followed by DSC-TGA

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Mixtures of $ZrO_2$ and C were prepared by high-energy ball milling. Powders were milled for times from 0 to 120 minutes in air atmosphere. As milling time increased, surface area of powders increased, indicating significant particle size reduction. The thermal treatment cycle included heating at 10 °C/min to 1600 °C followed by an isothermal hold for 2 hours under the vacuum (~20 Pa) in a resistance-heated graphite element furnace. This first step of the process promoted carbothermal reaction of the starting materials.

DSC-TGA was used to follow the carbothermal reaction. The onset temperature does not seem to change for non-activated and activated powders. The change in peak area may be related to the amount of the powder that reacts at this temperature. The catbothermal reaction was split into two parts for powders activated 60 and 120 minutes. Only part of the powder reacts at the initial reaction, and then higher temperatures are required for full reaction.

# Study of an alternative binder based on the carbonation of ladle furnace slag

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The carbonation curing of cementitious materials has received growing attention in recent years, especially in light of the reduction of carbon dioxide emissions. It allows the rapid hydration of conventional binder, such as ordinary Portland cement, and additionally provides great potential for the activation of suitable industrial wastes with non-hydraulic phases. The possibility of using ladle furnace slag (LFS) as an alternative binder has been studied. Ladle furnace slag shows only minimal hydraulic properties, but its components can react with $CO_2$ to form carbonates that bind the slag particles to a compact solid unit.

This work is focused on the investigation of the chemical processes during carbonation of ladle furnace slag. The main mineralogical phases of LFS, β-dicalcium silicate ($\beta$-$C_2S$) and γ-dicalcium silicate ($\gamma$-$C_2S$), were synthesised for the study. The carbonation reactivity of these phases was examined by perfusion calorimetry. A significantly higher reactivity with $CO_2$ for $\gamma$-$C_2S$ was observed. The carbonation and hydration products of these phases were characterized using X-ray diffraction analysis (XRD), thermogravimetric and differential thermal analysis (TG/DTA), and scanning electron microscopy (SEM).

# Flash Joule Heating-Boro/Carbothermal Reduction (FJH-BCTR): an approach for the instantaneous synthesis of transition metal diborides

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Transition metal diborides ($TMB_2$), such as $ZrB_2$ and $HfB_2$, are a class of ultra-high temperature ceramics (UHTCs) that have attracted considerable attention due to their performance in extreme environments [1-3]. This work reports the synthesis of several $TMB_2$ by what we termed as the Flash Joule Heating Boro/carbothermal Reduction (FJH-BCTR). This methodology is based on the traditional boro/carbothermal reduction reaction by which these kinds of UHTCs are commonly synthesized assisted with an electric field. This new electrothermal strategy allows the selective heating of reactants at high temperatures and rapid heating and cooling rates, enabling the kinetic control of chemical reactions and the formation of materials whose conventional preparation requires high-energy consumption [4, 5].

Unlike the traditional boro/carbothermal reaction, which requires temperatures above 1500ºC for several hours, FJH-BCTR does not need any extra source of heating rather than that generated by the electrical current, saving up to 80% of the energy input required for the preparation of these materials. The immediate synthesis is attributed to the Joule heat generated by the current, enabling extremely fast heating and cooling rates and, therefore, avoiding grain growth and boron volatilization. It is demonstrated that several phase-pure $TMB_2$ compounds, and even composites, with submicron microstructure can be prepared in a matter of seconds, proving the universality of FJH-BCTR.

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# The influence of the preparation method on the thermal, optical, and magnetic properties of $Bi^{3+}$ doped CAS glasses

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Calcium aluminosilicate (CAS) glasses of gehlenite composition, doped with different concentration of $Bi^{3+}$ (0.25, 0.50 and 1.50 mol. %) were prepared by two different methods, and impact of the way of preparation on thermal, optical, and magnetic properties was studied. In the first method, the combination of solid-state sintering (SSS) and flame synthesis (FS) was used, and glasses were prepared in the form of glass microspheres. For comparison, the conventional melt quenching technique (second method) was used, and glasses were prepared in form of bulk.

All prepared samples were X-ray amorphous. DSC records of glasses prepared by conventional melt-quenching technique revealed only one exothermic peak, with maxima in interval 943-982 °C, and the peak temperature decreased with increasing content of $Bi^{3+}$. In case of DSC curves of glass microspheres presence of significant effect in temperature interval 973-996°C (depending on the $Bi^{3+}$ content) and hints of another exothermal effect at 930°C (0.5 mol.% $Bi^{3+}$ addition) and at 884°C (1.5 mol.% $Bi^{3+}$ addition) were observed. This indicates the lower thermal stability of glass microspheres and two step crystallization of gehlenite phase in samples prepared by FS. Also, the higher tendency to crystallization was observed for both types of glasses with increasing addition of $Bi^{3+}$, which could indicate the role of Bi as a nucleating agent in the systems.

The photoluminescence properties of prepared systems were studied in visible spectral range. The all-prepared systems exhibited broad emission in spectral range from 350 to 750 nm centred at ~485 nm in case of glasses prepared by conventional melting and at ~ 425 nm in case of glass microspheres. From the comparison of the magnetic properties of the prepared systems, it was found that the glasses prepared by conventional melting do not exhibit such complicated magnetic properties as the glasses prepared by FS. In case of glasses prepared by melting, the diamagnetic (at 300K) and the paramagnetic (at 2 K) component of magnetization prevails, even at low magnetic fields. The glass microspheres were diamagnetic or weakly ferromagnetic at 300 K and paramagnetic or weakly ferromagnetic/antiferromagnetic at 2 K.

## Acknowledgements

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# Thermo-Optic-Phase-Shifter Using Silicon Rib Technology

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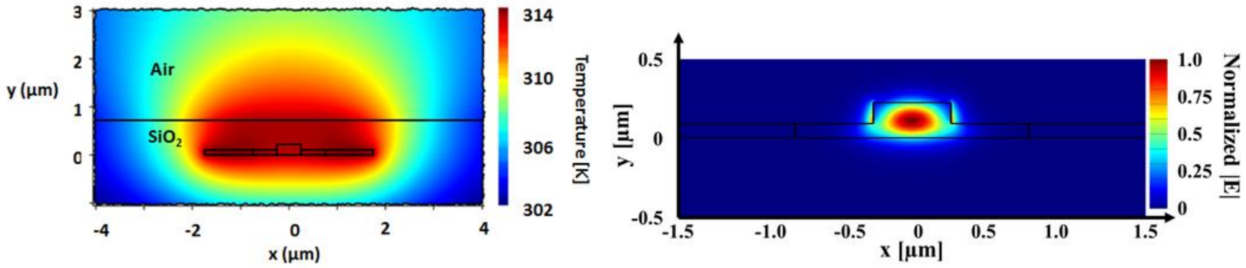
Thermo-optic phase shifter (TOPS) based on doped silicon (Si) heaters is commonly used to compensates device structure imbalance of high-speed Mach-Zhender modulator (MZM) due to fabrication errors. The modulator uses PN phase shifter to control the output gain. To maximize the performances and the linear operation range of the MZM, it is designed to work on quadrature bias-point (QBS). Some imperfections caused by manufacturing process might add some constant phase shift to the system and shift the QBP in some amount, thus requiring tuning to reach this optimal working point. This tuning can be achieved by using thermal tuners such as TOPS. However, this functionality required more electrical power for setting the MZM to be active around the linear transfer function at π/2 phase shift. To solve this issue, we proposed an optimal design of doped Si heaters using the standard commercial 220 nm Si layer in rib waveguide structure which can improved the electrical energy efficiency and reduced the optical losses [1-2]. Numerical simulations and optimizations were carried out on the key parameters, heater locations, doping concentration, etching depth and laser wavelength drift. Results show that the optimal design has a low power consumption of 19.1 mW for obtaining phase shift of π with a good time constant of 2.47 µs and low optical losses of 2.37 dB/cm at the 1550nm operated wavelength. Thus, an excellent figure of merit (FOM) of 47.2 mWµs is obtained for the optimal design. Also, the proposed device has a good stability to the laser wavelength drift effect in the C-band range. This TOPS can be very useful for improving the transmitter system performances that based on high-speed MZM technology.



(a) (b)

Figure 1: Heat distribution simulation at (a) $P_\pi$ and (b) Optical Field E distribution for the fundamental mode TE.

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# Poster Session 1

# Dilatometric study on phase transformations in non-deformed and plastically deformed medium-Mn multiphase steels with increased Al and Si additions

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Medium manganese steels belonging to the third generation of advanced high strength steels (AHSS) have received much research attention due to their outstanding mechanical properties. The ultimate tensile strength at a level of 1600-1800 MPa in a combination with total elongation ~10-15% can be obtained [1]. The retained austenite (RA) is a key microstructural constituent providing high strength and ductility of medium-Mn steels due to its strain-induced martensitic transformation (SIMT) during plastic deformation [2, 3]. The effectiveness of SIMT is closely related to the amount and stability of RA. The production of steels containing retained austenite requires the detailed characterization of the effect of plastic deformation and cooling conditions on the kinetics of phase transformation.

The aim of this study was to investigate an effect of plastic deformation in the austenite region on continuous cooling transformation (CCT) and temperature–tm – transformation (TTT) in 0.17C-4Mn-1Al-0.9Si-0.05Nb and 0.17C-5Mn-0.9Si-0.8Al-Nb TRIP-aided alloys. The differences in the kinetics of phase transformations and final microstructures were observed and compared in both investigated steels. The critical temperatures of steels and ranges of phase transformations of supercooled austenite in the undeformed and deformed states were determined using dilatometry. The obtained microstructures were observed using light microscope. The microstructural observations were assessed together with hardness measurements.

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# Effect of hot deformation on microstructure and precipitation kinetics in M789 cobalt-free maraging steel produced by SLM

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The presented work aims to evaluate the effect of hot deformation on microstructure, martensitic transformation kinetics and precipitation behaviour in an additively manufactured M789 cobalt-free maraging steel. The steel samples produced by the SLM method were subjected to deformation using the Gleeble 3800 thermomechanical simulator in a wide temperature range (600–1000 °C). The hot deformation temperature range was established according to dilatometry analysis, where phase transition temperatures were determined based on inflections from tangents to the curve. Afterwards, a series of heat treatment operations were conducted using a BAHR dilatometer 805A/D. The following characterization techniques were used: optical microscopy (OM), Scanning Electron Microscopy (SEM), Electron Backscatter Diffraction (EBSD) and Vickers microhardness test. The findings demonstrated that the deformation favoured the refinement of martensitic lathes and blocks in a form proportionate to the reduction in sample dimension and a preferred alignment towards the centre of the sample. The flow stress of the additive manufactured M789 maraging steel decreased with increasing temperature. With increasing deformation temperature, the grain size increases, accompanied by an increase in the width of the martensite laths. Deformation increased the kinetics of precipitation and reverted austenite formation during the ageing process.

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# Fe spinel-based materials and their CLOU properties

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Nowadays, promising combustion technology namely the Chemical looping is a technology where the needed oxygen is provided by an oxygen carrier. It offers prospective carbon dioxide sequestration-ready stream and also nitrogen oxides emission significant reduction. Thermogravimetric analysis (TGA) allows to determine properties of materials in the different atmospheres (neutral, oxidizing, reducing) which is critical for oxygen carriers.

An Oxygen carrier (OC) is a material (usually d-block metal oxide) used as a medium delivering oxygen needed for combustion process. OC should show out acceptable oxygen transport capacity and good reactivity toward fuels, as well as good mechanical strength. Ability of spontaneous releasing oxygen due to change of its partial pressure, so called CLOU effect, is desirable especially for fossil fuels combustion.

In this paper OCs were tested using TG to determine their reactivity toward selected fuels, and CLOU properties were profoundly evaluated.

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# New storage materials based on carbon nanotubes and metal alloys

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Storage the hydrogen in the solid materials is safe and effective way to store energy. This type of cell can be used both for stationary and mobile equipment.

Synthesis of hybrid materials will be based on; a) simultaneous sintering of mono- and multi-walled carbon nanotubes with intermetallic compounds One method of the synthesis of hybrid materials will be based on simultaneous sintering mono- and multi-wall carbon nanotubes with intermetallic compounds. The second method will involve the sintering of intermetallic alloy and then trituration it with MWCNT and SWCNT. Synthesis of alloys will be performed using resistance furnace and electric arc furnace. The resistance heating furnace will be prepared alloys with lithium content more than 50 of atomic%. Alloys of lithium content below 50 of atomic% will be prepared in an arc furnace under an atmosphere of spectrally pure argon.

Modification methods of metal alloys by MWCNT used by our group provide the possibility to use functionalized MWCNT in devices powered by electricity. Preliminary tests have shown a very positive influence of d- and p-electron elements on the corrosion resistance and extension of the life of hydrogen storage materials. Our proposed test procedure (synthesis - the phase composition - crystalline and electron structure and the properties of absorption and catalytic) will allow to select the most optimal configurations of hybrid materials for practical use. Since the main goal of the project is to obtain new materials from the point of view of their practical use.

# Structural and enhanced hydrogen storage properties of Mg-Co-Ga system

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Magnesium-based materials are considered one of the most promising systems for hydrogen storage. Currently, the biggest challenge in the development of these materials is the formation of stable hydrides, as well as the high temperature and pressure required for hydrogen absorption/desorption. Our main purpose of the study is to bring together experimental and theoretical insights of new MgTM (T=Mn, Fe, Co, Ni, Cu; M=B, Al, Ga) magnesium phases with unique properties by combining standard chemical techniques with advanced physics methods, such as hydrogen sorption properties of Mg-based alloys, electrochemical experiments with electrode materials of Mg-ion batteries and Mg-based materials. We have successfully obtained the first experimentally confirmed and practical metal hydrides based on Mg-Ni-Ga systems. They meet the requirements of modern hydrogen storage materials, such as hydrogen absorption/desorption at low temperatures, pressures close to atmospheric, and most importantly, relatively low material cost and environmental safety. Our strategy is to obtain alloys based on Mg and group p and d elements. We are confident that the newly formed systems will allow for the creation of new materials for hydrogen storage. Our main research is focused on the synthesis of new systems, gas and electrochemical hydrogenation, studies of sorption-desorption kinetics, and hydrogen capacity.

Magnesium alloys and intermetallic compounds have very useful properties that makes them attractive to manufacture products that are widely used in engineering, especially as aerospace construction materials, energy storage and superconducting materials. However, some difficulties in the synthesis of Mg-based alloys still exist and therefore these alloys are not yet sufficiently studied up to now. The presentation show our research associated with improve and optimize methods of synthesis of magnesium alloys (Mg-Ni-Ga system), determine its phase content and phase relations, crystal and electronic structures peculiarities, to conduct further physical and electrochemical properties investigations. The research shows that there are great possibilities to overcome the limitations described above.

# Preliminary comparative numerical analysis of three-layer hemp concrete wall with a layer enhanced with microencapsulated PCM

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The building sector in developed countries faces challenges to be more eco-friendly and energy efficient. Building materials with bio-additives could help transform into a more sustainable building sector. Hemp concretes are eco-friendly bio-based building materials that can help in this transformation. In these materials, agricultural or industrial wastes or manufacturing process by-products such as hemp shives could be used as fillers. Hempcrete has a low or even negative $CO_2$ footprint and has well hygro-thermal properties. Building envelopes made of hemp concrete might supply adequate thermal insulation with well vapor buffering properties and regulate microclimate indoors.

The paper presented the results of numerical simulations of an external building wall created from hemp concrete. The wall consists of three layers of hempcrete with different densities. The middle layer had a lower density (200 $kg/m^3$) than the external and internal ones (400 $kg/m^3$). Simulations were performed for constant wall thickness (40 cm) and different thicknesses of the middle layer. The wall with a layer with microencapsulated PCM additives and without was analyzed. Moreover, the wall made of aerated concrete was considered for comparison reasons. In the simulations, constant parameters, i.e., temperature and relative humidity, were assumed on the internal side of the wall. On the external side, temperature and humidity were changed according to the meteorological data for Warsaw.

The in-house numerical heat, air, and moisture (HAM) transfer model was used to conduct analyses. The model considered hemp concrete as a hygroscopic porous material with three phases, i.e., solid, bounded water, and moist air. Vapor and dry air transfer were considered separately. Thermal equilibrium between components (solid, bounded water, vapor, and humid air) was assumed. Hygric non-equilibrium between vapor and bounded water was considered, leading to a finite sorption-desorption rate. The model was implemented in the ANSYS Fluent software by using advanced user customization interfaces, i.e., User-Defined Function (UDF), User-Defined Scalar (UDS), and User-Defined Memory (UDM).

# Field horsetail (Equisetum arvense) - a functional additive to elastomer biocomposites

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The aim of the research was to recognize, study and explain the effectiveness of field horsetail (*Equisteum arvense*) as a source of active functional compounds for the modification of elastomeric composites of natural rubber. The research activity provided information on the characteristics of the successively separated products of horsetail processing: plant biomass, liquid natural extracts, biogenic silica and their influence on the properties of the produced biocomposites.

The research was carried out in three stages:

- Stage 1. Mechanical modification of the dried plant material and its incorporation as a fibrous filler into elastomeric mixtures. Investigation of the properties of the produced vulcanizates and evaluation of the activity of field horsetail as a modifier of biocomposites.
- Stage 2. Solvent extraction of field horsetail with isolation of active compounds contained in plant material. Characteristics of plant extracts, their freeze-drying and their use as compounds for anti-aging and microbiological protection of natural rubber.
- Stage 3. Obtaining biogenic silica contained in field horsetail using a two-stage method (hydrolysis and thermal treatment). Verification of the effectiveness of the obtained bio-additive as a filler for elastomer composites.

The implemented research was the recognition of the topic of the characteristics of the field horsetail as a source of active functional compounds for the modification of natural rubber. The results obtained are optimistic. Each of the proposed stages (modified fibrous filler, extracts with anti-aging and antibacterial properties, biogenic silica) confirmed the validity of the research assumptions. All stages ended with receiving not only extremely interesting conclusions, but also motivation to act and expand the research spectrum, for example with new plant centers such as elderberry or common nettle or other elastomers.

**The most important achievements:**

- In-depth characteristics of the field horsetail, which as a plant fibrous bioadditive can act as an active natural rubber filler, influencing a number of functional properties of biocomposites.
- Isolation of natural horsetail extracts, which after the freeze-drying process can be active natural rubber modifiers affecting the stabilization of vulcanizates, ensuring anti-aging and microbiological protection.
- Repeatable method developed by two-step hydrolysis and treatment of high-temperature biogenic silica, which is an excellent alternative to commercial fillers.

# Biochar as an alternative filler for elastomer composites

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In this study, to obtain novel natural rubber based biocomposite, oat straw was utilized as a plant source of carbon filler. Traditionally used as a filler of elastomer composites, carbon black is produced in an environmentally unfriendly process of acetylene incomplete combustion. Acetylene derivation from fossil fuels is not sustainable. In proposed procedure carbon filler is produced in more environmentally friendly way. Plant material was prepared by two step grinding, followed by the pyrolysis process that was carried out for two hours. Two temperatures were tested, 600°C and 900°C. Process was carried out under nitrogen atmosphere to prevent any oxygen entering the system.

To study biochar properties and compare it with commercially available carbon black, following technics were applied: TGA, FTIR, BET, SEM, granulometry. Furthermore, produced biocarbon was then mixed into rubber matrix, using standard technics to investigate its influence on composite final properties. Vulcanization process, mechanical strength, crosslinking density, gas permeability and aging were evaluated. Compared to rubber that contains commercially available carbon black, composites filled with biochar obtained from oat straw in pyrolysis process exhibited higher strength values. This work investigates alternative natural source of carbon filler for rubber matrix. As the results are promising, further research into other rubber types and different plant materials is needed to better understand the relationships between rubber matrixes and biocarbons with unconventional origin.

# Synthesis and thermal properties of $(RE^1_{0.5}RE^2_{0.5})_2Zr_2O_7$ zirconates

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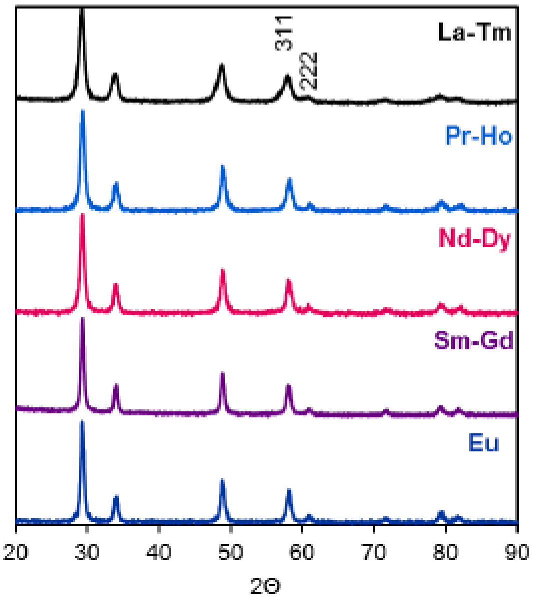
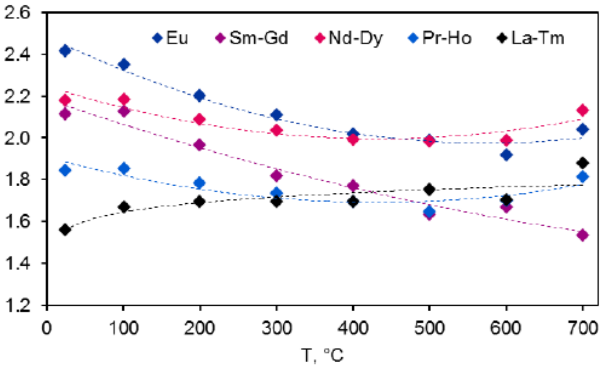
The article presents the thermal diffusivity and conductivity of dual-rare earth elements zirconates as a function of the temperature. All analysed systems were synthesised by solid-state reaction (SSR) and polymerized-complex method (PCM). The $(Sm_{0.5}Gd_{0.5})_2Zr_2O_7$, $(Nd_{0.5}Dy_{0.5})_2Zr_2O_7$, $(Pr_{0.5}Ho_{0.5})_2Zr_2O_7$ and $(La_{0.5}Tm_{0.5})_2Zr_2O_7$ were analysed. The rare earth element selection criteria were the mass and cation size distortion. The border condition was also the pyrochlore type of lattice, which is related to the ratio of rare earth elements and zirconium cation size. Short characterisation of density, phase constituents, and microstructural homogeneity after different variants of sintering were also presented. The average grain size was measured as well. To determine the value of the thermal diffusivity and conductivity, the pulsed laser LFA method was used (allowing to determine the value of thermal diffusivity in a wide temperature range). The heat capacity was determined by the Neumann-Kopp rule.

Obtained data revealed that rare earth elements substitution caused a lowering of the thermal conductivity of dual-element zirconates. This effect is incredibly intensive when a high cation size distortion is observed.



Phase constituents of calcinated powders



Thermal conductivity corrected by porosity

# Thermal diffusivity/conductivity of Pr, Eu and Ho zirconates

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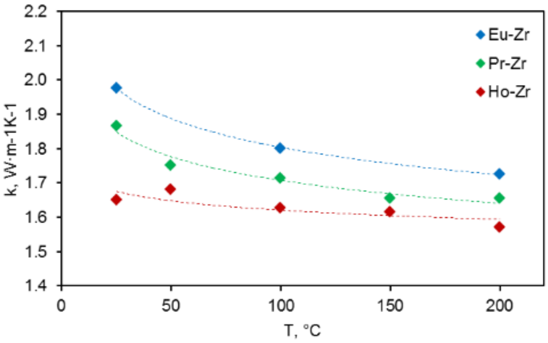
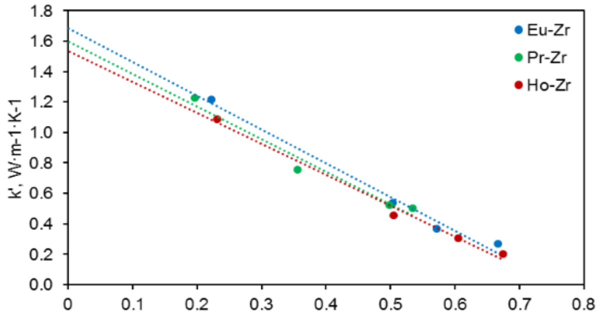
The article presents the thermal diffusivity and conductivity value of rare earth elements (Pr, Eu, Ho) zirconates as a function of the temperature. All analysed systems were synthesised by polymerized-complex method (PCM) with $Zr(NO_3)_4$ used as a precursor. The rare earth cations $RE^{3+}$ were introduced as nitrate compounds. The products of the primary stage of synthesis were calcinated and milled. As a final product, the monophasic pyrochlore zirconates of Eu, Pr and Ho were obtained with a pyrochlore type of lattice, confirmed by XRD analysis of phase constituents. In the next step, the theoretical density and the specific hate were calculated (Neumann-Kopp rule). Based on these data and thermal diffusivity measurements (laser-flash method), the thermal conductivity was calculated for all considered compounds.

Obtained data were used to determine the thermal conductivity value in the function of porosity. Based on the approximation procedure, the thermal conductivity of pores-free compounds was calculated.

It can be assumed that the presented research revealed the thermal properties of Pr and Ho zirconates, which are very narrowly presented in the literature. It should also be noted that thermal conductivity's tendency to decrease correlates with the cation size of rare earth elements used in zirconate compounds. Moreover, the relatively low influence of temperature on thermal conductivity thermal course suggests the strong influence of the phonon scattering mechanism.



Thermal conductivity of analysed zirconates



Thermal conductivity in the function of porosity

# Effect of the intercritical annealing temperature on the austenite formation in 5Mn alloy: Thermodynamic analysis

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Nowadays a lot of focus is put on tailoring mechanical properties of advanced high strength medium-Mn alloys. One of the way is to form the microstructure composed of various phases and retained austenite. Retained austenite undergoes strain induced martensite transformation during metal forming operations enhancing the mechanical properties of steel [1]. The easiest way to form microstructure composed of high retained austenite fraction is intercritical annealing. This heat treatment includes three steps: heating to a designed temperature, holding in this temperature for some time and then cooling to room temperature. In this way the final microstructure is composed of ferrite and retained austenite [2].

To control the heat treatment it is important to understand the initial conditions of austenite formation during intercritical annealing step. The knowledge on the transformation kinetics, an amount of the retained austenite and its thermal stability, allows to control the heat treatment parameters such as annealing temperature and time [3]. From the industrial point of view it would be ideal to use the lowest possible temperature and shortest time to obtain the best mechanical properties.

The work presents results of the thermodynamic analysis and dilatometric studies of the influence of the intercritcal annealing on the austenite formation, its thermal stability and Gibbs free energy changes, which control the austenite formation.

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# Rare earth elements zirconates` thermal and mechanical properties determination based on DFT simulations data

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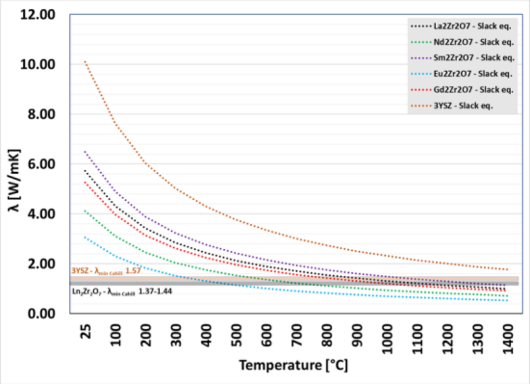
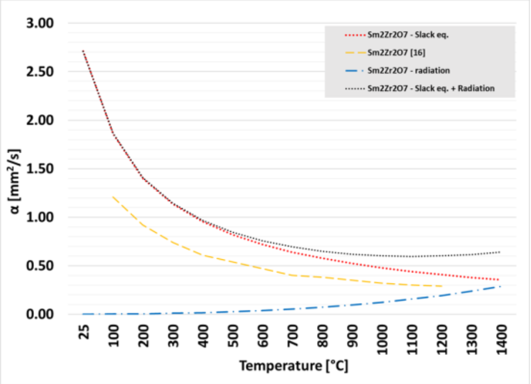
The article presents the methodology for determining the different mechanical and thermal properties of zirconates compounds with the overall pyrochlore formula $A_2B_2O_7$ based on density functional theory simulations results expressed by single-crystal elastic coefficients - $c_{ij}$. The sources of DFT simulation data are the literature information. On this base, the bulk elastic constants are calculated (Helmholtz, Kirchhoff modulus) and the sound speed in pyrochlore crystals. Detailed descriptions of chemical constituents and lattice structures are needed for those calculations.

Those data are the starting point for basic mechanical properties calculations such as Young modulus, hardness level, fracture toughness, and structural anisotropy. The second group of properties, which can be calculated in this procedure, are thermal properties such as Debye temperature and frequency, minimal thermal conductivity, specific heat, coefficient of thermal expansion, and thermal conductivity/diffusivity coefficient related to the phonon mechanism of heat transfer. The radiative component of heat transfer can also be calculated based on phonon-free path length. Lattice anisotropy of mechanical and thermal properties can also be determined.



Thermal conductivity coefficient and minimal thermal conductivity value



Thermal diffusivity in the function of temperature with the radial component of heat transfer: DFT simulation vs LFA measurement

# On thermodynamic modelling the effect of martensite on phase transformation kinetics in medium-Mn bainitic steel

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A cooling rate from the austenitization and isothermal holding temperature have a decisive influence on the obtained structure and properties of bainitic steels [1]. The former must be sufficient to omit ferritic and pearlitic transformations and in case of hot rolled steels results in a recrystallization degree of the austenite before phase transformations upon cooling. The later determines the fraction and size of bainitic plates and also stability of remaining austenite [2,3]. With the decrease of isothermal holding temperature the bainite and austenite are refined, which improves the mechanical properties of the alloy. However, the lower the holding temperature, the longer the bainitic transformation period is, which adversely affects prolonging the technological process. The formation of small fraction of martensite prior to the isothermal holding may significantly influence the kinetics of bainitic transformation.

The present work aims at analysing the phase transformation kinetics in 3Mn steel using thermodynamic calculations and dilatometry. The investigated steel was initially characterized using modelling and thermodynamic calculations and next subjected to dilatometric tests characterized by a number of isothermal holdings in a bainitic transformation range, both above and below the $M_s$ temperature. It was to investigate the effect of martensite on the kinetics of bainitic transformation and resulting morphology and phase composition of the alloy. The structural constituents and phase composition of the steel were identified using light and scanning electron microscopy techniques. The quantitative analysis of the fraction of RA in the microstructure was carried out using X-ray diffraction.

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# Thermal stability and irradiation resistance of LPBF AlSi10Mg alloy post-processed via KoBo extrusion method

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Nanocrystalline (NC) materials are expected to exhibit exceptional resistance to irradiation owing to their significant volume fraction of grain boundaries. However, a notable drawback is their susceptibility to grain coarsening when exposed to elevated temperatures. This limitation significantly impedes their practical application as irradiation-resistant materials, particularly in scenarios where they need to operate at relatively high temperatures.

In this study, an $AlSi_{10}Mg$ alloy, prepared using laser powder bed fusion (LPBF), underwent post-processing through the KoBo extrision method. This resulted in the production of a nanotwinned aluminum alloy with a high fraction of low-Σ twin boundaries. The KoBo processed sample had an average grain size of ~500 nm with a high density of coherent twin boundaries (CTBs).

To investigate the impact of nanotwins on thermal stability, a comparative characterization study was conducted on two types of samples: those with nanotwins and those without. Furthermore, the irradiation experiments were carried out by 60 keV He+ ions to $5 \times 10^{17}$ ions $cm^{-2}$ at 130 °C. Then the microstructures of the specimens were examined in a Transmission electron microscope.

# Hot deformation behaviour of additively manufactured and conventional maraging steels

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Hot working, as an important group of post-processing routes for additive manufacturing technology (3D printing), is used to reduce the solidification/processing defects and anisotropy of properties, grain refinement, improvement of mechanical properties, processing of pre-formed parts, and increasing the applicability domain.

In this study, hot compression tests were conducted on additively manufactured and conventional 18Ni-300 maraging steels using the Gleeble thermomechanical simulator. The tests were performed over a wide temperature range (900-1200 °C) and at strain rates of 0.001 to 10 $s^{-1}$. Microstructural analysis of the samples was carried out using light microscopy and scanning electron microscopy with electron backscatter diffraction (EBSD). The results revealed that dynamic recrystallization (DRX) was the dominant mechanism at high strain rates and elevated deformation temperatures. In contrast, dynamic recovery (DRV) prevailed at lower deformation temperatures and strain rates.

Furthermore, the experimental flow stress data was utilized to evaluate the material constants in a constitutive relationship. The results demonstrated that the specimens exhibited favorable hot workability and exhibited similar activation energy for hot working when compared to conventionally fabricated specimens.

The findings of this research provide valuable insights and can be utilized to develop innovative hybrid post-processing technologies. These technologies have the potential to enable single-stage net shape forging/forming of additively manufactured maraging steel components. Such processes can be performed at reduced forming forces, while achieving improved density and enhanced mechanical properties.

# Investigation of biomass waste carbonization process supported by TGA for solar-thermal energy conversion applications

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Sustainable technologies and the utilization of potential waste materials gain more attention as they take an approach to green and circular economy. Solar energy conversion and utilization is becoming one of the leading research topics. Utilization of biomass waste and incorporation of phase change material (PCM) allow to create a material that can be used in solar energy harvesting devices [1, 2].

The porous carbon structure obtained after carbonization of biomass can enhance solar energy harvesting and thermal conductivity of PCM. In addition, infiltration of PCMs into the micropores can prevent leakage and improve shape stability of the PCM composite [3]. Different types of biomass require proper carbonization parameters to obtain porous carbon materials with desired properties. For this purpose, thermogravimetric analysis (TGA) can be used as a method to support the design of the carbonization process especially in terms of temperature [4].

The aim of this work was to obtain a porous carbon matrix that could act as a carrier of PCMs and improve their properties. Different types of biomass were used to obtain a porous carbon materials by the carbonization process programmed according to the TGA results of the raw biomass. The obtained carbon porous structures were then infiltrated under vacuum with a melted PCMs based on poly(ethylene glycol), paraffins, fatty alcohols and acids.

The thermal properties of obtained PCMs infiltrated into the biomass delivered porous carbon materials were further analysed using differential scanning calorimetry (DSC) and thermogravimetry (TG). Furthermore, material samples were examined with scanning electron microscopy (SEM) and a leakage test was performed to establish their shape stability and leakage under increased temperature.

Research project supported by program “Excellence initiative—research university” for the AGH University of Krakow

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# Thermal analysis of the carbonized citrus fruit biomass infiltrated with sugar alcohols-based PCMs

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In recent years sugar alcohols as phase change materials (PCMs) are becoming more and more popular. This is due to research showing that these materials have almost two times higher the latent heat of fusion than other organic materials [1]. An advantage of sugar alcohols is their price and the ability to store energy over a long period of time due to the cold crystallization [2].

The main disadvantage of phase change materials with the solid-liquid phase transition is leakage during the phase transition process [3]. To avoid leakage above the PCM melting point different methods of shape stabilization, e.g. production of a biomass-derived carbonaceous aerogel/mannitol phase change composite, have been elaborated and tested. It is known that application of carbonized biomass as a shape-stabilizing foam has positive effect for supercooling, thermal conductivity, thermal stability, and thermal reliability of PCM composite [4, 5].

The main goal of our current research was to obtain a phase change material with shape stabilization for long-term energy storage. For this purpose, sugar alcohol-based PCMs modified with carbon nanotubes were prepared and infiltrated into carbonized orange peel. To characterize the obtained PCM composites differential scanning calorimetry (DSC), modulated temperature differential scanning calorimetry (TOPEM DSC), thermogravimetric analysis (TGA), and microscopy were used. Also, the percent of infiltration of the carbonized citrus fruit biomass by sugar alcohols was calculated.

"Research project supported by program “Excellence initiative—research university” for the AGH University of Krakow".

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# The study on the new biopolymer/natural dye hybrid pH indicators: preparation, characterization, and application

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Biopolymer-based pH indicators have been recently become very popular due to the great performance in the monitoring of food freshness conditions. The pH bio-indicators are generally developed from biological macromolecules such as proteins or protein isolates (e.g. gelatine), lipids (e.g., carnauba wax), as well as polysaccharides (e.g., pectin,) [1]. These biomaterials can carry natural compounds (e.g., natural dyes) with bioactivities and physicochemical properties that make them usable to develop smart, functional, and bioactive composites [2]. A very large variety of biomaterials obtained from nature in the form of different biopolymers or natural pH-sensing dyes and pigments is a valuable source of biocomponents for the design of eco-friendly, functional hybrid pH indicators intended for various applications, e.g. in packaging industry.

In this study, pH sensitive hybrids were successfully synthesized from red anthraquinone chromophores and carbohydrate polymers (chitosan and chitin). The relationship between the type of biomaterials used for modification and the structure, stability and pH-sensing activity of the designed pH indicators were evaluated based on the XPS, FTIR, SEM, TGA and UV-Vis measurements. The colorimetric measurements indicated that prepared hybrid pH indicators showed rapid and clear color change response upon the exposure to acidic (HCl) or alkaline ($NH_3$) vapours. In addition, the applicative studies revealed a high potential of designed materials as new multifunctional pH-responsive colorants for polymer composites. When introduced into the ethylene-norbornene copolymer, colorants based on biopolymers and anthraquinone dyes exhibited high resistance to UV radiation and showed a reduced tendency to migrate from the polymer matrix compared to pure natural dyes.

The effects of this study may have an important contribution into the designing of novel functional pH indicators based on biopolymers and natural dyes.

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# Thermal properties of polymeric phase change materials modified with selected nanoadditives

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One of the most interesting types of functional materials are phase change materials (PCMs). These materials can be a relatively inexpensive and efficient solution for thermal energy storage applications. They are also used to improve efficiency or completely eliminate the need for heating or cooling systems. The use of a phase change material, for example in construction, is shown in Figure 1. The phase change material in this case is designed to store heat during the day when the outside temperature is higher and then release it at night when the temperature drops [1].

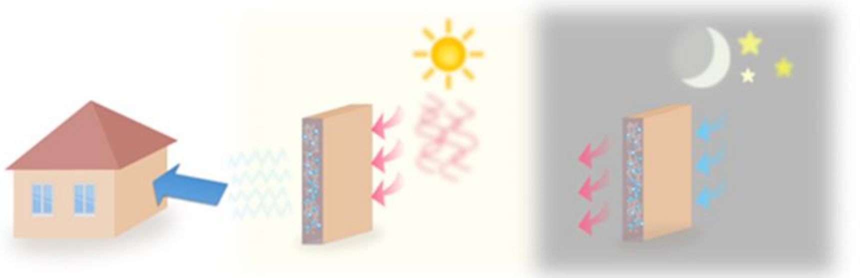

**Fig. 1** An example of a phase-change material operation scheme used in construction

This work focusses on the design, manufacture, and investigation of thermal properties of phase change materials modified with selected nanoadditives such as magnetite, boron nitride, or carbon nanomaterials. To determine the thermal properties of the phase change materials various thermal analysis methods (DSC, TOPEM DSC, TG) were used. The results show the effect of nanoadditives on the temperature and heat of the phase transition and thermal stability of obtained PCMs.

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*Research project supported by program "Excellence initiative—research university" for the AGH University of Krakow.*

# Thermal properties of thermochromic phase change materials modified with boron nitride

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Latent heat storage by phase change materials (PCMs) is one of the most preferred forms of thermal energy excess storage. PCMs use the latent heat of phase change to control temperatures within a particular range [1]. Organic phase change materials are among the most commonly tested. The incorporation of the thermochromic properties enables observation of the color changes of thermochromic phase change materials (TPCMs) during the phase transition. It makes the visualization of the phase change process more intuitive and simpler [2]. The boron nitride modifier is intended to improve the thermal conductivity of TPCMs [3].

This work aimed to study the thermal properties of thermochromic phase change materials with an inorganic modifier. Stearic acid, behenyl alcohol, and bromocresol purple were used as components of the thermochromic system and boron nitride was used as an additive. A thermogravimetric analysis was carried out to obtain data on the thermal stability of obtained samples, which is crucial for materials that will be subjected to temperature changes during their applications. Differential scanning calorimetry is an essential testing method for PCMs as it allows the determination of parameters of phase change processes both melting and crystallization. The results of this research showed that the tested materials have great potential as thermochromic phase change materials.

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https://doi.org/10.1016/j.enbuild.2016.09.022

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# Heat treatment thermal parameters` determination of Co-(Ni)-Al-Mo-Nb-X superalloys

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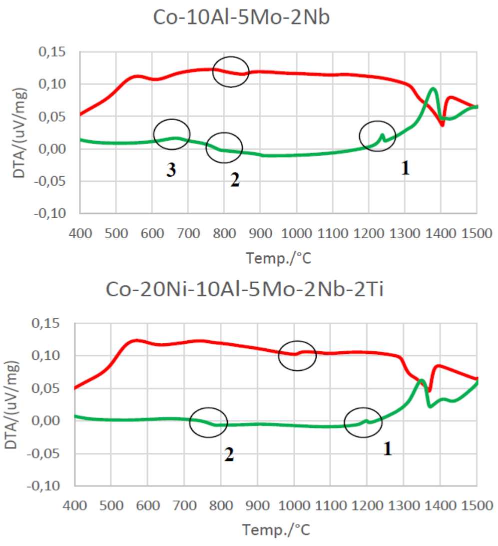
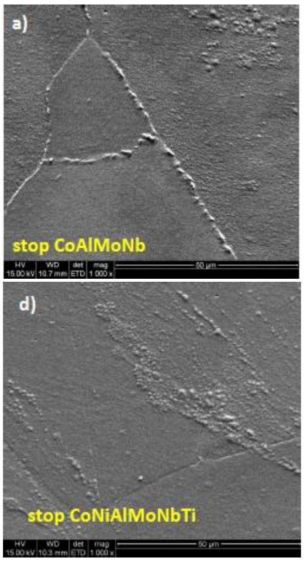
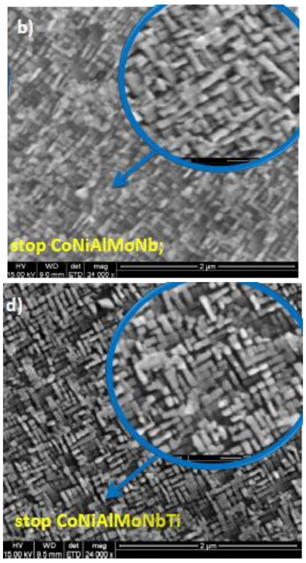
The article presents the thermal analysis results of new Co-based superalloys of new tungsten-free Co-(Ni)-Al-Mo-Nb-X Co-based superalloys where X = Cr, Ti and V. The data obtained during these investigations revealed the crucial temperatures such as incipient melting point, *solidus* and *liquidus* of alloys and *solvus* temperatures connected to the order/disorder transformation of strengthened L1$_2$ phase with overall formula Co$_3$(Al,X). These data determined the characteristic temperatures of homogenization treatment, solutionizing window, and ageing treatment. It was additionally revealed that Ni and Ti addition strongly increased the *solvus* temperature. The influence of V is much weaker. Still, adding Cr does not influence the order/disorder transition. The microstructural characterization of alloys after heat treatment based on the determined thermal parameters was also presented.



*DTA results*



*Solutionizing 1250°C/5h*



*Ageing 850°C/5h*

# Thermogravimetric analysis of new tungsten-free Co-based superalloys with rare earth elements additions

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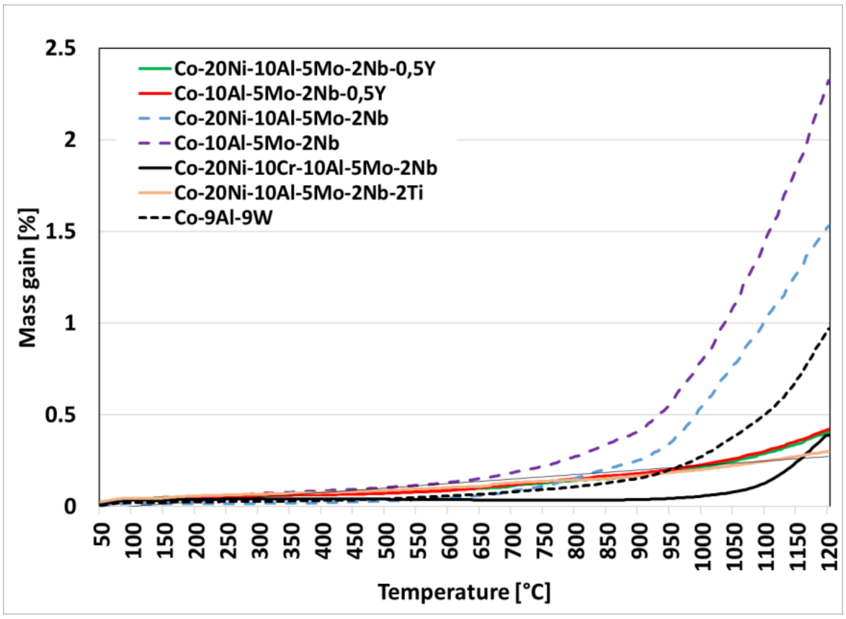
The article presents the thermogravimetric behaviour of new Co-based superalloys of tungsten-free type (Co-(20Ni)-10Al-5Mo-2Nb) with the addition of reactive elements of yttrium. The following alloys` variants were analyzed: Co-10Al-5Mo-2Nb as a basic alloy, its modification with yttrium – Co-10Al-5Mo-2Nb-0.5Y, nickel and simultaneously nickel and yttrium - Co-20Ni-10Al-5Mo-2Nb and Co-20Ni-10Al-5Mo-2Nb-0.5Y respectively and alloyed with Cr and Ti (Co-20Ni-10Cr-10Al-5Mo-2Nb, Co-20Ni-10Al-5Mo-2Nb-2Ti). The Co-9Al-9W alloy was used as a referential material. The results showed that using the Y significantly improved the oxidation behaviour of Co-(Ni)-Mo-Nb alloys, which is still comparable to Ti-modified alloys. The most beneficial effect was obtained in the case of Cr-added alloys, which is caused by an increasing tendency to chromia scale formation. The detailed characterization of microstructure was also performed for analysed alloys.



# Characterization of Nanofluids for Biomedical Applications: Study of Density and Viscosity Properties

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Nanofluids have several applications in the Biomedical area, either in the diagnosis of pathologies through images in which nanofluids were used to improve contrast [1], or in the treatment of diseases such as cancer, through methods like hypothermia using magnetic fluid. Other applications in which nanofluids are used are, for example, in antibacterial applications, transport of drugs, medical dressings and cryopreservation [2].

The present study focused on the application of nanofluids to aid in the characterization of the optical properties of biological tissues, through spectroscopy techniques. This technique makes it possible to identify differences in pathological tissues, when compared to tissues in healthy state [3]. To do this, it is necessary to know the refractive index, density, and viscosity of the nanofluid as a function of temperature. For the optical characterization to be measured, it is necessary that the nanofluid's refractive index is close to the refractive index of the biological tissue under study. For this, several concentrations were prepared in volume of graphene in physiological serum, and the density and viscosity were measured as a function of temperature [4]. The nanoparticles used were 11-15 nm with CAS 7782-42-5 from the commercial house MK-nano, and the techniques used for density measurement were the pycnometry, and for viscosity, the Cannon-Fenske viscometer.

It was found that with increasing temperature the viscosity of the nanofluid decreased exponentially, and with increasing concentration of nanoparticles in the base fluid, the decrease in viscosity was more pronounced.

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# Thermal analysis of a pump used in an innovative installation for cementing and special operations at the oil well intended to improve the efficiency of the extraction of conventional energy resources

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The paper presents a study conducted by the authors for investigating the thermal behaviour during operation of the parts of a pump used in an innovative installation for cementing and special operations at the oil well intended to improve the efficiency of the extraction of conventional energy resources, in connection with the structural analysis of that parts in a simulation driven design process [1].

The research looked at the influence of the degree of finishing and the thermochemical treatments of the surfaces of the parts in contact during operation on the thermal regime of these joints in motion and the resulting degree of wear.

Simulations were made, using finite element analysis programs, and experimental investigations were done, and comparative studies were carried out.

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# Thermogravimetric characterisation of various agriculture biomass residues prior to valorisation by thermal methods

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Biomass is a necessary and reliable energy resource, since it is the only renewable energy material with unlimited supplies, from trees to crops and animal wastes. Bioenergy is the chemical energy harvested and stored by plants through photosynthesis from solar energy (sunlight). The production of bioenergy from bioproducts could provide a clean alternative to traditional fossil fuels, such as coal, crude oil, or natural gas and, consequently, contribute to environmental and economic sustainability. Specific types of biomass as potential candidate feedstock for energy production include energy grasses, forestry residues, agricultural crops, urban wood waste, animal manure or algae crops. In particular, biomass waste from agriculture, which are often burned on-site with associated pollution problems, have received increasing attention as valuable materials.

Samples of vegetal agriculture residues were collected from a very narrow area (virtually a farm garden in east of Romania) to minimise, as much as possible, the effect of geographical, climaterical and pedological factors that affect the growth and development of biomass and the properties of the generated materials. Stalks, hulls, shells and pits, with high lignification degree and which are rarely valorised but left unused for natural decay were considered as representative biomass waste. Thermogravimetry was used to determine the thermal behaviour, prior to their valorisation by thermal treatments.

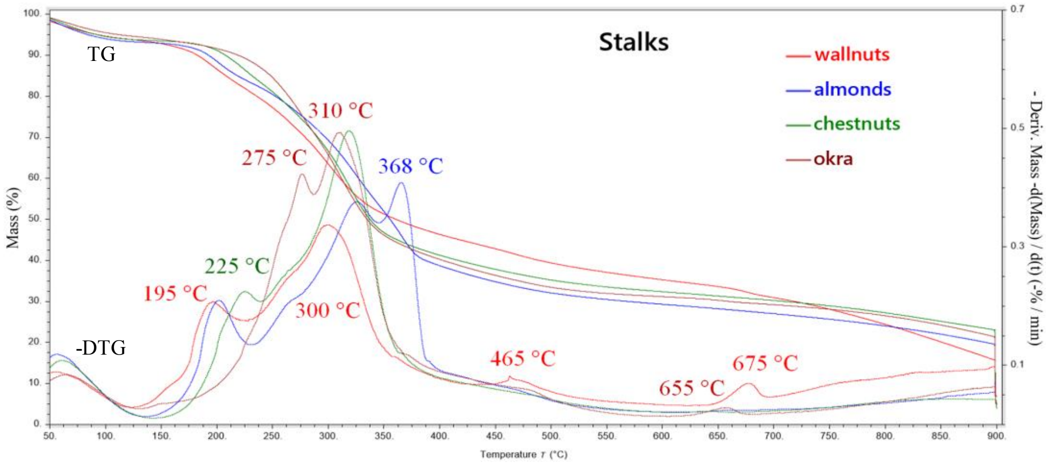

Fig. 1. The TG and DTG curves of stalks from various sources.

Acknowledgements: Support by the Ministry of Research, Innovation and Digitization, CNCS/ CCCDI-UEFISCDI, through the project PN-III-P4-PCE-2021-1141, within PNCDI III is gratefully acknowledged.

# Biocomposites based on hydroxyapatite loaded with amoxicillin for bone tissue repair and regeneration

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Currently, defects and bone diseases represent a serious problem for many patients. Research in bone tissue engineering is in a permanent search and development of new biomaterials with the role of bone graft [1]. In tissue engineering, the scaffolds, signals and cells are fundamental, and these elements can be used independently or, preferably, can be combined in various arrangements to create new tissues [2]. Scaffolds can be made of simple or composite materials, natural or synthetic, nonresorbable or resorbable. Various signals (internal or external), like biological, chemical, mechanical and electrical cues, can be used for tissue regeneration. To prevent the infections development and to stimulate healing, chemical cues are most often used. These are active principles (drugs) and are encapsulated in the scaffold structure to be implanted in the living tissue [3].

In this study, the new biocomposites based on nanohydroxyapatite (as carrier of antimicrobial units and bone filler), chitosan and collagen (as matrix) and amoxicillin (as chemical cue - drug) were prepared. The hydroxyapatite nanopowder was obtained by the wet chemical precipitation method, showing an average crystallite size of 58.3 nm and pore size of about 1.6 nm. The porous scaffolds from these new biocomposites were obtained by the phase inversion process and were characterized by XRD, SEM and EDX methods. In vitro drug release of amoxicillin as a molecular model-drug indicated that these hybrid biomaterials can provide a prolonged release of bioactive agents in physiological conditions. The therapeutic role of the composites is demonstrated by the antimicrobial test against the yeast strain Candida albicans. These composites loaded with amoxicillin exhibited an inhibition effect on the Candida albicans growth, suggesting thus their clinical potential use with a great appeal for the treatment of localized infections. The results suggested that these biocomposites with a controlled release capacity of bioactive factors may be of use in bone tissue engineering for enhancing the bioactivity and bone inductivity for the regeneration of bone defects.

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# Antibiotic-loaded bioceramics for bone tissue healing

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For a very large number of people, especially elderly people, the life quality is greatly affected by health problems related to the bone defects caused by trauma or some diseases. In restorative medicine, to solve the problems that occur at the level of the bone structure, in addition to biological bone grafts, implants made of synthetic biomaterials that try to imitate the bone structure are used. Among them, bioceramic materials are widely used, and this is because they have excellent biocompatibility and mechanical properties suitable for their clinical use in orthopedics and dentistry [1].

A problem that can arise after the implantation of a biomaterial in a bone structure is the appearance of bacterial infections. Therefore, it is extremely important that the bioceramic implant also has an antibacterial function to prevent or treat a possible infection associated with the bone implant. In recent years, a series of studies have been carried out regarding the creation of bioceramics that incorporate antibiotic-type active principles, precisely to induce antibacterial activity of the implant [2].

In our study, to achieve antibacterial aims, hydroxyapatite scaffolds doped with silver ions were prepared for long-term release of antibacterial ions. In addition, an antibiotic (amoxicillin) was introduced into the apatitic bioceramic to act quickly on pathogenic bacteria that could develop on the implant. The porous scaffolds were obtained by the phase inversion process and were characterized by XRD, SEM and EDX methods. In vitro drug release of amoxicillin and silver ions indicated that these hybrid biomaterials can provide a prolonged release of bioactive agents in physiological conditions. The results suggested that these biomaterials with antibacterial function may be of use for the regeneration of bone defects and bone tissue healing.

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# Analytical prediction of the curing overheating and overshoot

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Due to the exothermic nature of the curing reaction and the relatively low thermal conductivity of thermosets, overheating and even thermal runaway can occur when the sample exceeds a critical thickness. Thermal runaway occurs when heat dissipation cannot compensate for heat generation. Below this critical thickness, heat dissipation equals heat generation and the system reaches a steady state, this is the so-called subcritical state [1,2]. Still, the formation of temperature gradients in the subcritical state leads to non-uniform curing and even matrix degradation and delamination [3-6]. In this contribution, we determine the critical thickness related to a given overheating, as well as the maximum overheating before the steady state becomes unstable. The validity of the solution was verified by comparing it with numerical results.

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# An overview of viscosity of several nanoparticles enhanced liquids

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This study will be focused on polyethylene glycol PEG 400 used as base fluid for nanofluids preparation. In case of nanofluids, it has been shown that the addition of solid nanoparticles to various fluids can increase the thermal conductivity and can influence the viscosity of the suspensions by tens of percent. The aim of this paper is to make a comparison regarding the viscosity of the PEG 400 as base fluid in combination with three types of oxide nanoparticles. In this experimental study, all the nanofluids were made by the two-step method.

Regarding the properties of PEG 400, it has a CAS number of 25322-68-3 and a molecular weight of 380-420 g/mol. The MgO nanoparticles have a molecular weight of 40.30 g/mol, dimensions of ≤ 50 nm, and a density of 3.580 g/cm$^3$. The other nanoparticle properties are detailed in Chereches et al. [1,2]. The rheological analysis was performed using a Physica MCR 501 modular rheometer (Anton Paar, Austria) equipped with a Peltier temperature control system in the range 283.15–333.15 K. The measurements were performed on a planar geometry. The diameter of the plate used is 50 mm. The distance between the plates was set to 0.5 mm. The obtained results were interpreted with the help of the RHEOPLUS v.3.40 software [3]. The experiments performed to determine the viscosity assumed the estimation of both the rheological behaviour of the fluids at ambient temperature and the variation of viscosity with temperature. Considering the experimentally results, this research is focused on viscosity of PEG 400 – MgO, ZnO and $Al_2O_3$ nanocolloid, in the range of mass concentration of up to 5 % wt. This comparative study is to verify how the viscosity is influenced by the nanoparticle type because this topic is at its beginnings and more studies are necessary to shed some light on their thermophysical properties. Concluding, the addition of nanoparticles increase the viscosity of nanofluids, but this increase depends on the type of nanoparticles and their concentrations. Also, viscosity decreases at heating.

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Acknowledgments

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# Morpho-structural properties of thermally treated iron oxide nanoparticles synthesized by laser pyrolysis using ethanol as sensitizer

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The laser pyrolysis technique was used in the synthesis of magnetic iron oxide nano-powders with ethanol vapours as sensitizer. This technique uses the energy coming from a $CO_2$ laser working in C.W at 9.25 microns wavelength which is transferred to the reactive precursors via the excited ethanol molecules, generating a rapid heating of the $Fe(CO)_5$ vapours in the presence of oxygen. For a parametric study, different samples were prepared by changing the percentages of sensitizer in the reactive mixture. Moreover, the raw samples were thermally treated at different temperatures and their morpho-structural and magnetic properties were investigated. The results indicated a high degree of crystallinity (mean ordered dimension) and enhanced magnetic properties were detected at high percentages of ethanol vapours. On the contrary, at low ethanol concentrations, due to a decrease in the reaction temperature, nanoparticles with a very low ordered dimension were synthesized (up to 2.4 nm). The particles obtained were in the range of 3 to 10 nm in diameter (TEM). Most of them exhibited superparamagnetic behaviour at room temperature with saturation magnetization values up to 60 emu/g. The samples consist mostly in maghemite with a decreased carbon presence (up to 8 at%) when compared with the experiments with ethene as sensitizer. On the particles surface, C generated functional groups such as C-OH or C=O that act as a supplementary hydrophilic agent in water-based suspension were detected. Using the as-synthesized and thermally treated nano-powders, water suspensions were prepared by means of a horn ultrasonic homogenizer at 0.5 mg/ml concentrations. DLS analyses revealed a great stability in time of some powder suspensions having around 100 nm mean agglomerated size, 4.8 to 5.3 pH and more than 40 mV zeta-Potential values.

# Differential thermal gravimetric analysis for plants growth soil with different salt concentration

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The first part of our experiments was to test the sensitivity of our equipment. The first sensitivity test consists in determinate the minimum amount of organic material that can be measure with enough precision. The second test consists in the evaluation of the influence of compacting the organic compound. The main propose of the experiment was to visualize the impact of salt soils on the plant grow. In this experiment we are using the Shimadzu thermal differential gravimetric DTG-60 equipment, to view the internal chemical modification and evaporation of components.

For this experiment the pumpkin seeds ware planted in three type of different salinity soil. The first analysis has been done when we had a height of only a few centimetres. The final analyse has been done when the plant has one month old.

# Thermal and FTIR characterization of medicated jelly with betulin and betulinic acid

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Medicated jelly can be found in solid dosage forms with application in treatment of different type of diseases for children and elderly. The market offers different types of medicated jelly, like medicated jelly with calcium gluconate, metformin hydrochloride, acyclovir, alendronate, etc[1].

Betulinic acid [BA] and betulin [B] are triterpenes, both present important biological activities like anti-inflammatory, antitumor effects [2]. Betulinic acid proves over the years a good activity into induction of apoptesis and antiangiogenic response for tumour cells [3].

For the current study, we consider important to study the interactions between the most used materials in medicated jelly formulation (pectin, gelatine, etc.) with betulinic acid and betulin. Thermal induces interaction for binary mixture between the most common materials used in medicated jelly formulation, betulin and betulinic acid was studied using a TG/DTG/HF and FTIR analysis (see Fig.1 and Fig. 2).

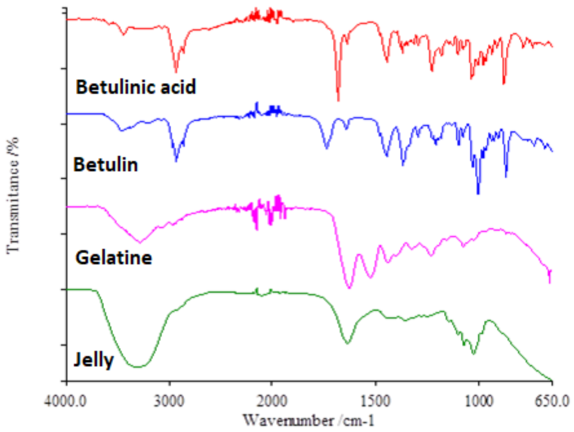

Fig. 1: FTIR spectra for betulinic acid, betulin, gelatine and for jelly.

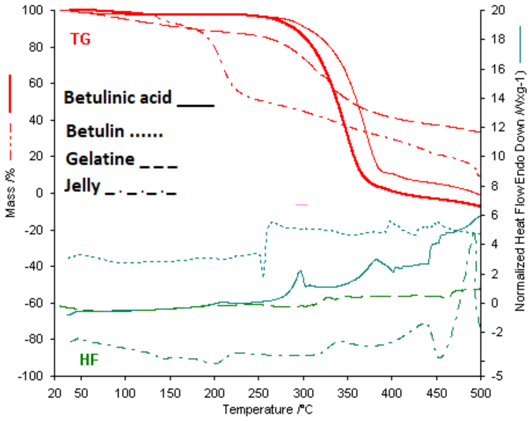

Fig.2: TG/DTG/HF curves for betulinic acid, betulin, gelatine and for jelly

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# Absorption of phosphorus from water, use of hydrogels based on biopolymers

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Excess phosphorus is a concern for most aquatic ecosystems [1]. Phosphate removal by adsorption has been investigated in recent years using different sorbents, which include bioadsorbents [2].

In this study, we prepared and analyzed: hydrogels based on polyvinyl alcohol (PVA), and polyvinylpyrrolidone (PVP), in which we included, in turn, the constituent polysaccharides: chitosan, carrageenan, or alginate with/without egg shells, in different ratios [3-5].

The main aims of this study were:

• optimization of the preparation of absorbent material with/without eggshells and the conditions for removing phosphorus from water.

• characterization of the absorbent material using the following techniques: FT-IR, Thermal Analysis, SEM Microscopy [6].

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# Evaluating the thermal regeneration processes of spent activated carbons used in winemaking

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Activated carbons play a crucial role in the wine industry, particularly in the purification and filtration processes, as they are highly effective in removing impurities and undesirable compounds from wine.

The thermal regeneration process involved subjecting spent activated carbons, previously used in winemaking, to high temperatures to remove adsorbed substances and regenerate their adsorption capacity. The regeneration conditions, including temperature, time, and heating atmosphere, were optimized to ensure the efficient restoration of the activated carbons' performance. Characterization of the regenerated activated carbons was conducted using various techniques. Surface area analysis, pore size distribution measurements, and scanning electron microscopy (SEM) were employed to evaluate the structural and morphological properties of the regenerated activated carbons. Additionally, Fourier-transform infrared spectroscopy and thermogravimetric analysis (TGA) were utilized to determine their chemical composition and thermal stability.

The results demonstrated that the thermal regeneration process effectively restored the adsorption capacity of the activated carbons. The regenerated activated carbons exhibited comparable surface areas, pore structures, and adsorption properties to those of initial activated carbons, indicating their potential for reuse in winemaking processes. Furthermore, the characterization results provided valuable insights into the structural and chemical properties of the regenerated activated carbons. These findings contribute to a better understanding of their performance and suitability for wine purification applications.

In conclusion, the thermal regeneration and characterization of activated carbons used in winemaking offer a sustainable approach to their reuse and contribute to the optimization of wine production processes. The regenerated activated carbons, with their restored adsorption capacity and favorable properties, can play a significant role in improving the quality and consistency of wines while minimizing waste and environmental impact

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# Preparation and characterization of carbonaceous adsorbents from solid industrial waste

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Solid carbon residue, also known as carbon black, is the carbonaceous material left after rubber degradation during the pyrolysis process. It is a potential human carcinogen, and short-term exposure to high concentrations can cause discomfort in the upper respiratory tract, leading to mechanical irritation. Industrial waste poses a significant environmental challenge, and finding effective methods to utilize and mitigate its impact is of paramount importance.

Activation is one of the methods used to modify carbonaceous materials and involves the partial oxidation of carbonized layers in its structure, using water vapor, carbon dioxide, hydroxides, or carbonates of alkali metals as activation agents.

The aim of this study was to develop and characterize adsorbent materials derived from solid industrial waste. A series of carbonaceous adsorbents were obtained from the pyrolysis residue of tires. Various techniques such as physical, chemical, and thermal treatments were employed to modify the waste materials and enhance their adsorption properties. Activation was carried out in a horizontal reactor, using water vapor as the activation agent, as well as pre-treatment with KOH, $H_3PO_4$, and $HNO_3$. The obtained adsorbents were characterized using gas adsorption, IR spectroscopy, and thermal analysis. The results obtained indicate the possibility of obtaining carbonaceous adsorbents with economic potential from solid waste generated during tire pyrolysis. This study highlights the feasibility of obtaining and characterizing adsorbent materials from solid industrial waste. The utilization of such materials not only offers a sustainable solution for waste management but also presents an opportunity to address environmental concerns and promote cleaner industrial practices.

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# Optimizing the thermal treatment in order to obtain a single hexagonal phase of $YMnO_3$

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Hexagonal ternary manganese oxides constitute an important class of materials with potential applications in electronic devices such as sensors and non-volatile random access memories [1]. Moreover, the hexagonal $YMnO_3$ is a good candidate for non-volatile memory device application owing to having stable intrinsic charged domain walls [2]. In addition, the catalysis properties of $YMnO_3$ are also grabbed considerable attention due to its high catalytic activity, low cost, and environmental friendliness and having narrow optical band-gap properties [3].

In this work, we report a series of yttrium manganese compounds which have been synthesized via sol-gel technique, and heat treated at different temperatures: 600 °C, 800 °C and 1000 °C, for 6 h. The obtained materials were studied morpho-structural by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM/EDX), and (DTA)/(TG) analysis. X-ray diffraction analysis showed that at the temperature of 600 °C, the XRD peaks were not obvious, which revealed that the sample was mainly amorphous. However, for the samples calcined at 800 °C and 1000 °C the XRD spectra are consistent with JCPDS: 25-1079 from the database for $YMnO_3$ having the hexagonal perovskite structure and space group P63cm without other impurities.

The physico-chemical properties of perovskites materials obtained through sol-gel method have been analysed with the aim of studying the relationships between structure and properties in this class of materials the influence of the thermal treatment on the induced properties.

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# Properties of manganese yttrium oxide: Influences of dopants on the thermal, structural and optical properties

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**Abstract:**

The materials of the perovskite-type oxides such as: $YMnO_3$, $YFeO_3$, $BiMnO_3$, $BiFeO_3$ and $YCrO_3$ show a distorted structure and crystallize in either orthorhombic or hexagonal structure, depending of synthesis conditions [1].

Manganese perovskites of the $AMnO_3$ type generally crystallize in orthorhombic structure when the A cation in the $ABO_3$ arrangement has a large ionic radius while if A has a small ionic radius manganites crystallize in a hexagonal structure with space group P63c [2,3].

In this paper we report a comparative study between undoped and Co or Sn doped yttrium manganese oxide ($YMnO_3$) samples synthesized by the sol–gel technique, followed through subsequent heat treatment done at 800 °C for 6 hours. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray energy dispersive spectroscopy (EDX), Fourier transform infrared spectroscopy (FT-IR), ultraviolet-visible (UV–Vis) spectroscopy. The thermal behaviour of the undoped and Co or Sn doped $YMnO_3$ compounds were investigated by (DTA)/(TG) simultaneous analysis. Thermal analysis techniques were used to study various phase transitions and other properties in perovskite materials. The XRD pattern of the prepared samples confirmed the formation of a single hexagonal phase of $YMnO_3$ undoped, while in the Co or Sn doped samples can be observed a secondary $YMn_2O_5$ perovskite phase.

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# Thermal and mechanical properties of ash powder/glass fiber reinforced polyamide hybrid composites

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The automotive industry is undergoing a huge shift to resolve significant issues that affect both consumers and the climate. Reducing the weight of vehicles through the employment of composite materials represents an effective way to diminish both fuel consumption and hazardous emissions [1]. Glass fiber reinforced polymer composites are often used in automobiles due to their great strength-to-weight ratio as well as their lower weight compared to metallic car components [2]. Reducing the amount of glass fiber in polymer composites should be possible with the introduction of aluminosilicate materials but without compromising the overall qualities necessary for these materials in automotive applications [3]. In this study, ash powder (C) is used as a reinforcing agent in polyamide 6 (PA6)/ bio-polyamide 10.10 (PA10)/glass fiber (F) hybrid composites and its influence on the thermal, mechanical and nanomechanical properties is thoroughly investigated. Samples containing15-30% F and 15-25% C were prepared in dynamic conditions through extrusion and injection molding for physico-mechanical (Impact testing, DMA), thermal (TGA, DSC) and tribological characterization (Nanoindentation and nanoscratching). TGA analysis presented in Figure 1 showed small changes regarding the thermal stability of the composites with the introduction of C while the residue at 700°C correlates with the quantity of reinforcing agent present in each sample. The DSC thermogram showed in Figure 2 displays a shift in material crystallinity with the introduction of C. The melting temperature and enthalpy of the composites with C decreases gradually compared to neat glass fiber polyamide hybrid.

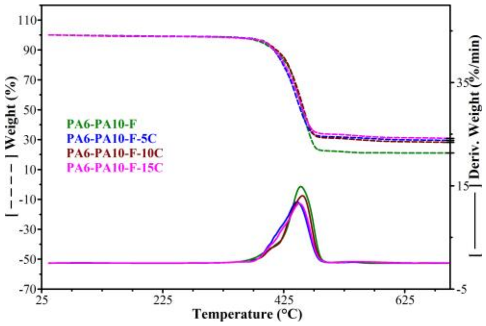

Fig. 1 TGA analysis of polyamide hybrid

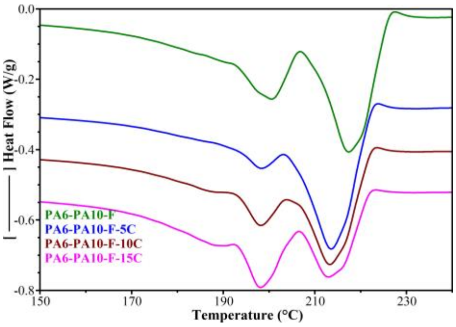

Fig. 2 DSC analysis of polyamide hybrid composites
composites

The introduction of ash powder helps minimize the amount of glass fiber used while also giving a waste item a purpose that would otherwise be abandoned and contribute to environmental damage.

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# A cold/chemical sintering process for manufacturing Zn foams from spherical powders

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Cold sintering (CSP) of Zn powders offers a simple and effective process to manufacture Zn metallic foams by utilising dissolution/reprecipitation mechanism to transfer material in the particles contact points and so to create the sintering neck between them, assuring the needed mechanical properties.

As an alternative to the classical sintering process, the cold sintering process uses chemical solutions to dissolve the passivation layer covering the metal surface and facilitate the self-exchange of metal atoms. Aqueous acetic acid solutions have been shown to cold sinter Zn powders in the production of conductive inks [1], however limited attention is focused on the development of porous Zn material by cold (chemical) sintering [2]. The present work focuses on the manufacturing of cold sintered zinc foams. The influence of the porosity, pressing temperature (RT, 60ºC, 100ºC, 150ºC) and concentration of the liquid additive was investigated and compared with Zn foams made by the classical powder metallurgy route.

The manufactured samples were analysed by scanning electron microscopy (SEM), X-ray diffraction, porosimetry and the corrosion behaviour was also evidenced.

The sintering of the Zn particles was evidenced in the SEM images, the sintering necks were formed but there are in an initial stage of sintering. This fact explains the lower compression strength of the cold sintered specimens compared to the classical sintering method (400ºC/3 h).

During the cold sintering process, a Zn acetate is forming, its decomposition was studied by thermal analysis and FTIR spectroscopy.

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# Throughout thermal characterization of ester-grafted nanocellulose

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Situated at the present in the golden age of its development, nanocellulose (NC) is a highly valuable material that has found its way as a key component in a variety of applications due to its magnificent characteristics such as its provenience from renewable resources, high surface area, excellent mechanical strength, biocompatibility, biodegradability, and the plenitude of -OH groups from its surface which open numerous possibilities for chemical modification. Describing generically any cellulosic material that has at least one dimension in the nano range, NC has been exploited since the 1990s as a reinforcing agent for polymer matrices [1]. However, the use of NC as a reinforcement for polymers at a larger scale has been severely limited by its strong hydrophilic character, which elevates compatibility issues with most organic solvents and the polymeric matrices. This problem generated a quest towards finding different routes to chemically modify the surface of NC for enhancing its surface hydrophobicity and increase its interactions and compatibility with the polymer matrices that are generally hydrophobic [2].

In this work, we proposed the one-step isolation and esterification of NC by hydrolysis with a weak aliphatic hydroxyacid derived from natural resources, to increase its surface hydrophobicity and compatibility with different polymeric matrices. The Fourier transform infrared spectroscopy revealed the appearance in the NC's spectrum, of new peaks characteristic to the C=O bonds from the ester moieties, confirming that the chemical modification of NC with the hydroxyacid took place successfully. The scanning electron microscopy (SEM) images showed that NC maintained its nano diameter following the chemical modification reaction. Thermogravimetric analysis was employed to thoroughly study the thermal stability and the kinetics of the thermal degradation of the esterified NC by comparison with those of unmodified NC.

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# Thermal stability of aliphatic polyesters recovered from hot embossing substrates

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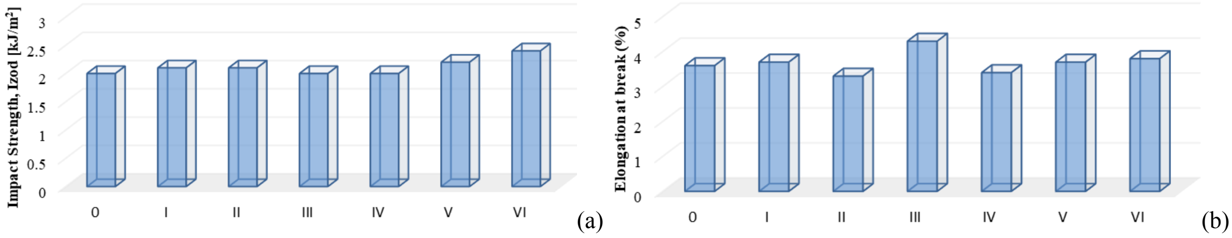
Reuse and recycling are important components of a circular economy and they are increasingly penetrating into the activity of each company, where the new products are designed to last several lifecycles. Biobased and biodegradable polymers are disposed under composting conditions, however reuse and recycling can be regarded as a more interesting option before composting. In the anti-counterfeit sector, hot embossing polymeric substrates is an efficient and cheap method in the technological cycle from the fabrication of security labels [1]. Polymethylmethacrylate or polycarbonate, which are usually employed as substrates for hot embossing, are not currently recycled or reused, due to the decay of their thermal and mechanical properties. In this work, a biobased polyhydroxyacid was tested as polymeric substrate at the hot embossing phase and recycled for determining the number of lifecycles.

The biobased polyhydroxyacid was melt processed in plates by compression molding, then the plates were hot embossed for imprinting the desired model and grounded in a mill to obtain the first grounded material that must be recycled. This cycle was repeated six times, after each cycle the material being injection molded into specimens and characterized through mechanical (tensile strength, Young's Modulus, elongation at break, and impact strength) and thermal (differential scanning calorimetry and thermogravimetric) analyses (Figure 1). Following these analyses it was concluded that the studied biopolymer can be reused six times as substrate for hot embossing because its thermal and mechanical properties are not significantly affected by recycling and reuse.



(a) (b)

Figure 1. Mechanical properties after recycling: impact strength (a), and elongation at break (b)

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# Analysis through hyphenated techniques of Pottery samples from the settlements and burial ground at Pecica – East site (Pecica, Arad County, Romania)

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The study presents the results from the analysis of pottery samples from the archaeological sites (Pecica East-Forgaci/Lucaş, Pecica-East/Duvenbeck) at Pecica-East (Pecica, Arad County, Romania). The sites are settlements and burial grounds in use during the Neolithic, the Copper Age (Aeneolithic to Bronze Age transition), as well as during the Medieval period [1-3].

The analyzed samples come from 12 pottery sherds, belonging to the Aeneolithic period (Tiszapolgár culture) and Copper Age (Bodrogkeresztúr culture). The samples cover the main types (fine, semifine, coarse and painted ware). The purpose of the analysis was to determinte the composition of the wares and firing temperatures.

The analysis was conducted using complementary techniques (TG/HF, FT-IR, XRD, SEM and XRF) [4-7].

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# Synthesis and characterisation of some metals doped hydroxyapatite with different applications

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Influence of the different metals on the doped hydroxyapatite was studied by using thermal analysis and FT-IR spectroscopy. The samples were prepared as following:

- a solution containing trimethyl phosphate calcium acetate monohydrate and in distilled water was added drop-wise in 30 minutes and at room temperature, under sonication, solutions containing zirconyl chloride hexahydrate, or barium acetate, or cadmium acetate dihydrate, or stibium trichloride, or aluminium nitrate, or kalium phosphate or silver nitrate. Molar ratio Metals/P was in all cases 1.67. After sonication, the mixture was dried.

One example of TG/DTG/Heat Flow is presented in Fig.1. with corresponding FT-IR spectra obtained before and after thermal treatment in Fig. 2.

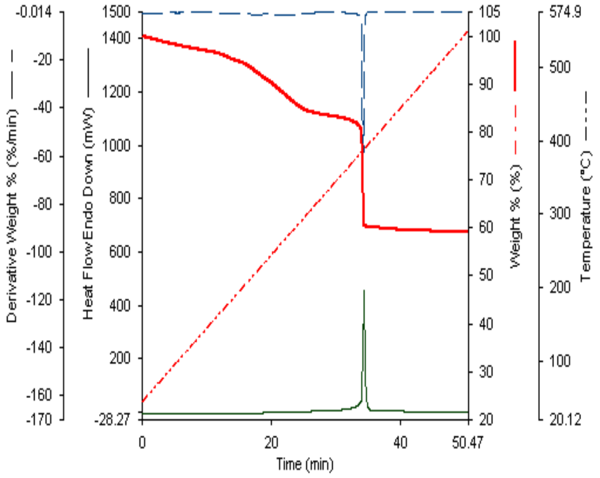

Fig. 1 TG/DTG/HF curves for sample with Zr

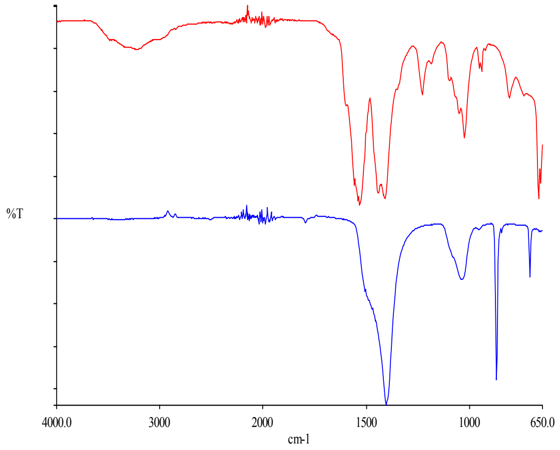

Fig.2. FT-IR spectra for sample with Zr before and after thermal treatment

[1] S. S Bandgar, T. V. Kolekar, S. S. Shirguppikar, M. A. Shinde, R. V. Shejawal, S. R. Bamane, "Synthesis, Characterization of Silver Doped Hydroxyapatite Nanoparticles for Biomedical Applications", Materials Science and Engineering: C, 9(3) (2017) 78-84.

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# Analysis of late Neolithic pottery and clay samples from the Ronaț-Triaj site (Timişoara, Timis County, Romania) using hyphenated techniques

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The study aims to analyze prehistoric ceramics consisting of pottery samples from the archaeological site Ronaț-Triaj (Timișoara, Timiș county, Romania), a late Neolithic site (4750-4500 cal BC), also inhabited during the Late Antiquity.

The analyzed samples come from 7 pottery sherds, belonging to the Foeni cultural group (dated to cca. 4920/4675-4580/4460 cal BC, the equivalent of the phase C-phase D Vinča culture). The samples cover the main categories of the Foeni cultural group (black, orange, red, including painted ware) and types (fine, semifine, coarse). To determine whether the wares were locally produced, clay samples from the site were also studied. [1-4].

The analysis was conducted using complementary techniques TG (Fig.1), FT-IR, XRD (Fig.2), SEM, XRF and LIBS) in order to determine details regarding production technology and origin of the raw materials [1, 5, 6].

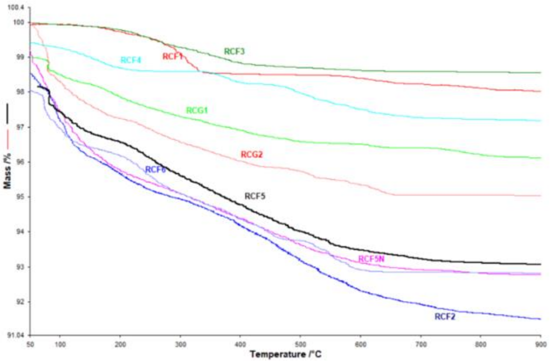

Fig.1. Comparative thermogravimetric data of ceramics samples

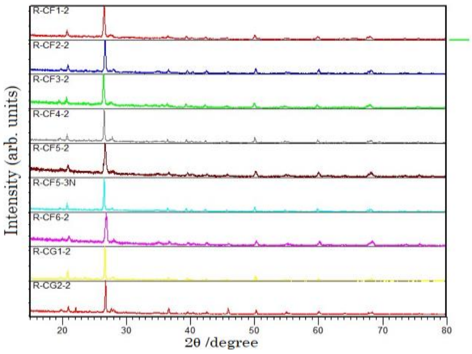

Fig.2. XRD data of ceramics samples

[1] Vlase D., Rogozea O., Moșoiu C., Vlase G., Lazău R., Vlase T. J Therm Anal Calorim 2019;
[2] Lazaraovici G. 2012; 34: 55-71.
[3] Drașovean, F. Praehistorische Zeischrift, 1997; 72: 54-80.
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[5] Shoval S, Beck P. J Therm Anal Calorim, 2005; 82: 609–616.
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# Analysis by multiple techniques of some fragments of Dacian ceramics, discovered near the Dacian fortress of Alun-Piatra Roșie (Hunedoara county)

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The 16 samples presented in this work come from the research carried out on the surface of a terrace arranged on the southern slope of the Piatra Roșie hill, in the village of Alun, Boșorod commune, Hunedoara county, Romania. In that place, a construction made of wood was identified, on the surface of the ground, having the appearance of a household. The vessel fragments come from containers specific to Dacian pottery. The archaeological literature recorded the results of research, as well as some isolated discoveries, in the form of a monograph (1) and several studies, larger or smaller in size (2).

The analysis was conducted using complementary techniques TG/DTA, FT-IR (Fig.1), XRD, SEM-EDS, XPS, X-ray Computed Tomography (XCT) (Fig. 2) and high-performance micro-focus X-ray, in order to determine details regarding production technology and origin of the raw materials.

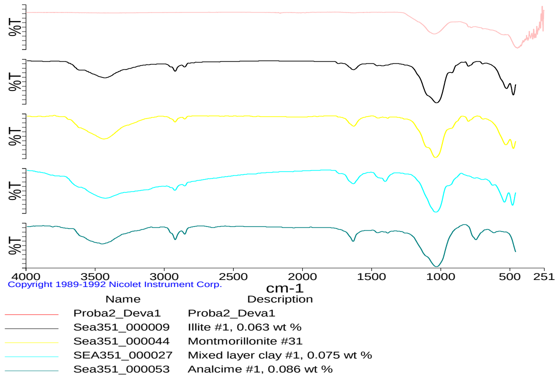
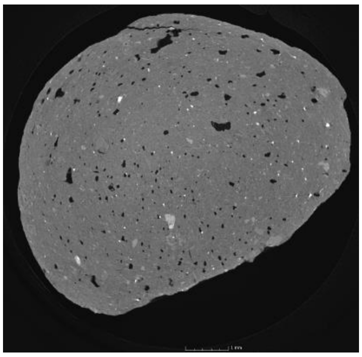


Fig. 1. FT-IR sample 2



Top view
Inclusions of up to couple of tens of microns (bright spots ) and pores up to couple of hundredts microns (black holes)

Fig. 2. Microtomography cross-sections of Sample 2

[1] Daicoviciu 1954, Constantin DAICOVICIU, Dacian Citadel from Piatra Roșie. Archaeological monograph, Ed. of the Romanian Popular Republic Academy, Bucharest, 1954.
[2] Pețan 2021, Aurora Pețan, The fortified terraced ensemble from Alun-Piatra Roșie, Archeovest IX, 2021, p. 387-419

# Influence of La additions on solidification and microstructure in the as-cast state of the alloy EN AW-7175

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The high-strength aluminium alloys of the 7xxx series, which belong to the Al-Zn-Mg-Cu system, are known for their exceptional properties and are often used for strength, fatigue resistance, stress corrosion resistance and wear resistance. The alloy EN AW-7175 requires an understanding of the precipitation process during solidification and cooling, where different phases are formed depending on the Zn/Mg ratio and cooling rate. Microstructural defects in the as-cast state affect the mechanical properties, prompting the investigation of La additions to refine the microstructure and improve the mechanical properties. In this study, the influence of La additions on the solidification and microstructure of the alloy EN AW-7175 in the as-cast state is investigated. Thermodynamic calculations, DSC and SEM analyses were performed. Samples with La additions (0.05-0.17 mass%) were compared with a reference sample (0 mass% La). La additives have only a minimal effect on the liquidus temperature and show minor differences in the solidus temperature in equilibrium calculations. The solidification interval decreases slightly compared to the reference sample, which is consistent with the Scheil simulations. The DSC results show reduced liquidus and solidus temperatures, while the solidification interval remains largely unchanged by the addition of La. The addition of La alongside $Al_{13}Fe_4$, $Mg_2Si$ and the eutectic $\alpha(Al) + \sigma[Mg(Zn, Cu, Al)_2]$ leads to the formation of two new La-based phases: $Al_{20}Cr_2La$ and $LaSi_2$. $Al_{20}Cr_2La$ modifies the $Al_{45}Cr_7$ phase and solidifies first, while $LaSi_2$ modifies $Mg_2Si$. As the La content increases, the $Mg_2Si$ content decreases until it completely disappears when the La content exceeds 0.1 mass%. On the contrary, according to literature [1-3], the grain size increases somewhat with a higher La content.

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[2] W. H. Yuan, B. L. An., Adv. Mater. Res., 152-153 (2010) 1810–1813
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# The influence of La and Ce additions on the solidification of alloys from the Al-Fe system

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Aluminium alloys are popular in modern applications due to their lightweight, high strength and ductility. Alloys in the 8xxx series have similar properties to those in the 1xxx series, but are stronger, more malleable, and have higher stiffness. The addition of rare earths (RE) can further improve the microstructure, corrosion resistance and mechanical properties of aluminium alloys at room and high temperatures.

The effects of rare earth (Ce and/or La) additions to Al-1.4Fe alloys were investigated. Thermal analysis of the solidification behaviour of the reference alloy showed the occurrence of three reactions corresponding to the formation of α-Al, eutectic (α-Al + Al-Fe phase), and Fe intermetallics, respectively. The results showed similar reactions for the Ce and/or La modified alloy, but at slightly different temperatures, indicating a change in the forming phases due to the addition of Ce and/or La. In all cases, the microstructures were typically hypoeutectic, consisting of the primary α-Al and the eutectic (α-Al + Al-Fe phase). The effect of grain refinement of the primary α-Al grains of the as-cast alloy was observed by the addition of RE, while La showed the strongest effect. The effect of the RE additions showed no obvious differences in the morphology of the eutectic Al-Fe phase, although they were present in these phases. When Ce and/or La were added, (α-Al + $Al_{11}Ce_3$) and/or (α-Al + $Al_{11}La_3$) eutectics were formed, while Fe was not detected in these eutectics.

# Synthesis of Calcium Aluminate Hydrates, their characterization and dehydration

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Calcium aluminate phases (CAP) are the main components of Calcium Aluminate Cement and the important part of Ordinary Portland Cement [1]. The hydration of CAP can be influenced by various conditions such as pH, particle size distribution, temperature, etc. The key role in the hydration of CAP plays the temperature that can influence the course of hydration as well as the formation of hydration products [2].

The aim of this work is to synthesize the pure calcium aluminate hydrates by hydration of pure CAP at different temperatures and then characterize their structure and thermal behaviour. Four CAP – CA, $C_3A$, $C_{12}A_7$ and $CA_2$ were prepared by solid-state reaction [3] and amorphous citrate sol-gel method. The purity was verified by XRD analysis. CAP were hydrated for 48 hours at different temperatures ranging from 5 to 60 °C. After hydration arresting, the products were identified by XRD analysis. The microstructure was determined by SEM. The thermal behaviour, mainly the dehydration, was measured by TG-DTA.

Hydration of $C_3A$ and $C_{12}A_7$ at high temperatures led to the formation of cubic $C_3AH_6$. $C_3AH_6$ dehydration is represented by two peaks on the DTG curve with maximums 290 – 310 °C and 425 – 440 °C. The hexagonal $CAH_{10}$ was formed during the CA hydration at 10 °C. Its dehydration is represented by the peak with maximum at 110 – 120 °C on the DTG curve. As a hydration product at other temperatures, $C_2AH_8$, $AH_3$, $C_4AH_{13}$ and $C_4A\bar{C}H_{11}$ were identified. These phases did not manage to separate, and they occurred only in a mixture.

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# Thermal analysis of two new coordination polymers based on 4,4′-bis(1H-imidazol-1-ylmethyl)biphenyl

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[2]University of Craiova, Department of Biology and Environmental Engineering, Craiova, Romania
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Coordination polymers with desired structures possess interesting functionalities and have been one of the most attractive areas in crystal engineering and supramolecular chemistry [1]. A subclass of these is the metal-organic frameworks (MOFs) - coordination networks with organic ligands containing potential voids. Research into MOFs has been motivated by the prospect of discovering new structures with enhanced functional properties such as high thermal stability that will make these materials eligible in technical processes involving heating. A suggestive method for this purpose is thermal analysis.

Two new coordination polymers have been synthesized and thermogravimetric characterized: $\{[Zn(Lig)(2,4\text{-}PyDC)]\cdot 2H_2O\}_n$ (**1**), $\{[Zn_2(Lig)(3,4\text{-}PyDC)_2]\cdot 3H_2O\}_n$ (**2**), where Lig = 4,4′-bis(1H-imidazol-1-ylmethyl)biphenyl, 2,4-PyDC = 2,4-pyridinedicarboxylate and 3,4-PyDC = 3,4-pyridinedicarboxylate. Measurements were done in a dry nitrogen atmosphere and the compounds were heated from the room temperature to 1000 °C at a rate of 10 °C/min.

Thermogravimetric trace for **1** and **2** allowed to identify the number of water molecules in the external sphere of the complexes. Both compounds lose water molecules up to 200 °C: 2 water molecules (6,2%) from (**1**) and 3 water molecules (6,5%) from (**2**). One interest was to see the effect of water removal from channels within the structures - in the absence of the guest molecules the compounds are thermally stable up to 310 - 320 °C, after that a sudden loss of 50% for (**1**) and 40% for (**2**) up to 430 °C occurs, then the compounds gradually decompose.

High thermal stability can make these materials eligible in technical processes involving heating.

**Acknowledgements:** This work was funded by the Project ANCD/20.80009.5007.04. "New materials based on coordination compounds of metals with polyfunctional ligands as porous polymers, catalysts, biologically active substances and nanostructured compounds".

# Kinetics studies on oxygen D2 diffusion in $Ag_2O$ doped YBCO-123 material

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TG and DSC analyses were performed on $Ag_2O$ doped YBCO 123 composite (0%, 5%, 10%, 15% and 20% Ag) during the whole cycle: heating with a rate of 0.17 $Ks^{-1}$, to 1373.15 K in flowing air atmosphere; cooling down to room temperature, by intercalating 12 isothermal: at 1233.15 K, 1073.15 K, 1023.15 K, 973.15 K, 923.15 K, 873.15 K, 823.15 K, 773.15 K, 723.15 K, 673.15 K, 623.15 K and 573.15 K.

The TG results were selected for the thermo kinetic (TK) analysis in terms of oxygen diffusion-controlled kinetics [1-3]. The fraction of the sample decomposed (dimensionless quantity, $\alpha$), was employed to establish the characteristic mathematical form of $g(\alpha)$ (given by Eq. 1) that was used in a (D2) diffusion model [1].

$$g(\alpha) = \alpha + (1-\alpha)\ln(1-\alpha) = \kappa t \tag{1}$$

The thermo kinetic (TK) analysis of TG-data of pure YBCO-123 sample demonstrated that the strongest oxygen accumulations occurred during two of the isotherms (at 1023.15 K, and at 723.15 K, respectively) due to D2 oxygen diffusion taking place in the framework of normal crystal lattice of the YBCO-123 phase or along the crystal surfaces and channels or fissures of imperfect product crystals. The Horowitz–Metzger [2] reasonable approximations facilitates the representation of $\ln(g(\alpha))$ over $\theta = T - T_S$ ($T$ is temperature under consideration, and $T_S$ is the inflection temperature).

A linear fit for the plots giving $\ln(g(\alpha))$ versus $\theta$ was obtained in the 1034.92 ─776.15 K range in the case of pure YBCO-123. The inflection temperature, $T_S$=1234.34 K, was established as the point from TG curve, when the mass begins to increase on cooling process. It was estimated for the activation energy a value of 1.068 eV, in a non-isothermal oxygen diffusion (in 1034.92 ─ 776.15 K range), in good agreement with Gallagher results [3].

For 5 % of Ag doping, the (D2) diffusion model was applied well for all isotherms fixed at temperatures less than 1023.15 K, for an inflection temperature of 1087.68 K. The others $Ag_2O$ doping will be also discussed.

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# Poster Session 2

# Influence of cooling rate and crystallisation temperature on the phase development in deuterated tripalmitin using DSC

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Triglycerides are important fats in defining textures of foodstuffs, in particular, chocolate, through controlling the phase behaviour during processing. Our group has carried out a number of model studies on the triglyceride, tripalmitin, by following the phase development during crystallisation using neutron diffraction [1-3]. Additionally, the influence of shear on the crystallisation was investigated. In order to carry out neutron diffraction studies, the tripalmitin used was deuterated. This paper furthers these investigations by following the crystallisation of the deuterated tripalmitin using isothermal and controlled rate crystallisation of the deuterated tripalmitin. In addition, a commercially sourced tripalmitin (Sigma Aldrich) was also investigated. Results on the influence of cooling rate as well as crystallisation temperature are reported.

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# Coupled dielectric spectroscopy and DSC for ferroelectric materials

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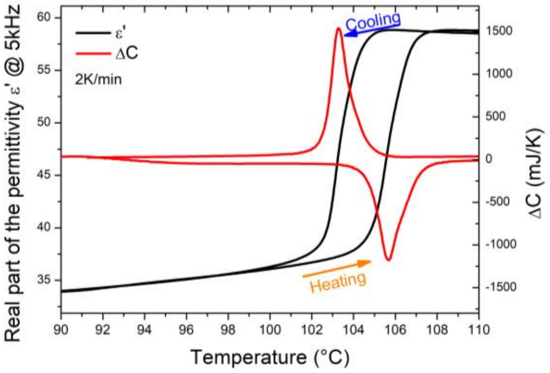
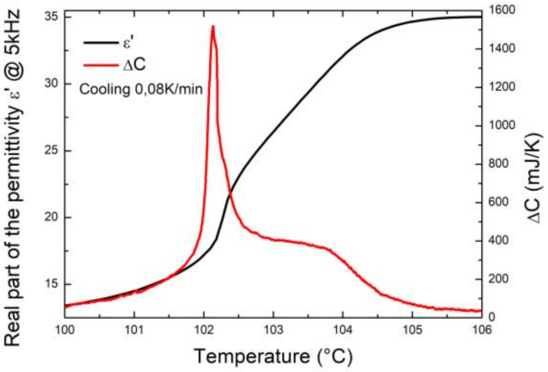
Differential scanning calorimetry allows to measure the thermodynamic parameters of phase transitions. DabcoH$^+$A$^-$ is a lead free hybrid organic-inorganic ferroelectric family of material simply synthetized from commercial and low cost molecules, namely tetragonal acids (such as $HBF_4$, $HClO_4$ or $HReO_4$) and DABCO (1,4 diazabicyclo[2.2.2]octane). Below its Curie temperature (105°C for dabcoHBF$_4$) where a great permittivity jump and an excess large specific heat are witnessed, it displays ferroelectric characteristics [1]. To better understands the coupling between the structural and dielectric phase transition we developed a differential scanning calorimeter able to record thermodynamic and dielectric properties in operando.

The system operates between -10°C and 130°C in a controlled atmosphere. The sensitivity of the instrument is typically of the order of 0.4 V/W while its time constant is about 10 s. The system has no closed crucible or pan and is based on planar sample and reference cells which are placed symmetrically within an oven. The temperature of the oven is scanned at rates ranging from ±0.005 °C/min up to ±3°C/min. The cold source is generated by a thermoelectric module. First measurements, performed on approximatively 100 mg of DabcoH$^+$BF$_4^-$ pressed powder, are shown in figure 1 and are in accordance with literature [2] [3]. Low scanning speeds and high sensitivity allow the deconvolution of fine structures that are correlated in both signals suggesting that multiple transitions occur in these materials. Perspectives of development focus on increasing the signal to noise ratio to characterize thick films of few micrometres. We present possible strategies.





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# Novel isothermal macrocalorespirometer for measuring soil microbial activity

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Calorespirometry integrates calorimetric and respirometric measurements, enabling simultaneous assessment of the overall metabolic activity of soil microorganisms by monitoring in real-time heat ($R_q$) and $CO_2$ ($R_{CO2}$) production rates. Using this method, it is possible to study the turnover of substrates and soil organic matter (SOM) at the microbial level. The current calorespirometric method follows a purely calorimetric approach, where $R_{CO2}$ is indirectly measured by quantifying the heat released during the absorption reaction in a NaOH solution ($CO_2$ trap) contained within the sample vessel alongside the soil sample [1]. This approach presents a few drawbacks, including i) indirect $CO_2$ measurements, ii) small sample size ($\geq$ 4.5 g), iii) low sample throughput, iv) unnaturally low $CO_2$ partial pressure, and v) limited oxygen availability. We present a newly developed, early-engineered isothermal macrocalorespirometer with multiple channels (up to 24 measuring units) to address these limitations. This device consists of a respirometric unit (cell filled with KOH solution for $CO_2$ adsorption) and a sample vessel with the soil sample (10 g) placed on a heat flow sensor (calorimetric unit). The heat flow sensor maintains direct contact with the heat sink, forming a complete channel. As a result, the heat release is independent of the $CO_2$ trapping. Moreover, the issues related to oxygen depletion and saturation of the $CO_2$ trap are overcome thanks to the large headspace (> 100 mL). The development process of this novel isothermal macrocalorespirometer is supported by state-of-the-art numerical simulations based on the finite-element method with COMSOL, which provide valuable insights into the instrument's sensitivity and performance. The applicability of this device was already successfully demonstrated using soil samples spiked with glucose, and numerical solutions were validated against experimental data obtained from the self-built multichannel macrocalorespirometer under laboratory conditions.

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# Selection of kinetic Method for analysis of Decomposition, Curing and Crystallization of Polymers by NETZSCH Kinetics Neo Software

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The different kinetic approaches are used in the literature for analysis of kinetic processes in polymers [1]. Therefore, the mostly frequent question must be answered: what method should be selected for specific polymer process. The work formulates the general rules for selection of kinetic method for decomposition, curing and crystallization in polymers. Additionally, we added here the mostly probable reaction type of fitting method for these polymer processes.

The decomposition of polymers can be well measured by Thermogravimetry. Easiest way for kinetic analysis is the model-free method, like Friedman, Vyazovkin or numerical. Ozawa or Kissinger methods were created for the single-step reactions and therefore usually produce good fit only for the first reaction step in multi-step reactions. Other possible method is the model-based method, but here the user must assume the reaction types. The decomposition of polymers is usually n-th order reaction, where n=1 for decomposition in liquids, and n is non-integer for phase-boundary reactions in solids. The mixture of independently decomposed materials can be described as the independent reaction steps.

Another polymer process is the curing or cross-linking. The main measurement technique of study is DSC for the exothermal effect. Additional measurement type is rheometry, which provide information about the viscosity increase during curing. The curing reactions are typically autocatalytic, where reaction rate is proportional to the product concentration. They can be described by the model-based method with Kamal-Sourour equation or its simplified forms. Additionally, some curing reactions takes place in the glass transition range where reaction rate is diffusion controlled. The vitrification and diffusion control depend on the current glass transition temperature and therefore could not be described by model-free methods. In this case we usually selects the kinetics according to diffusion control with given dependence of Tg vs conversion according to diBenedetto equation.

Crystallization process in polymers is the kinetic process too. This exothermal process can be measured by DSC and analysed by kinetic methods as well. The crystallization in the small temperature range just below melting point can be easy described by Arrhenius approach. If the crystallization for cooling should be analysed, then the influence of diffusion region near glass transition should be taken into account. Classical model is the Nakamura model with Hoffmann-Lauritzen theory and Avrami dependence on conversion. But the better solution for many polymers is obtained by Sbirrazzuolli model [2] with Hoffman-Laurithen theory for diffusion and Sestak-Berggren model for nucleation term.

The work contains many kinetic application examples for each of these processes.

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# Thermal Inspection of a ‘Green’ Epoxy Adhesive

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Epoxy resins are versatile materials widely used in manufacturing industries, since they provide excellent mechanical properties, adhesion, and chemical resistance. They are characterized by formation of strong, durable bonds, which makes them indispensable in numerous applications [1]. The current work investigates the thermal behaviour of a ‘green’ epoxy resin cured in the presence of different diamines. Both Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) are utilized for the study. The first technique reveals the enhanced thermal stability of the crosslinked network, compared to the structure prior to polymerization. On the other hand, the subsequent method displays the exothermal events of curing, as well as the variation in the polymerization peak, the curing completion temperature and the glass transition temperature, depending on the diamine involved in the procedure. Differential Scanning Calorimetry is further used in the evaluation of isothermal experiments, aiming in the determination of the time needed for the crosslinking to evolve. Once cured, epoxy adhesives form a rigid and durable structure, making them appropriate for demanding applications [2]. As a result, a comprehensive thermal evaluation is crucial when targeting in upgraded end product properties.

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## Funding information

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# Evaluating the thermal performance of selenides synthesized by ball milling and pack cementation for thermoelectric applications

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The operation of internal and external operating lifts and elevators requires the installation of additional functions in the elevator cars, including air conditioners, towards people's comfort. However, the use of conventional air conditioners has a detrimental effect on the construction level, energy consumption, noise level in the car, and the environment. An innovative method that can be applied alternatively in order to overcome most of these problems is the use of suitable thermoelectric air conditioners. In this direction, thermal storage plays a key role to lower building energy consumption. The thermoelectric materials community has made significant progress on nanostructured and process-able materials to improve efficiency and flexibility, reducing manufacturing costs. Selenide compounds, such as $Ag_2Se$ and $Cu_2Se$, have received a lot of attention because of their promising capabilities in thermoelectric applications. Additionally, Ag, Cu, and Se are less toxic than common materials used for thermoelectrics (such as Bi, Pb, Sb, and Te), while Se is about 10 times more abundant than Te.

Two different methods for the synthesis of $Ag_2Se$ and $Cu_2Se$ compounds have been used. The first one is the high-energy ball milling (HEBM) process, which is a powerful solid-state synthesis/powder mechanical alloying method, using different milling times (1-20 hours). The second one is the simple, cost-effective, and eco-friendly technique of chemical vapor deposition by pack cementation (CVDPC). In this case, the synthesis of samples is the result of a reactive diffusion process due to the reaction of the donor materials with the products of the halide activator.

The structural and morphological characterization of the synthesized selenides was studied by Fourier transform infrared spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy and scanning electron microscopy. The thermal stability of the prepared samples was examined by thermogravimetric analysis (TGA). Both the thermoelectric $Ag_2Se$ and $Cu_2Se$ phases were successfully synthesized, by HEBM and –for the first time- by CVDPC. Furthermore, $Ag_2Se$ synthesized with both methods was remarkably stable up to 400 °C, considering its maximum Figure of Merit at 40 °C, as reported from previous studies.

**Acknowledgments:**
This research was carried out as part of the project «Design and implementation of innovative lift's air-conditioning systems by using thermoelectric devices» (Project code: KMP6-0074109) under the framework of the Action «Investment Plans of Innovation» of the Operational Program «Central Macedonia 2014 2020», that is co-funded by the European Regional Development Fund and Greece.

# In-situ monitoring the curing evolution of pMDI with soy-bean protein using a DRIFT environmental chamber

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Polymeric diphenylmethane diisocyanate (pMDI) is a formaldehyde-free resin that shows great promise as an adhesive for wood and wood-composite applications. Soybean protein, a commonly extracted by-product during the production of soybean oil, is chosen to act as the filler in order to align with circular economy principles and to reduce cost expenses.

The aim of the present study is to explore the ability of diffuse reflectance FTIR (DRIFT) spectroscopy (Fig. 1a) to follow the *in-situ* curing of resins. To address measurement issues stemming from contamination of the environmental chamber's sealing window, various sample crucibles and gas flows were employed. The study is further supported by differential scanning calorimetry (DSC), thermogravimetry (TGA), and conventional attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy.

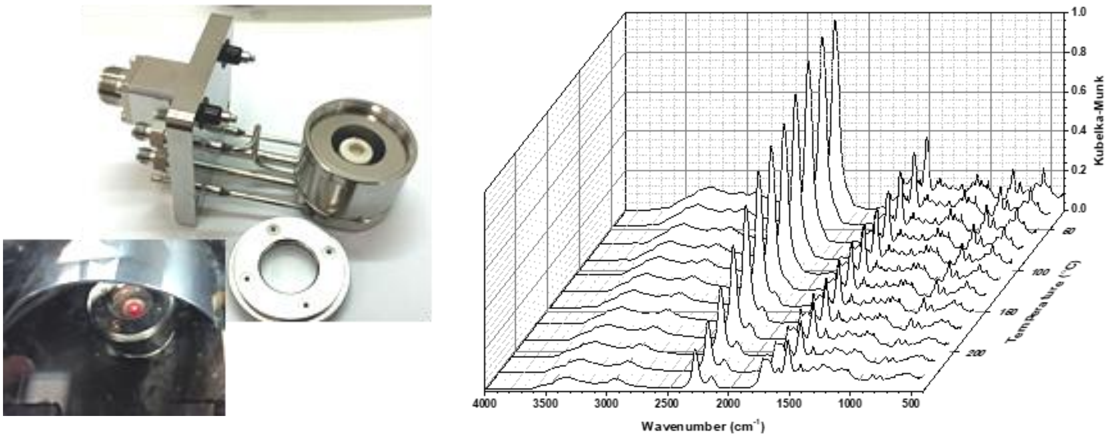

**Figure 1.** DRIFT environmental chamber (a) and *in-situ* collected DRIFT spectra showing the curing evolution of pMDI with soy protein.

The results showed the successful *in-situ* observation of pMDI curing with soy-bean protein (Fig. 1b), because of the decrease in isocyanate and hydroxyl groups at 2274 and 3300 cm$^{-1}$, respectively, and the emerging of a new band at 2140 cm$^{-1}$, suggesting the formation of a carbodiimide group. Restrictions regarding the type of crucibles used, the applied gas flow, and the sample/KBr ratio for the measurements are noted.

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# Investigating the impact of PACAP on thermal stability of G-actin by differential scanning calorimetry

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Pituitary adenylate cyclase activating polypeptide (PACAP) is a bioactive peptide known for its diverse effects within the nervous system. While numerous studies have demonstrated the neuroprotective properties of PACAP, its role in tissue regeneration and potential as a therapeutic agent remains to be fully understood. Specifically, the understanding of PACAP's impact on cytoskeletal dynamics, particularly the organization and disorganization of actin filament networks, is limited due to the scarcity of *in vitro* studies in this area. Additionally, the interaction between PACAP and actin has been minimally explored, and the influence of PACAP on the thermal stability of actin is completely unknown.

To address these gaps, the current study aimed to investigate the impact of different forms and fragments of PACAP on the thermal denaturation and renaturation of $Ca^{2+}$-G-actin using a differential scanning calorimetry (DSC) approach. Our primary objective was to determine whether PACAP modulates the thermal stability of $Ca^{2+}$-G-actin and establish a temperature-dependent pattern of any structural alterations that may occur as a result of PACAP interaction.

In PACAP38 + $Ca^{2+}$-G-actin mixture the DSC scans exhibited a mild decrease of actin denaturation temperature compared to the control, plus an exotherm appeared in the high-temperature range with a significantly increased calorimetric enthalpy. The truncated PACAP27 produced a slight increase in actin denaturation temperature with the same exotherm without significant alteration in enthalpy. In PACAP6-38 there was no change in denaturation temperature of actin and no plus exotherm, but significant $\Delta H_{cal}$ was observed. The PACAP6-27 modification exotherm was absent but the actin denaturation temperature and enthalpy increased compared to the control actin.

Through this research, we sought to elucidate the underlying mechanisms of PACAP's effects on actin dynamics and provide valuable insights into the potential therapeutic applications of PACAP in the context of cytoskeletal organization and neuronal regeneration. The findings of this study may contribute to the development of novel strategies targeting actin-related processes for neuroprotection and neural tissue repair.

# $Ca^{2+}$ dependent thermal sensitivity of bacterial MreB assemblies

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In the bacterial cells, the actin homolog, MreB manages the cellular motions and morphology. Play an important role in cell-wall growing and cell shape determination. In vivo studies with fluorescence microscopy images of bacterial cells have shown that the MreB polymer, forms cable-like structures that spiral around the periphery of the cell. As we presented earlier, the thermal motion of the ribbon-like MreB polymers was slowed down by the addition of 2 mM $Ca^{2+}$. The rapid calcium depletion, via EGTA treatment, reordered the polymers into extensive sheets in the presence of magnesium, and further treatment with calcium led to fissured monolayer sheets and the dissociation of filaments into web-like structures which attached to the glass surface.

E.coli MreB was heterologously expressed and purified from E.coli using a filtration method to prepare MreB polymers. The heat denaturation of MreB assemblies, under varying $Ca^{2+}$ concentrations, were investigated by DSC, and the $Ca^{2+}$ dependent MreB polymer rearrangement rates were assessed by isoperibol calorimetry.

Here, we measured $Ca^{2+}$ dependent thermodynamics of prokaryotic MreB assemblies. Under high ionic strength, the MreB polymers show multiple thermal components around 60 °C and 82 °C, as less and more stable components, respectively. MreB polymers with a relatively slow exothermic kinetics turned to be more stable due to adding 2 mM $Ca^{2+}$. However, changing the calcium concentration from 0.2 to 0 mM and subsequently recovered it to 0.2 mM initialized endothermic remodelling of MreB assemblies and the majority of them showed higher stability than before the treatment.

Presumably, the final cell shape will be a product of the MreB properties and the ionic milieu. Calcium concentration-induced changes of MreB structure may also participate in membrane remodelling during prokaryotic cell division or osmotic adaptation.

# The influence of temperature and sulfation on Funori gel formation

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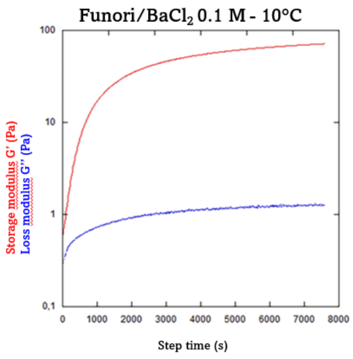
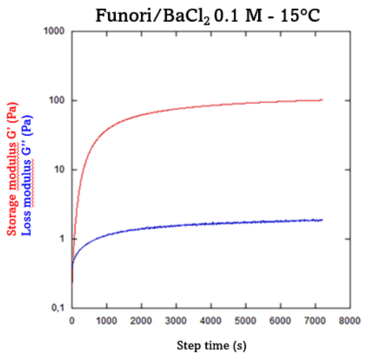
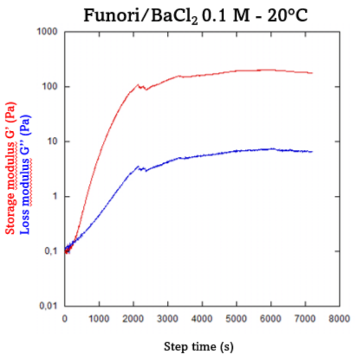
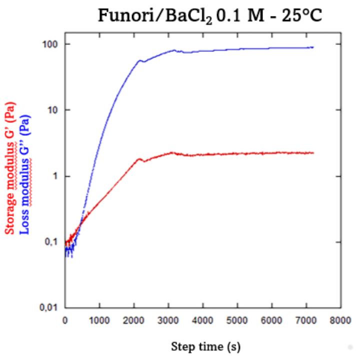
The thermal properties and rheology of Funori, the polysaccharide derived from red algae *Gloiopeltis,* were investigated in this study. It has been demonstrated how metal ions enhance funoran gelation with $Ba^{2+}$ ions having a clearly higher gel-inducing effect [1]. For this reason, the aim of this work is to study the effects of the addition of $BaCl_2$ on 1% *w/w* Funori solutions observing the process of gelling kinetic at different temperatures (10, 15, 20, 25 °C) and salt concentrations (0.05 M, 0.1 M, 0.2 M). The samples were characterized by differential scanning calorimetry and dynamic rheometry. $BaCl_2$ solutions exhibited a strong effect on the gelling formation: with enhancing salt concentration, storage modulus (G') and loss modulus (G'') increased in the selected concentration range. Observing Funori gelling kinetics it was found a directly dependence of gelling point by both concentration and temperature, firstly reached enhancing concentration and decreasing temperature. The addition of $BaCl_2$ and its relative sulfation remarkably affects Funori rheological properties. It does not gel without added ions, but it is able to form strong gels with a relatively high amount of inorganic cations. Decreasing temperature and enhancing concentration a strong gel is obtained. The good ability to form transparent and strong gels makes Funori a promising hydrocolloid for cultural heritage surface cleaning, especially in those cases where high temperatures must be avoided.









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# Clay-Based Drug Delivery: Advancing Controlled Release with Montmorillonite and Kaolin

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In recent years, the field of pharmaceutical sciences has shown growing interest in controlled drug release, a crucial area of research. Regulating drug release over time offers significant advantages in enhancing therapeutic efficacy and ensuring patient compliance. One promising approach in this research is the utilization of clays like montmorillonite and kaolin for developing controlled drug delivery systems.

Clays are naturally occurring minerals with unique physicochemical properties such as high surface area, porosity, and ion exchange capabilities. These attributes make clays highly attractive as carriers for various pharmaceutical compounds. Montmorillonite and kaolin clays, in particular, have received considerable attention due to their abundant availability, low cost, and biocompatibility, making them ideal candidates for pharmaceutical applications.

By incorporating drugs into clay-based matrices, controlled drug release can be achieved through mechanisms like diffusion, ion exchange, and clay structure swelling. The interlayer spaces of clay minerals provide an optimal environment for trapping and sustained drug release. Additionally, modifying the surface properties of clays can enhance drug loading capacity, control release kinetics, and improve drug formulation stability.

This work aims to explore the potential of montmorillonite and kaolin clays for controlled drug release applications. To achieve this, soluble and poorly water-soluble drugs were studied, with Metronidazole antibiotic and Nile Red representing these two classes of compounds. Nile Red, a cost-effective model drug with behaviour sensitive to the surrounding medium similar to chemotherapy pharmaceuticals, was used in place of actual pharmaceutical compounds for this project.

Equilibrium and kinetic adsorption studies were performed to examine the impact of external and internal factors (type of clay, pH levels, adsorption protocols, adsorbent doses, and initial drug concentrations..) on drug adsorption.

The prepared clay-drug hybrids were extensively characterized using techniques like XRD, FT-IR, DSC, TGA, and UV-Vis spectroscopy. These analyses provided insights into the kinetic and equilibrium behaviours of the systems and helped identify the most effective clay-based drug delivery system. Such a system not only facilitates drug delivery but also protects against photodegradation and oxidation processes.

The study also investigated drug release under conditions simulating oral drug administration. The analysis demonstrated that the novel drug/clay systems improved drug bioavailability and targeted release, mitigating common adverse side effects associated with chemotherapy and antibiotic therapy.

# Thermodynamic study of 1,4-bis(3-methylimidazolium-1-yl)butane bis(triflyomethylsulfonyl)imide ([C4mim][$NTf_2$]$_2$) from 6 to 350 K

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Since the beginnings of the research on ionic liquids (ILs), the classes of organic salts with a 1,3-dialkyl imidazolium cation and the bis(trifluoromethyl)sulfonylimide ($NTf_2$) anion is one of most widely investigated among aprotic ILs [1]. The reason is probably due to their high thermal stability, closely related to the scarce nucleophilicity of the anionic portion [2]. In searching for improved variants of the well-known alkylimidazolium $NTf_2$ ILs with lower volatility and good thermal stability at relatively high temperatures, ILs with a dipositive cation (DILs, Dicationic Ionic Liquids) were more recently considered. In these $NTf_2$–based compounds, the doubly charged cation with two alkylimidazolium rings linked by a $(CH_2)_n$ chain, with $n$ ranging from 1 to 10, or more. It was recently shown that DILs have some physical and chemical properties potentially more attractive for applications than those of their monocationic counterparts [3]. Despite this interest, the thermodynamic characterization of DILs is presently very scarce in the literature. To the best of our knowledge, the only studies reported so far are focused on the evaporation of the DIL with the $n = 3$ linker and a methyl group on the imidazolium rings [4,5]. In particular, no study is reported on the heat capacity of any member of this family and no thermodynamic functions are currently available both in the condensed and in the vapor phase.

Therefore, in the present study, the molar heat capacity of solid 1,4-bis(3-methylimidazolium-1-yl)butane bis(triflyomethylsulfonyl)imide dicationic compound ([$C_4$mim][$NTf_2$]$_2$) has been measured over the temperature range from 6 to 350 K by a precise automated adiabatic calorimeter. The standard thermodynamic functions of the studied compound, namely, the heat capacity $C°_{p,m}(T)$, the enthalpy change $[H°(T) – H°(0)]$, the entropy $S°(T)$ and the Gibbs free energy change $[G°(T) – G°(0)]$, have been calculated on the basis of the experimental data for the temperature range explored.

Keywords: dicationic ionic liquids; $NTf_2$ anion; heat capacity; adiabatic calorimetry

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# Blends of biodegradable polymers: morphology, mechanical and thermal properties

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Biopolymers, and more specifically biodegradable polymers, are considered as the potential substitute of petroleum-based polymers to comply with the objectives of the Zero Pollution Action Plan, which is one of the policy areas of the EU Green Deal. The renewable resource origin of biopolymers and their biodegradability or compostability provide an advantage over conventional polymers [1]. Among biodegradable polymers PLA, PBAT and PHBV are noteworthy but they show advantages and disadvantages. PLA is the most used thanks to its high biodegradability and acceptable cost, but the low elongation, low impact strength and low heat of deflection temperature have been reported in literature. PBAT is a biodegradable copolymer with high flexibility, which allows its use only in specific applications while PHBV has similar properties to polypropylene but it is stiff and brittle. The blending concept of polymers is an effective, and economical alternate way of acquiring new materials with acceptable properties [2]. The effective blends can provide advantage over the individual polymers in terms of physical and mechanical properties. Despite several works on binary blend formulations are available in the literature that highlight limitations on the improvement of mechanical properties [3], only a few authors have studied the properties of PLA/PBAT/PHBV ternary blends.

In this work binary/ternary biodegradable polymer blends of PLA, PHBV and PBAT were fabricated by a twin-screw extruder followed by injection molding. A successful attempt has been taken to obtain PLA/PHBV/PBAT blends with properties comparable to that of certain commodity polymers. Mechanical properties have been studied by tensile, bending and Charpy impact tests, while the thermal properties by DSC and TGA analyses. In particular, new insights are provided into their thermal degradation kinetics and mechanisms and how the blend composition affects their thermal stability.

Keywords: biopolymers; thermal properties; thermogravimetric analysis; kinetics; mechanical properties

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# New DSCvesta2 with cutting-edge $\chi$ sensor® and self-diagnosis function

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Rigaku has developed a new DSCvesta2 equipped with a cutting-edge Sensor Technology, $\chi$ sensor® and a self-diagnostic function.

**Cutting-edge $\chi$ sensor®**: Equipped with the ground-breaking "$\chi$ sensor®", Rigaku's DSC is a new model that combines toughness and high sensitivity, enabling atmospheric measurements up to 600°C. The $\chi$ sensor sample stage features guide prongs for enhanced sample pan positioning reproducibility, ensuring high-precision results for everyone. Moreover, our unique signal processing technology significantly reduces noise levels.

Fig. 1 Cutting-edge $\chi$ sensor®

**ΔBlock**: Adopts the revolutionary "ΔBlock" structure, which controls heat transfer between the furnace and cooling unit based on temperature zones. It efficiently conducts heat in low-temperature ranges and insulates in high-temperature ranges, enabling efficient cooling and heating. This unique design allows us to harness the maximum cooling performance of the cooling unit, achieving a heating capability up to 725°C when any cooling units are installed.

**Vestaeye**: Equipped with the industry-first self-diagnostic feature, "vestaeye", our device provides numerous benefits through constant monitoring of its status.

1. Self-diagnosis begins upon device start up, ensuring peace of mind even during measurement initiation.
2. Avoid sample loss due to errors during the process by detecting anomalies before starting measurements.
3. Verify the device's normal operation before executing measurements after a period of inactivity or prior to night time operations.
4. Identify specific areas of concern when abnormalities occur in the device.
5. Achieve seamless service support through clear identification of device status.

**Sample observation capability**:
The temperature range for DSC measurements is extended to -70°C to 725°C even when the sample observation unit is installed, and the measurements can be performed in combination with an auto sample changer (ASC).

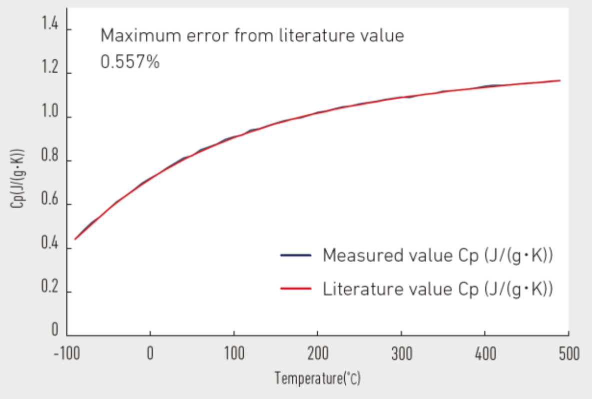

Fig. 2 Cp measurement example of sapphire

# Preparation of α-alumina by combustion synthesis and observation of the thermal behavior of its formation process

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Alumina ($Al_2O_3$) is one of the most widely used materials in various industrial applications, such as ceramic materials, catalyst supports, and adsorbents. In particular, α-alumina is the most chemically stable form, and there has recently been demand for higher functionality through finer particles.

In this study, we attempted to prepare α-alumina through combustion synthesis [1] using mixtures of aluminum nitrate and various types of fuel as starting materials. The fuels used included urea, hydroxyl urea, methyl urea, dimethyl urea, and guanidine nitrate. This method enables α-alumina to be obtained at lower temperatures compared to the conventional method, which involves using aluminum hydroxide as a starting material and heating it to temperatures over 1200 °C.

The mixtures were heated in a furnace ranging in temperature from 300 °C to 1150 °C, and the resulting combustion residues were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM).

As a result, α-alumina could be obtained at relatively low temperatures of 400 °C to 900 °C only when the urea and hydroxyl urea as fuels were mixed in double the amount of the oxidizer, aluminum nitrate. Low-temperature α-alumina formation prevents particle agglomeration and produces submicron particles.

Thermogravimetry-differential thermal analysis/mass spectrometry (TG/DTA/MS) measurements were performed on each sample to investigate the reaction mechanism of α-alumina formation. The results suggested that the key to the formation of α-alumina is the reaction of isocyanic acid derived from urea or its intermediates with the alumina precursor formed from aluminum nitrate.

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# Individual effects of water vapor and carbon dioxide on the thermal decomposition of calcium carbonate

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The reversible reaction of the thermal decomposition of $CaCO_3$ and carbonation of CaO has attracted attention because of its potential for a sustainable energy storage technology. Kinetics of the thermal decomposition is affected by both water vapor and $CO_2$. The universal kinetic description over different atmospheric conditions is necessary for better kinetic understanding. This can be done by introducing an accommodation function (AF) in the kinetic equation.[1,2] In this presentation, kinetic parameterizations of the effect of atmospheric water vapor and carbon dioxide on the thermal decomposition of $CaCO_3$ are demonstrated.

The thermal decomposition of $CaCO_3$ was tracked by TG under various heating programs in a stream of $N_2$–$H_2O$ mixed gas or $N_2$–$CO_2$ mixed gas characterized different partial pressure of water vapor ($p(H_2O)$) and $CO_2$ ($p(CO_2)$), respectively. The reaction is accelerated by the atmospheric water vapor, which is expressed by the kinetic equation with the AF of $p(H_2O)$.[1)]

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right) f(\alpha)\left(p(H_2O)\right)^a \qquad (1)$$

Whereas, atmospheric $CO_2$ retards the reaction. Moreover, the self-generated $CO_2$ can also affect the kinetics. The kinetics in the presence of $CO_2$ is expressed by using an AF of $p(CO_2)$ and equilibrium pressure ($P_{eq}(T)$) with four parameters ($a$, $b$, $c$, $d$).[2)]

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right) f(\alpha)\left(\frac{1}{p(CO_2)}\right)^a \left[1-\left(\frac{p(CO_2)}{P_{eq}(T)}\right)^b\right] \qquad (2)$$

$$;\, p(CO_2) = c \cdot p(CO_2)_{SG} + d \cdot p(CO_2)_{ATM}$$

Based on Eqs. (1) and (2), the thermal decomposition of $CaCO_3$ can be universally described under individual conditions of water vapor and $CO_2$, as illustrated for the universal isoconversional kinetic relationships in Fig. 1.

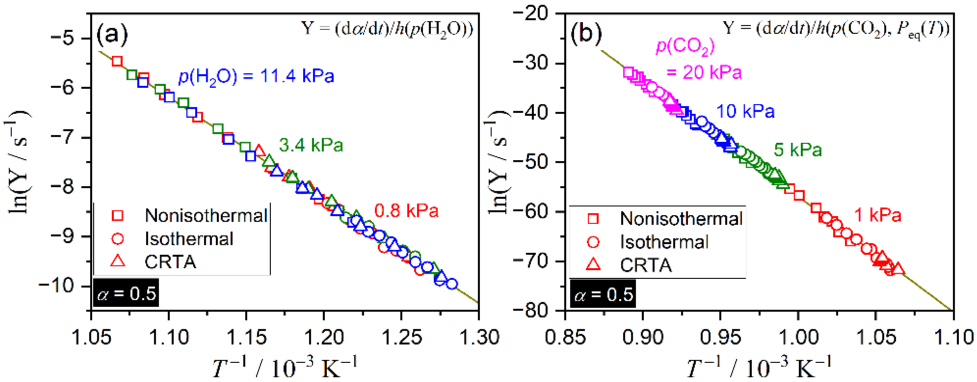

**Figure 1.** Universal Friedman plot for the thermal decomposition of $CaCO_3$ considering the effect of atmospheric gas: (a) water vapor and (b) carbon dioxide.

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# Effect of self-generated carbon dioxide on the thermal decomposition of zinc carbonate

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The thermal decomposition of $ZnCO_3$ is retarded by $CO_2$ attributed to the reversible reaction scheme: $ZnCO_3 \rightleftarrows ZnO + CO_2$. Introduction of an accommodation function comprising $CO_2$ partial pressure ($p(CO_2)$) values and equilibrium pressure ($P_{eq}(T)$) makes it possible to analyse kinetic data universally over different $p(CO_2)$ conditions and temperatures [1,2]:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right) f(\alpha)\left(\frac{1}{p(CO_2)}\right)^a \left[1-\left(\frac{p(CO_2)}{P_{eq}(T)}\right)^b\right] \qquad (1)$$

Furthermore, effective $p(CO_2)$ value during the reaction is calculated by estimating the respective contributions of self-generated and atmospheric $p(CO_2)$ ($p(CO_2)_{SG}$ and $p(CO_2)_{ATM}$, respectively) based on the eq.(2) [2].

$$p(CO_2) = c \cdot p(CO_2)_{SG} + d \cdot p(CO_2)_{ATM}, \qquad (2)$$

where $c$ and $d$ are the contributions of $p(CO_2)_{SG}$ and $p(CO_2)_{ATM}$, respectively. A universal kinetic description based on eqs.(1) and (2) was achieved through kinetic analyses of TG curves for the thermal decomposition of $ZnCO_3$ in a stream of $N_2$–$CO_2$ mixed gas characterized by different $p(CO_2)_{ATM}$ values, i.e., 5, 10, 20, and 40 kPa, by optimizing ($a$, $b$, $c$, $d$) in eqs.(1) and (2) (Fig.1 (a)). The established kinetic relationship can be extrapolated to the reaction in an inert gas atmosphere, enabling to estimate the effect of $p(CO_2)_{SG}$ on the thermal decomposition in an inert gas atmosphere. This novel procedure to estimate the effect of $p(CO_2)_{SG}$ was successfully demonstrated for the thermal decomposition of $ZnCO_3$ in a stream of dry $N_2$ and air (Fig. 1(b)).

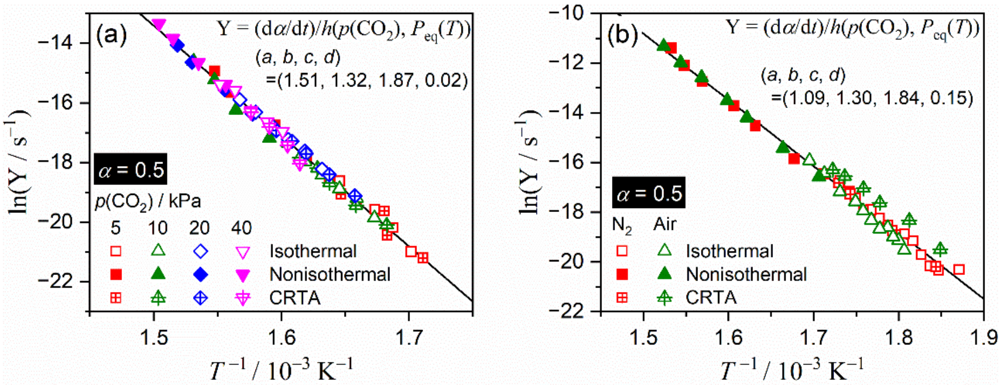

**Figure 1.** The universal Friedman plots of thermal decomposition of $ZnCO_3$ at $\alpha = 0.50$ using the optimized exponents ($a$, $b$, $c$, $d$) in eqs.(1) and (2): (a) in a stream of $N_2$–$CO_2$ mixed gases and (b) in a stream of dry $N_2$ and air.

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# Effect of induction period on activation energy of fluorine containing elastomer obtained by ISO 11358-2

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The thermogravimetric analysis (TGA) of tetrafluoroethylene-propylene elastomer (TPE) was studied with the authority of ISO 11358-2 [1] to obtain the activation energy of the thermal degradation. But the activation energy obtained by the analysis of TG curves of the higher heating rate was different from that of the lower heating rate [2]. This article tried to find out this reason. To investigate this matter, four kinds of thermally pre-aged samples were prepared by changing the thermal aging time at 250ºC. The aging time was 24 h, 49 h, 120 h and 240 h. The weight retained after the aging was 99.7%, 99.0%, 94.0%, 75.0% restrictively. TG curves of each sample were measured, and analysed with reference to ISO 11358-2.

Figure 1 shows the analysed result of the TG curves whose pre-aged time was 24 h. The bending point was observed, which tendency was same as non-pre-aged sample [2]. On the other hand, the analysed result of the sample whose pre-aged time was 120 h showed the straight line as shown in Figure 2. This result satisfied the requirement of this standard which say that the line shall be straight and has to be parallel each other. The difference between the result shown in Figure 1 and Figure 2 might be due to the induction period. An induction period is completed by the thermal aging for 120 hours at 250 ℃.

As mentioned above, the effect of the induction period should be considered for obtaining the activation energy using ISO 11358-2.

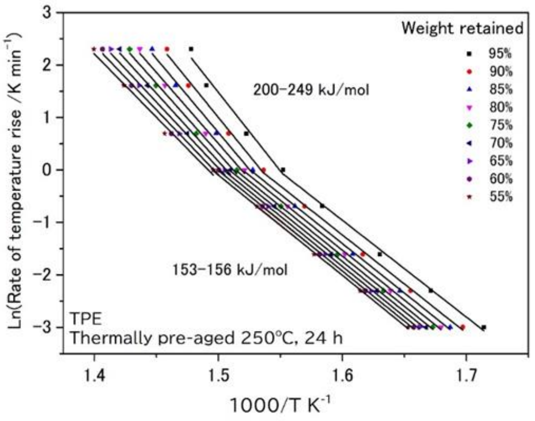

Fig.1 Sample of pre-aged for 24 h

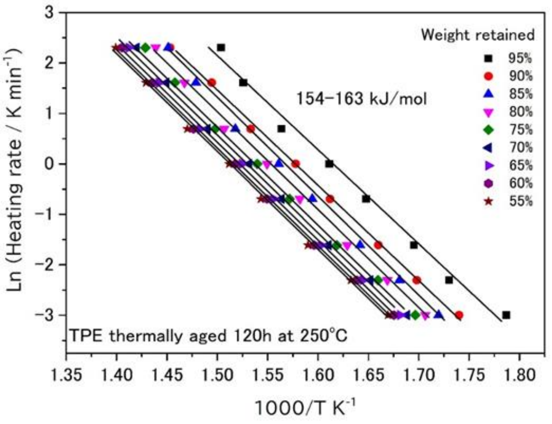

Fig.2 Sample of pre-aged for 120 h

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# Physico-geometrical mechanisms and kinetics of the thermal dehydration of sugar hydrates accompanied by liquefaction

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Thermal decomposition/dehydration of solids exhibits complex kinetic behaviours, when various physical phenomena including melting, glass transition, and cold crystallization of reactant and products participate at a specific stage of the reaction. Contribution of a physical phenomenon dramatically alters the reaction behavior due to the changes in the state of reactant/product and geometrical constraints of the reaction [1,2]. Thermal dehydration of sugar hydrates shows such type of behavior. Herein, physico-geometrical mechanisms and kinetics of the thermal dehydrations of β-maltose monohydrate (BM-MH) [3], trehalose dihydrate (TH-DH) [4], and D-glucose monohydrate (DG-MH) [5] are discussed and compared.

Upon linearly heating these sugar hydrates, the partial liquefaction occurs midway through the thermal dehydration in all cases. The liquefaction is owing to the glass transition of the amorphous surface product in BM-MH, whereas melting of the reactant occurs during the thermal dehydrations of TH-DH and DG-MH. In both cases, certain core–shell structures are produced by the liquefaction: solid reactant core–supercooled liquid shell in BM–MH and molten reactant core–solid product shell in TH-DH and DG-MH. The subsequent thermal dehydration proceeds in a complex manner with the physico-geometrical constraints owing to the respective core-shell structures. The reacting particles coalesce and further form a dome in the thermal dehydration of BM-MH [3] exhibiting the corresponding changes in the mass loss behavior. In the case of TH-DH, melting of α-trehalose anhydride in the surface product layer and crystallization of β-trehalose anhydride occur to complete the thermal dehydration before the melting of β-trehalose anhydride [4]. DG-MH also exhibits two-step mass loss process after the core–shell structure was developed.

The solid-state thermal dehydration of these sugar hydrates can be followed at temperatures lower than the glass transition temperature of amorphous BM anhydride or the melting point of TH-DH and DG-MH. The solid-state thermal dehydrations of these sugar hydrates are described by different physico-geometrical mechanisms. The thermal dehydration of BM-MH shows the diffusion-controlled rate behavior with the apparent activation energy ($E_a$) of ~140 kJ mol$^{-1}$ [3]. The physico-geometrical consecutive surface reaction and phase boundary-controlled reaction (SR–PBR(*n*)) is applicable to the thermal dehydration of TH-DH [4]. Presence of the induction period and subsequent auto-catalytic mass loss behavior are characteristics of the thermal dehydration of DG-MH.

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# Dismantlability of epoxy adhesive containing inorganic/organic composite fine particles

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In recent years, with the growing need for recycling, there has been much research on dismantlable adhesives that enable joints to be separated by providing a stimulus such as heating after a period of use[1]. The author's previous research revealed that epoxy adhesives mixed with inorganic salts containing halogens in their structure, such as ammonium iodine ($NH_4I$), lost their adhesive strength by heating at 270°C, lower than that of filler-free epoxy adhesives [2]. These adhesives are expected to be used as dismantlable adhesives.

In this study, we focused on composite particles as a novel filler to reduce the dismantling temperature. The filler was prepared by spray-drying $NH_4I$ and 3 wt% carboxymethyl cellulose ammonium salt (CMCA) solution. Moreover, we evaluated the dismantlability and decomposition characteristics of epoxy adhesives containing the prepared $NH_4I$/3 wt% CMCA composite.

Measurements of the adhesive strength before and after heating clarified that the adhesive containing $NH_4I$/3 wt% CMCA composite had a lower dismantling temperature (250°C) than filler-free adhesive (350°C) and the adhesive containing pure $NH_4I$ (270°C), which is a relevant result meeting the purpose of this study. On the other hand, the initial strength before heating also decreased in the samples with $NH_4I$/3 wt% CMCA composite compared to the filler-free adhesive. This drawback was overcome by increasing the content of CMCA in the composite particles or using guar gum instead of CMCA. Adhesives with composite particles containing 5 wt% and 7 wt% CMCA and 3 wt% guar gum retained their initial strength close to that of filler-free adhesive, and so are suitable as dismantled adhesives.

The results of thermal gravimetric-differential thermal analysis (TG-DTA) showed that pure $NH_4I$ decomposed at around 320°C with mass loss due to decomposition. In contrast, with the $NH_4I$/CMCA composite, the mass loss occurred at approximately 30°C lower temperature. The fact that epoxy adhesives with the filler decomposed at almost the same temperature suggests that the reaction between $NH_4I$ and CMCA or its decomposition products triggered the decomposition of the epoxy adhesives.

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# The adsorption kinetic parameters of phosphorus by calcium silicate hydrated based adsorbent

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Although phosphorus is an essential nutrient for plant and animal growth, excessive levels of phosphorus in water degrade water quality and lead to eutrophication [1]. Phosphorus enters mainly water systems through agricultural runoff and wastewater discharge [2]. For this reason, it is necessary to remove excess phosphorus from contaminated water sources and control its concentration in wastewater. Both objectives can be achieved by creating and applying adsorbents with high selectivity and adsorption capacity for phosphorus [3]. In addition, these adsorbents should not be toxic. Such adsorbents can be produced using calcium silicate hydrates. For this reason, this work aims to synthesise adsorbent based on calcium silicate hydrates and determine its adsorption kinetic parameters for phosphorus.

The absorbent was synthesised under hydrothermal conditions (200 °C, 16 h) using suspension of fine grounded and calcined polonite (Ecofiltration sp. z o.o., Poland) and fine grounded calcium oxide. The molar ratio of calcium oxide and silicon dioxide was equal to 1.5 while the water to solid ratio was 10. It was determined, that during hydrothermal treatment, the intensive interaction between primary compounds proceeded resulted to the formation of calcium silicate hydrates (tobermorite, α-C2SH, C-S-H(I), and C-S-H(II)).

Bath experiments were used for the adsorption of phosphorus ions by synthetic adsorbent, that is, 10 g of adsorbent were poured into 1 L of $KH_2PO_4$ solution, in which the phosphorus concentration was 0.1, 0.2, 0.5, 1.0, 1.5, 2.6, and 5.0 g of $P^{5+}$/L. The duration of adsorption was up to 1 week. It was determined that the synthetic adsorbent strongly chemosorbed phosphorus ions from liquid medium, while its adsorption capacity was more than 50 mg of phosphorus per 1 g of adsorbent. The adsorption kinetic parameters were determined by using Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich adsorption equilibrium models and by pseudo-first- and pseudo-second- order adsorption kinetics models.

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# Microwave-Assisted Synthesis of Monetite in the Temperature Range of 25–200 °C

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Calcium phosphates are salts of phosphorus that can be found in nature or synthesised in the laboratory [1]. Calcium phosphates are one of the most important compounds used in various fields: as an additive to animal and bird feed, in the production of ceramics and abrasives, in the glass industry, and in other traditional and modern fields [2]. The chemistry of main calcium phosphate – hydroxyapatite is widely discussed in the scientific literature; however, insufficient data are available on the formation and properties of other calcium phosphates [3-4]. Thus, this work aims to synthesize monetite in $CaCO_3$–$H_3PO_4$–$H_2O$ system in a temperature range of 25–200 °C by using the microwave method.

For the synthesis of calcium phosphates, the mixture consisted of calcium carbonate, phosphoric acid, and water was used. The molar ratio of Ca and P of the initial mixture corresponded to 1.67. The required amount of calcium carbonate was mixed with diluted phosphoric acid to obtaine liquid to solid ration equal to 10 ml. The resulted solution was left for 30 min at room temperature to remove $CO_2$ formed during the neutralization reaction. The prepared mixture was placed in a microwave reactor "Monowave 300", where treatment was carried out in the temperature range of 25–200 °C for 2 h. The reaction temperature was reached in 3 min and the mixture was stirred at 200 rpm during the reaction.

It was determined that the mineralogical composition and thermal properties of formed compounds strongly depends on the synthesis temperature. It was found that at temperatures of 25 °C and 40 °C, brushite is formed, which recrystallizes into monetite when the synthesis temperature is increased to 60 °C. Monetite was dominated (>85%) in the products when the temperature of synthesis was equal to 140 °C. Also, raw materials were fully reacted under these synthesis conditions. Further increment of synthesis temperature do no influence the stability of monetite.

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# Influence of $Fe^{3+}$ ions on the formation and thermal stability of gyrolite

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Gyrolite ($Ca_4(Si_6O_{15})(OH)_2 \cdot 3H_2O$) is a calcium silicate hydrate, which can be found as a natural mineral or can be synthesised under hydrothermal conditions (50–350 °C and 16 h–42 days) [1]. Gyrolite is characterised by relatively large interlayer spacing (*d*–2.2 nm), therefore it can be used as an adsorbent for the removal of metal ions from wastewater [2]. It is known, that foreign ions can increase the adsorption capacity of calcium silicate hydrates [3]. Unfortunately, there is little data in the literature on the influence of trivalent ions on the formation and properties of gyrolite. For this reason, this work aims to determine the influence of iron ions on the formation of gyrolite under hydrothermal conditions and its thermal stability.

The synthesis of gyrolite with intercalated $Fe^{3+}$ ions was based on the hydrothermal method. The dry primary mixtures were prepared to match the gyrolite molar ratio of $CaO/SiO_2 = 0.66$. The iron ion concentration in the primary mixture was equal to 25, 50, 75, 100, or 150 mg per gram of the $0.66CaO+SiO_2$ mix. Hydrothermal synthesis has been carried out in unstirred suspensions under saturated steam pressure at a temperature of 200 °C for 4 to 72 h. XRD, in-situ XRD, DSC, TG, and FT-IR methods were used to characterise the products of synthesis.

The mineral composition of the products obtained during hydrothermal synthesis in the $0.66CaO\text{-}SiO_2 \cdot nH_2O\text{-}H_2O\text{-}Fe(NO_3)_3$ system depends both on the duration of the hydrothermal treatment and the initial concentration of $Fe^{3+}$ ions in the mixture. Up to 100 mg of $Fe^{3+}$ ions intercalate into the structure of gyrolite during hydrothermal synthesis. A higher concentration of iron ions leads to the formation of hematite. The results of in-situ XRD, DSC, and TG showed that intercalated ions change the thermal properties of gyrolite.

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# $Cu^{2+}/SO_4^{2-}$ ions adsorption by synthetic mayenite with intercalated $SiO_2$

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Mayenite ($Ca_{12}Al_{14}O_{33}$) has been recently stimulating research interest because of its high ions and waste immobilization efficiency [1] and catalytic properties in comparison with other calcium aluminates [2]. The application of mayenite depends on the employed method of synthesis and of quantity-intercalated ions. In previous work [3], it was observed, that in $CaO$–$Al_2O_3$–$H_2O$ suspensions, after 4 h of isothermal curing at 130 ºC temperature katoite was formed which 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. Meanwhile, to the best of our knowledge, no data has been published, and it is still completely unknown how intercalated $SiO_2$ in mayenite structure affect them adsorption properties. This work aimed to determine $Cu^{2+/}SO_4^{2-}$ ions adsorption capacity by pure mayenite and mayenite with intercalated $SiO_2$ when the initial concentration 1.5 g/l of copper ions. The synthesis was carried out in unstirred suspensions (130 °C temperature, 1 h), when molar ratios of the primary mixtures were $CaO/(Al_2O_3+SiO_2) = 2.8$, and $SiO_2= 0$ or 0.25. After synthesis products calcined for 1 h at 350 °C. 1 g of adsorbent was added to 100 ml of $CuSO_4$ aqueous solution (1.5 g/l of $Cu^{2+}$ ions).

It was estimated that $SiO_2$ additive react and enter into the structure of katoite. It was observed that $SiO_2$ additive had no influence on products (katoite) thermal stability, because in both systems, at 350 °C temperature synthetic katoite fully decomposed to mayenite. It was determined that $SiO_2$ additive affected mayenite adsorption capacity for copper ions and $SO_4^{2-}$ anions. It was obtained that, after 20 min of adsorption process, the amount of the adsorbed ions by pure mayenite was equal to 56 mg $Cu^{2+}$/l. Meanwhile, after 60 min duration, almost half $Cu^{2+}$ ions (66 mg/g) were adsorbed, and 95 mg of $SO_4^{2-}$ anions were intercalated into the structure of pure mayenite. It is worth noting that the $Cu^{2+}$ and $SO_4^{2-}$ adsorption capacity of mayenite with intercalated $SiO_2$ is higher, because after 60 min of this process, the determined values were equal to 115 mg of $Cu^{2+}$ions and 135 mg of $SO_4^{2-}$ anions, respectively. It was determined that, after all adsorption process, mayenite fully recrystallization and new crystallinity phases formed.

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# Synthesis and properties of cement additive made from biomass ash

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In order to reduce greenhouse gas emissions, additives are added to cement mixes to reduce the amount of cement clinker used [1]. The most common additive used in the cement industry for this purpose is coal fly ash, but with the global decline in the number of coal-fired plants, the availability of this additive is likely to decrease in future [2.] Biomass fly ash, on the other hand, is so far a practically unused alternative to coal fly ash [3]. As the number of biofuel plants is expected to increase in the future, the availability of this additive will also increase.

The aim of this research is to examine the use of biofuel fly ash as a cement additive after hydrothermal modification. Biomass fly ash was prepared by milling and washed. The effect of water content on the chemical composition of the milled fly ash was investigated. The fly ash additive was then hydrothermally synthesised using an autoclave, the $CaO/SiO_2$ ratio was modified by adding CaO. After studying the chemical and mineral properties of various additive iterations, an additive with a $CaO/SiO_2$ ratio = 1 was selected, and cement samples with different amounts of the additive were examined. The effect of the additive on the compressive strength of the cement is subsequently investigated after 2 and 28 days of hydration. The following methods were used in the course of the study of sample composition changes: XRD, XRF, DSC-TG, FT-IR, ICPMS and isothermal microcalorimetry.

It was found that the mineral composition of the ash was not affected by the duration of the intensive milling process. The $Ca^{2+}$, $K^+$, $Na^+$, $Mg^{2+}$ cations and $SO_4^{2-}$, $PO_4^{3-}$ anions leached predominantly from the ash milled for 1 and 7 min, and the amount of leaching, although not significantly, increased by increasing the water to solid material ratio. The synthesized additive was mainly composed of calcium hydro silicates and had shown to increase the hydration of tricalcium silicates. It was found that after 2 days of hydration, the specimens in which 5 wt. % of the cement had been replaced by the additive showed a 4 % increase in compressive strength compared with the ordinary Portland cement. After 28 days of hydration, the samples with additive were slightly weaker than the Portland cement, however, samples with 5-10 wt.% additive still belong to the same cement strength class (42.5).

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# The dependence of the amount of $Al^{3+}$ ions inserted into the 1.13 nm tobermorite structure on the synthesis conditions

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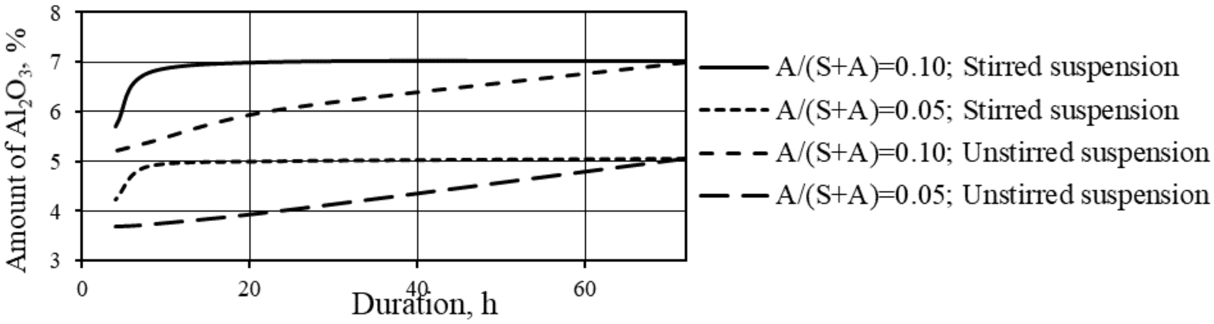
The 1.13 nm tobermorite $Ca_5Si_6O_{16}(OH)_2{\cdot}4H_2O$, calcium silicate hydrate of potentially highest practical importance, is formed in autoclaved aerated concrete, sand-lime bricks, fibre cement roofing products, heat-insulating materials, etc [1]. Another important application stems from its high sorption capacity for heavy and radioactive metal ions [2]. Its properties are significantly influenced by the intercalation of other metal, especially aluminum ions, into the crystal lattice [3]. The aim of this work is to study the kinetics of $Al^{3+}$ ions insertion into the structure of 1.13 nm tobermorite.

Analytical grade reagents were used in this work, which were ground to the appropriate fineness in a *Pulverisete 9* (Germany) vibrating disc mill: CaO (≥99.0%; $S_a$ = 575 $m^2{\cdot}kg^{-1}$), $SiO_2{\cdot}nH_2O$ (≥99.5%; $S_a$ = 735 $m^2{\cdot}kg^{-1}$), and $Al_2O_3$ (≥99%; $S_a$ = 525 $m^2{\cdot}kg^{-1}$). The composition of the initial mixtures corresponded to the molar ratios $CaO/(SiO_2 + Al_2O_3) = 0.83$ and 1.0; $Al_2O_3/(SiO_2 + Al_2O_3) = 0.05$ and 1.0. Hydrothermal syntheses were carried out in stirred (120 rpm) and unstirred suspensions (W/S = 10.0) at 180 °C in an autoclave *Parr Instruments*, model *4751* (USA). The products were examined by XRD, DSK, TG and SEM methods.

In stirred suspensions with C/(S + A) = 0.83, the majority of $Al^{3+}$ ions are inserted into the 1.13 nm tobermorite structure within the first 4 h of synthesis. After extending the duration to 8 h, all Al from the mixture with A/(S + A) = 0.05 is intercalated. In the mixture with A/(S + A) = 0.10, the maximum amount (7.0%) of $Al_2O_3$ replaces $SiO_2$ within 24 h of synthesis. In unstirred suspensions, intercalation occurs more slowly, but reaches the same values (Fig. 1).



In the mixtures with C/(S + A) = 1.0, the processes take place analogously, but slightly less aluminum is inserted (after recalculation to $Al_2O_3$ – 6.8%). At maximum intercalation, the ratio of Al atoms to Si atoms is 1:6, and the molar ratio $Al_2O_3/(SiO_2 + Al_2O_3)$ is equal to 0.08.

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# The supplementary cementitious material from used smectite clay and limestone ($LC^3$)

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The growing demand for cement encourages the search for new alternative materials to replace a part of the cement and reduce carbon dioxide emissionsin into atmosphere. Recently, much attention has been paid to the development of an $LC^3$ additive consisting of limestone, thermally activated clay and gypsum and to the conduct of various research studies to evaluate the influence of the $LC^3$ additive on the rheological properties of the cement mortar as well as the physical and mechanical properties of the cementitious stone. The scientific literature shows that replacing up to 50% of cement clinker with a mixture of 30 wt.% activated clay, 15 wt.% limestone and 5 wt.% gypsum, in addition to having similar mechanical properties to conventional cement, can reduce $CO_2$ emissions up to 30 % [1, 2, 3].

The main purpose of this research work is to explore the possibility of using limestone in combination with thermally activated smectite clay (like a waste after the oil bleaching process) as a cement substance ($LC^3$) for Portland cement.

The calcined smectite clay has been tested as a medium-activity pozzolanic substance (864 mg CaO/g) after thermal activation at 600 °C for 1h. Therefore, two cement materials, $LC^3$I, consisting of 50 wt.% activated smectite clay and 50 wt.% limestone, and $LC^3$II, with 60 wt.% of the clay and 40 wt.% limestone, were prepared in the work. These cement materials replaced from 10 to 50 wt.% of Portland cement and prepared $LC^3$I and $LC^3$II cements met the requirements for hydraulic activity.

It was found that the addition of 10-50 wt.% $LC^3$I or $LC^3$II delayed and prolonged the induction period of the cement samples and directly influenced the increase of the aluminate curve in cement samples with 40 wt.% and 50 wt.% $LC^3$I. In addition, $LC^3$ I and $LC^3$II cement specimens released less heat into the environment than OPC during 70h of hydration. It is important to note that the compressive strength of 28 days cured prisms formed of the cement samples with 10, 20 and 30 wt.% $LC^3$ II, possibly due to the more intense pozzolanic reaction between the activated clay minerals and the Portlandite, was either higher (52 MPa, 10wt.%) or very close (48 MPa, 30 wt.%) to the compressive strength of OPC (49 MPa). When up to 20 wt.% of cement was replaced by $LC^3$I, the compressive strength of 28 days cured specimens were 46 MPa.

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# Functionalized carbon nanotubes as new potential green electrodes

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One of the main problems of the modern world is the increasing demand for energy while facing deeper environmental restrictions. Although there are many sustainable sources of energy available, more efficient methods of production, processing, storage, and utilization are still being sought. Among the most commonly used energy storage systems are batteries and capacitors. The majority of research and technological efforts are currently focused on lithium-ion batteries (Li-ion). The demand is driven by the development of critical infrastructure, the demand for electric vehicles, continuous advancements in smart devices, and industrial automation. The production of highly efficient and affordable energy storage devices is currently an important area of research.

The aim of this work was to obtain new materials based on multi-wall carbon nanotubes (MWCNT) functionalized with phosphorus-organoselenium derivatives for potential use as components in lithium-ion batteries. The synthesis method for the new electrode materials was carried out in multiple steps. In the first step sodium (lithium) O,O-dialkyl(aryl)selenophosphoranes were synthesized through reactions with alcohols or alkali metal hydrides. The next step involved covalently attaching bromine to MWCNT to improve their chemical activity. Subsequently, the brominated MWCNT underwent chemical functionalization with phosphorus-organoselenium anions. The energy storage capability was tested in three-electrode cells (Swagelok® type) as well as in pellet cells through chronopotentiometry and cyclic voltammetry analyses. Additionally, polarization potentiokinetic curves were used to evaluate their susceptibility to corrosion.

As a result of the conducted reactions sodium (lithium) O,O-dialkyl(aryl)selenophosphoranes of and brominated MWCNT were obtained, which were used for the synthesis of their new selenophosphorus derivatives. The cells composed of nanotubes modified in this way exhibited greater operational stability and higher capacity compared to native forms. This provides the potential for using such electrode materials as components in lithium-ion batteries, replacing the commercially used graphite in anodes.

# New materials for hydrogen storage based on carbon nanotubes

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The main objective of this project is the development of a new generation of materials that can be used as a link in hydrogen storage friendly for environment. The specific aims of project are studies on the synthesis, structure determination and the physico-chemical properties and experiments aimed for use systems of MWCNT with lithium-sulfur or lithium ion, respectively, organic disulfide compounds or lithium salts of organic tiooxohetroacids and selenooxoheteroacids. The results of portion of the research conducted in the framework of these projects have led to experiments testing the use of derivatives of multi-walled carbon nanotubes (MWCNT) functionalized by substituents generated from organic phosphorus sulfur- and selenoacid as starting materials to construct the storage of hydrogen, generating at the same time suggesting the use of organic disulfide derivatives (in particular disulfides organophosphate) as one of the elements analogs lithium-sulfur. Full analysis of physicochemical obtained nanotube systems using thermal analysis DSC / TG, analysis using electron microscopy SEM with EDS analysis and NMR spectroscopy was carried out. The full analysis will be carried out sorption/desorption processes and testing the toxicity of these systems for natural environment (Microtox aparat, vegatation hall). Implementation of the proposed project leads to an increased library of "knowledge" on new materials for hydrogen sorption. The test materials are new, so they’re not described group of compounds in the chemical literature, in which creates a favorable possibility of inducing new features and provide the appearance of useful physicochemical properties of the derivatives obtained upon use as substrates in the chemistry of the "new materials" (in particular, "sorptional").

# Sr-doped BCY–LSCF composite cathodes: preparation, properties and electrochemical tests in ceramic proton-conducting fuel cells

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A solid oxide fuel cell (SOFC) is an electrochemical energy generator with very high energy conversion efficiency. Proton-conducting SOFC electrolytes show high ionic conductivity in the range of 500–650°C and at lower temperatures. Among them, $BaCe_{0.9}Y_{0.1}O_3$ (BCY) is very promising, but unstable in $CO_2$- or steam-containing atmospheres. This instability can be substantially reduced by partial replacement of ions $Ba^{2+}$ by $Sr^{2+}$ (BSCY), while ionic conductivities remain at an acceptable level. In this study we summarise a study of the electrolytic properties of $Ba_{0.95}$ $Sr_{0.05}Ce_{0.9}Y_{0.1}O_{3-d}$ samples, which are crucial for application with ceramic proton fuel cells. The utility of LSCF–SBCY composites as cathode materials for SOFCs is investigated, as well as the performance of ceramic fuel cells with LSCF–SBCY as composite cathodes in the temperature range 500–800°C, and the results presented and discussed.

The LSCF–BSCY composite slurry was prepared by mixing powders in the weight proportion 70:30 and ink vehicle then printed on the electrolyte half-disk using the doctor blade method. Two circular-shaped working and reference electrodes were screen-printed on one side, and LSCF counter-electrodes on the entire opposite side were deposited on each electrolyte half-disk ($Ce_{0.8}Gd_{0.2}O_{1.95}$ and $Ba_{0.98}Sr_{0.02}Ce_{0.9}Y_{0.1}O_3$). After sintering at 1100°C, the cells were tested in a three-electrode set-up by electrochemical impedance spectroscopy and cyclic voltammetry. Tests were performed in oxygen and in an oxygen–argon gas mixture. Recorded impedance spectra consist of up to three well-separated semicircles, with high frequency in relation to electrolyte grain boundary resistance and low frequency in relation to the electrode reaction process resistances. Obtained polarisation resistances ($R_p$) mainly slightly depend on the oxygen partial pressure in the range $0.1<P/P(O_2)<1$, while at lower concentrations of oxygen.

Electrochemical tests on Pt| LSCF–SBCY| SBCY|Ni–SBCY |Pt ceramic fuel cells supplied with pure hydrogen, and with identical cells supplied with mixtures of 0.5% vol and 1% $CO_2$ vol in $H_2$ gas, were performed in the temperature range 500–800°C. It was found that the power output $P_{max}$ of the investigated fuel cells was approximately 130–150 mW/cm$^2$ at 600°C. Stable operation of fuel cells was observed under prolonged electrical load.

# Thermal and mechanical properties of polymer composite powders for Additive Manufacturing

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Additive manufacturing (AM) is a broad term for the advanced technology of producing parts with desired geometry by making an object "by adding material layer by layer". Compared to conventional subtractive manufacturing technologies, AM can easily and quickly produce prototypes or functional components with complex geometries, greatly improving the design and manufacturing process. Rapid prototyping processes enable the production of relatively complicated parts based on 3D computer geometries. Most rapid prototyping processes can produce parts from a variety of common and specialised materials. The materials to be used depend on the type of rapid prototyping technology used. Some technologies use photosensitive resin that is cured with a laser or the light from a DLP projector (PolyJet and Stereolitography - SLA). Selective laser sintering uses a CO2 laser to sinter or fuse powdered material, usually plastic. Selective laser sintering (SLS) is one of the rapid prototyping (RP) technologies used in various fields and applications. The reason is that SLS enables the production of very complex parts with high accuracy, surface quality and good mechanical properties. SLS converts thermoplastic powders, such as polyamide 12 (PA 12) and polystyrene, into end-use parts using a laser to melt and fuse the particles. In this technique, the powder serves as both raw material and mould. Therefore, the unsintered powder can be recovered, screened and reused in subsequent designs, reducing manufacturing costs. However, one problem that stands in the way of a wider application of SLS is the limited variety of polymers that can be used. While traditional polymer processing methods, e.g. injection moulding or extrusion, have access to thousands of different formulations composed of several dozen base polymers, only a few dozen different formulations are currently available for SLS treatment.The aim of this work is to determine the influence of the thermal properties of selected polymers as well as composites consisting of a polymer matrix. The analysed results of DTA/TG and DSC/TG investigations were compared with the mechanical and geometrical properties of the printed moulds. The correlation between the parameters of the thermal properties of the starting powders used in 3D printing and the quality of the obtained products is analysed and discussed. The results can be used in practise to help SLS or FDM users improve the sintering process and produce higher quality surface printed materials.

# Thermal analysis of debinding and sintering process of FDM manufacture H13 steel

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Fused deposition modelling (FDM) using a filament containing solid metallic powder and multicomponent polymer binder enables indirect manufacturing of metallic components through subsequent debinding and sintering. This multi-step method has the benefits of being affordable and waste-free. It–can be also applicable for small and medium-sized production as well as individual workshops. However, to produce H13 steel parts using this comprehensive and economical method, the process of debinding of the polymer binder, which plays the role of the metal powder flexible matrix in the continuous filament, must be designed appropriately. The study involved selecting printing conditions, degradation, and sintering, and comparing them depending on the used filaments with a high filling of H13 steel powder. The chemical structure of binding polymers was also investigated using FTIR spectroscopy depending on the selected debinding parameters. The morphology and structure of the printed and sintered material were also examined using the SEM microscope. In addition, the density and flow rate index of the mixture were also measured. These findings offer an alternative method for producing isotropic, full-dense metallic parts by solid-state sintering and shed light on crucial processes for optimizing indirect additive manufacturing of metal parts.

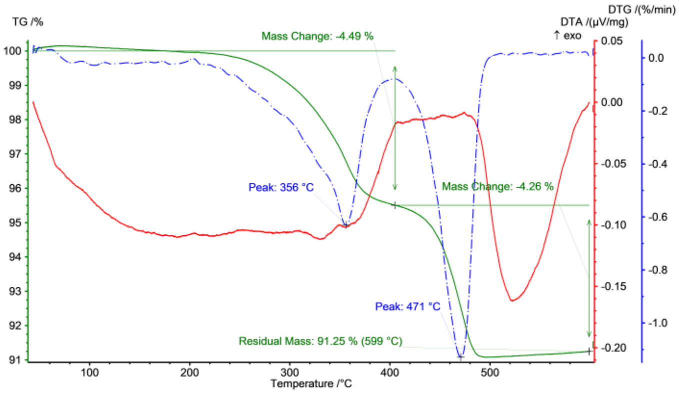

Figure 1. TG curve characteristics for Zetamix H13 steel filament

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# Dilatometric study of phase transformation in additively manufactured H13 hot work tool steel

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Tools and dies are increasingly being manufactured using additive manufacturing (AM); that's why in addition to optimising manufacturing, it is crucial to create the most suitable heat treatment conditions for the generated parts. In this paper, the dilatometric analysis of H13 hot work tool steel fabricated by three additive methods was conducted using a BAHR dilatometer 805A/D. This way, the selected manufacturing technology's influence on the phase transformation's kinetics during steel cooling was determined. The analysis compared samples produced by selective laser melting (SLM), fused deposition modelling (FDM) and conventional powder metallurgy methods. Additionally, the microstructure using Scanning Electron Microscopy (SEM) and Electron Backscatter Diffraction (EBSD) have been evaluated after manufacturing and in quenched and tempered condition. Heat treatment further results in a partial recovery of the solidification structure by removing the cellular/dendritic structure and the uneven local hardness. Dilatometry highlights the significantly different quenching and tempering behaviour of samples produced using SLM compared to FDM. These differences are most likely due to the difference in the carbon content of the steel. While in thermally degraded samples produced by printing with a high-filled filament, it can play the role of the so-called residual carbon, the laser beam can lead to steel decarburisation in the SLM method.

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# Effect of inhibiting butyrylcholinesterase activity by coffee extracts and fractions thereof digested in *in vitro* gastrointestinal tract

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Butyrylcholinesterase (BChE) is the enzyme that hydrolyses acetylcholine. It has a special role in cholinergic neurotransmission due to its concentration, higher than acetylcholinesterase. BChE participates in cholinergic neurotransmission as it can hydrolyze acetylocholine (ACh) in case of selective acetylcholinesterase inhibition. BChE participates in the formation of senile plaques and hydrolyses ACh. Selective inhibition of BChE activity can efficiently contribute to alleviating the symptoms of neurodegenerative disease and dementia that are characterized by reduced ACh levels [1,2].

Our previous studies have shown that coffee extracts and their various fractions are potential BChE inhibitors, prompting us to investigate how bioactive coffee extracts digested in the simulated gastrointestinal tract and absorbed in Caco-2 cells will interact with this enzyme.

The aim of the study was to assess the affinity for BChE and the enzyme inhibition efficiency of coffee extracts and fractions thereof after *in vitro* digestion. The digestion of extracts from coffee roasted to various degrees (green, light and dark) was carried out in a simulated digestive system, reproducing physiological processes of the gastrointestinal tract, introducing a mixture of selected probiotic bacteria and passing through the erythrocyte layer. The evaluation of BChE inhibition was assessed for coffee extracts and fractions taken after digestion on each of the four sections of gastrointestinal tract, i.e. in the stomach, small and large intestine and colon, and after passing through the layer of erythrocytes and performed using an isothermal titration calorimetry that allowed to determine the most effective coffee extract and fraction limiting the enzyme activity that protects acetylcholine from degradation.

Studies have shown that the highest bioavailability of compounds with high affinity to BChE was characterized by green coffee and their fraction of monochlorogenic acids due to the high content of hydroxycinnamic acids and it was additionally increased in the presence of microbiota. The research was funded by National Center of Science (project No. UMO-2018/29/N/NZ9/01160).

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# Evaluation of natural materials for sorbent applications

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The dynamic development of various technologies and industrial sectors has contributed to serious significant environmental changes on a global scale. In recent years, therefore, intensive activities have been carried out in order to employ efficient solutions to reduce the negative impact of humans on the environment, among others by management of solid, liquid, and gaseous waste, elimination of toxic substances from the environment, those stored in the landfill, together with the reduction of greenhouse gas emissions.

Here, we present a new engineering method and an attractive alternative to the storage of hazardous by-products and wastes from different industrial plants. We developed technologies for the production of highly effective sorbents and fillers useful in the cleaning of different post-production waste from harmful impurities. Particularly, our studies focused on the characterization of commonly available and cheap raw materials (including diatomite, clay, or coal shales) and their specific thermal modification in order to achieve desired features for optimized technological processes of sorbent production. The coupled TG-FTIR measurement methods were used in the study. The specific changes in properties of raw materials as a function of the temperature allowed us to select them directly as sorbents or evaluate them as useful raw materials for geopolymerization processes. On the basis of the obtained results, the processes and mechanisms occurring in different materials during their heating were also characterized. Some processes were indicated to be critical to optimizing technological processes dependent on the thermal treatment during the production cycle. Thanks to this information, it was possible to reduce the energy consumption of the process and shorten the entire production time.

Our studies provide tools for novel and integrated environmental management in line with the 'Cleaner Production' goal to reduce the production of waste while improving the use efficiency of energy, resources, and water.

Funding

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# Polyhalite as a possible potassium source in ammonium nitrate fertilizers – thermal stability assessment

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Potassium is one of three most important plant nutrients. It plays an important role in plant growth and development [1]. While potassium can be supplemented in forms of granules of KCl or $K_2SO_4$, spreading other macronutrient fertilizers on fields requires additional unnecessary operations to provide all nutrients required to plants [2]. Production of ammonium nitrate (AN) fertilizers comprising potassium salts is either costly or the final product can present an explosion hazard due to presence of chlorides [3,4]. Instead of common potassium salts, minerals like polyhalite (PH) can turn out to be a good alternative and a source of other important plant nutrients like calcium, magnesium and sulphur [5]. In this paper, thermal stability of AN – PH mixtures was determined and possibility of safe application of polyhalite as a fertilizer compound was evaluated. Differential thermal analysis coupled with thermogravimetry and mass spectrometry (DTA-TG-MS) has been applied in the presented research. Selected mixtures of PH and ammonium nitrate have been heated up to the temperature of 400 °C with a heating rate of 5 °C/min. The research was conducted on mixtures of AN and polyhalite in various proportions. The additive was added in raw or processed form. Processing of PH was performed by either water extraction and soaking, calcination or water extraction, soaking and calcination. Determination of selected elements concentration was performed using Atomic Absorption Spectroscopy method (AAS). The influence of the PH addition to AN systems was defined in terms of two main aspects – the possible chloride ions removal to increase AN thermal stability with various processing methods and the activation of potassium contained in PH to forms that remove the unwanted low temperature phase transition of ammonium nitrate and are easily available to plants.

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# Influence of titanium on thermal properties of Co-Ni-Al-W alloys

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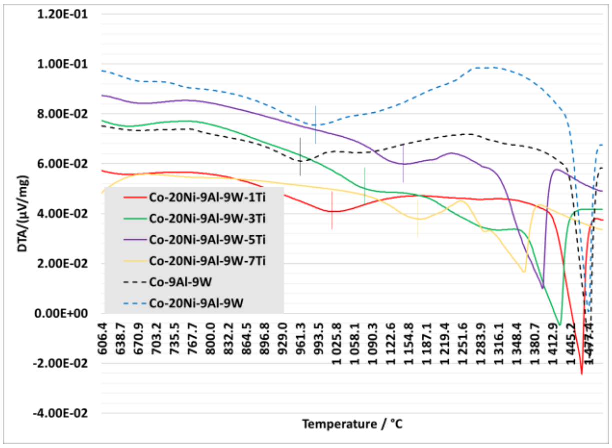
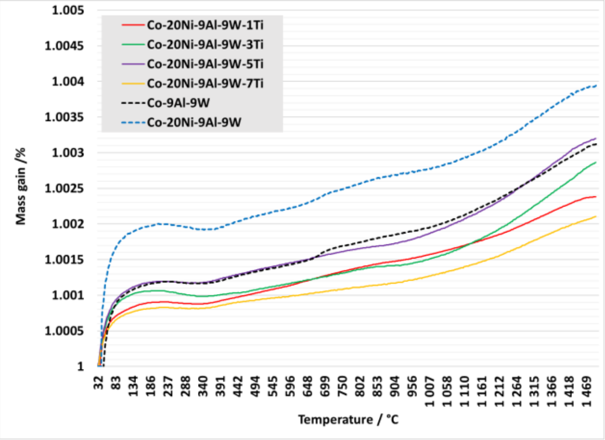
The article presents the thermal properties characterization of Co-20Ni-10Al-5Mo-2Nb-xTi alloys where x = 1, 3, 5 and 7. The differential thermal analysis (DTA) revealed very intensive effects of titanium on the thermal behaviour of described alloys. Those effects are expressed by decreasing both *solidus* and *liquidus* temperatures. Contrary to this, the *solvus* temperature significantly increased, which is a beneficial effect from the point of view of operating temperature. All those effects caused the limitation of the so-called solutionizing window, in which effective heat treatment should be realized. The introduction of titanium on the level of at least 3 atomic percent also caused the formation of many different topologically close-packed phases (TCP). Due to the strong tendency to TCP phase formation, the DTA results were compared to simulation results based on the CALPHAD method, where the different types of TCP phase formation are also revealed.

Additionally, the thermogravimetric behaviour of analyzed alloys was considered. Obtained results don't reveal a visible tendency between titanium concentration in alloys and oxidation behaviour under the condition of the DTG test. Still, it should be noted that the alloy with the highest level of Ti showed the most beneficial character during the test.





# Thermal diffusivity and conductivity of new Co-based superalloy

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The article presents the thermal diffusivity and conductivity characterization of new Co-based superalloys of two essential types: tungsten-containing Co-(20Ni)-9Al-9W and tungsten-free Co-(20Ni)-10Al-5Mo-2Nb alloys. Those materials are the most widely described in the literature and form the group of new creep-resistant materials considered an alternative to Ni-based superalloys. It should also be noted that practically there needs to be more information about the thermal conductivity (diffusivity) of alloys of this type.

In the first analysis stage, the thermal diffusivity was determined by the laser-flash method using the LFA 427 apparatus by Netzsch. The Cape-Lehman model was used for thermal diffusivity calculations. The measurement range was from 25 to 1000°C with 100°C steps. The density of alloys was calculated based on the chemical composition of alloys and their heat capacity (Neuman-Kopp rule). Based on these data, the thermal conductivity was calculated in the whole temperature, assuming the constant value of density and specific heat. The thermal diffusivity/conductivity results were compared to the DTA analysis of these alloys, with particular emphasis on the temperature range of order-disorder transformation.

Due to the essential influence of chemical constituents and microstructural aspects on the thermal conductivity of metallic materials, detailed descriptions of the microstructure of analyzed alloys were also presented. Special attention was placed on the chemical composition of solid solutions and the presence of different precipitations. The thermal diffusivity and conductivity measurements were realized for alloys in as-cast conditions and after solutionizing with rapid and slow cooling as a final heat treatment stage.

Obtained results revealed significant differences in thermal diffusivity and conductivity of analyzed alloys, which were connected to alloying elements concentration in solid solutions and different precipitations.

# Impact of pozzolanic additive on the microstructure and thermal chemistry of cement mortars

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In cement-based mortars and concrete, active or inert mineral additives are used in order to reduce the amount of Portland cement clinker and to improve certain characteristics or to achieve special characteristics. The decorative cement mortars' main advantage, besides being an artificial imitation of natural rocks, is better workability, but durability and stability are the key properties when used. To achieve good aesthetic surface and multilateral application of decorative cement (for example, 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 coloured fine and coarse aggregates is necessary. The abovementioned 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, defined by its ability to react with calcium hydroxide and create a cementitious phase (insoluble calcium silicates). Its incorporation in the cement mortars creates economic, engineering, and durable effects, typical for natural pozzolans. Unlike light in colour pozzolans (as silica fume, metakaolin, etc.), clinoptilolite is soft and ductile. Moreover, it modifies the rheological behaviour 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 coloured mortars preserves an ancient view due to the characteristic colour of clinoptilolite.

This study has investigated the effect of white Portland cement replacement by clinoptilolite with up to 10 wt% in different cement composites. The density of composite-structures at 1, 28 and 120 days of water curing was evaluated by measurements of physical-mechanical properties - density, compressive strength, and porosity. Crystal structures and sample morphology have been investigated by X-ray powder diffraction analysis, FTIR spectroscopy and Thermal analysis (TG/DTG-DSC). The applied complex of analytical techniques allows for the identification of the newly-formed solid phases in the hydrated cement composites, the definition of their structural characteristics, and the analysis of cement's properties.

The following has been determined: the sulphate/carbonate-containing solid phases; the dehydration, dihydroxylation, decarbonation, and desulphuration steps; sample reaction mechanism of thermal decomposition, which are the parameters revealing the influence of thermal activated clinoptilolite additive and water-to-cement ratio on the physical-chemical properties of cement composites.

Acknowledgements. This work was supported by the Operational Program "Science and Education for Intelligent Growth", co-financed by the European Union through the European Structural and Investment Funds under grant BG05M2OP001-1.001-0008 of the National Centre for Mechatronics and Clean Technology (V.P.)

# High energy milled and high temperature activation of $CaO$-$SiO_2$-$P_2O_5$ natural system

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In this study high energy milled (HEM) samples of natural phosphorites from Bulgarian and Estonian deposits were investigated. The activation was performed via planetary mill with Cr-Ni grinders with a diameter of 20 mm. This method is an ecological alternative, since it eliminates the disadvantages of conventional acid methods, namely the release of gaseous and solid technogenic products.

The aim of the study is to determine the changes in the structure to follow the solid-state transitions and the isomorphic substitutions in the anionic sub-lattice in the structure of the main mineral apatite in the samples from Bulgaria and Estonia, under the influence of HEM activation. It is also interesting to investigate the influence of HEM on structural-phase transformations on the structure of impurity minerals - free calcite/dolomite, pyrite, quartz, as well as to assess their influence on the thermal behavior of the main mineral apatite.

The effect of HEM is monitored by using a complex of analytical methods, such as chemical analysis, specific surface area (SSA), powder X-ray powder diffraction (PXRD), Fourier transformed infrared (FTIR) measurements and thermal analysis (TG/DTG-DSC) coupled with Pfeiffer Omnistar Mass Spectrometer.

The study of the activation effect shows that the mechanical activation has the following impacts at micro-level: (i) deformation of polyhedrons; (ii) smaller size of crystallites with an increased degree of structural defects leading to a metastable phosphorite with increased dispersity.

The obtained results prove the correlation in the behaviour of the studied samples in regards to their quartz content and bonded or non-bonded carbonate ions. After HEM activation of the raw samples, the A- and A-B type carbonate-apatites are formed. The new isomorphic phases (A- and A-B type carbonate-apatite) are decarbonized at temperatures of about 780-850 K and 1050-1100 K. In the presence of quartz, the decomposition temperature for carbonate ions in A-type is increased. In addition, the moisture and higher quartz content in the samples leads to a shift in the dehydroxylation temperature.

***Key words***: High energy milled activation, Carbonate apatite, Quartz, Isomorphic substitution, Thermal analysis

Acknowledgements. This work was supported by the Operational Program "Science and Education for Intelligent Growth", co-financed by the European Union through the European Structural and Investment Funds under grant BG05M2OP001-1.001-0008 of the National Centre for Mechatronics and Clean Technology (V.P.)

# Kinetic analysis for thermal decomposition reactions of $NH_4RhO_4$ for the recovery of high-purity Rh powders from the scrubber residue of molybdenum oxidizing roasting process

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Rhenium is a refractory metal which melts at 3180°C and shows no ductile to brittle transmission and this behaviour remains constant until its melting point. Rhenium and its alloys are widely used in the high-temperature industries such as nuclear industries, spaceships and semiconductors.

The feasibility of a dry thermal decomposition process for the recovery of high-purity Rh from the low-grade APR (Ammonium Perrhenate: $NH_4RhO_4$), which is generated from the scrubber residue of molybdenum oxidizing roasting process, was drawn by a thermodynamic analysis for a system consisting of H, N, O, K and Rh. This feasibility was experimentally verified by the TG analyses of a low-grade APR, consisting of $H_2O$, $NH_4RhO_4$ and much smaller amount of $KReO_4$, under inert and oxidizing atmospheres: a low-temperature pyrolysis under inert atmosphere decomposes this low-grade APR into the mixture of $ReO_2$ and $KRhO_4$ by emitting $N_2$ and $H_2O$, and the oxidation treatment at higher temperatures then converted this mixture into gaseous rhenium oxides such a $RhO_2(g)$ and $Rh_2O_7(g)$ and non-volatile $KRhO_4$. Volatilized rhenium oxides are condensed out into ultrafine powders of high-purity rhenium oxides, which are readily reduced into ultrafine high-purity Rh.

A stepwise dry thermal treatment processes was proposed and optimum operating conditions for reaction steps were established based on the nonisothermal kinetic analysis and the kinetic predictions for reaction steps involved in the proposed dry thermal decomposition process for the treatment of APR into high-purity Rh powders.

$$NH_4ReO_4 \rightarrow ReO_2 + 2H_2O(g) + 1/2N_2(g) \quad (1)$$
$$ReO_2 + 2.5O_2 \rightarrow Re_2O_7(g) \quad (2)$$
$$Re_2O_7(g) + H_2 \rightarrow Re + H_2O(g) \quad (3)$$

High-purity and ultrafine powders of Re can be obtained by reactions (1), (2) and (3) in order, which includes a unit process for reactive condensation of volatilized rhenium species into ultrafine aerosol particles.

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# Structural changes and gas evolution characteristics of strong acidic cation-exchange resins during the course of pyrolysis and carbonization to 1273 K

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Ion-exchange (IE) resin, an insoluble matrix in the form of microspheres, is used in water decontamination and demineralization processes. The pyrolysis characteristics of IE resins, which are made of polystyrene sulfonate, have been investigated for two purposes: pyrolysis to reduce the volume of radioactive spent IE resins for disposal and pyrolysis to derive carbon spheres to use them as a catalyst support or adsorbent. The pyrolysis of IE resin causes a loss of the ion-exchanging properties, the chemical decomposition of polymers that generates various gaseous species, and a wide variety of changes in the chemical structures according to the treatment temperature [1].

This study investigated the structural changes and gaseous evolution products of strongly acidic cation-exchange resins during the course of pyrolysis and carbonization in a wide temperature range up to 1273 K. The structural changes were investigated using high-resolution FTIR, C-13 NMR and XPS. The gas evolution characteristics during the pyrolysis and carbonization processes were investigated using TGA-QMS, TGA-FTIR, and multi-shot Py-GC/MS.

A plot of the derivative of TG (DTG) shows a pattern that is similar to the pattern of the Gram Schmidt intensity of the IR spectrum. The temperature and time positions of the peaks in the DTG plot are nearly identical to those of the peaks of the Gram Schmidt intensity. The relative intensity of each peak in the DTG plot was nearly proportional to the intensity levels of the corresponding peaks in the Gram Schmidt plot, as shown in the 2-D plots of the IR spectrum. Four reaction steps were identified in the DTG plot and IR spectrum. The structural changes in carbonization identified by high-resolution FTIR of pyrolyzed CER samples obtained after the completion of different reaction steps are in agreement with those by C-13 NMR. This revealed that the structure of the benzene ring remained as CER was carbonized after approximately 773 K after the third reaction step, emitting $SO_2$ and sulfur-bearing hydrocarbons such as thiophene. The results of a detailed examination of the structural changes according to NMR, FTIR and XPS were in agreement with the pyrolysis gas evolution characteristics as examined by multi-shot Py-GC/MS.

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# Corrosion behaviour of arc sprayed Zn15Al coatings: A comparative study of electrochemical, accelerated corrosion tests, and coastal railway exposure

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Arc sprayed Zn15Al coatings with different spraying parameters: arc current and spraying distance were studied. The corrosion behavior of the coatings was studied using an electrochemical impedance measurement, accelerated testing by cyclic corrosion test (CCT), and coastal railway exposure test. Corroded surfaces were characterized by scanning electron microscopy (SEM). The corrosion product formed on the coating was analyzed by X-ray diffraction (XRD) and scanning electron microscopy. From the potentiodynamic polarization test, the corrosion rate of the coating, using arc current of 100A and a spraying distance of 100mm, was 0.012 mm/year. The corrosion rate increased with increasing arc current and spraying distance. From the surfaces analysis after the CCT, Simonkolleite (Zn5(OH)8Cl2•H2O) was found on the coating surfaces. The corrosion behavior of Zn-Al coating depends on the dissolution of the η-Zn phase in the coatings, which is a form of selective leaching corrosion, while localized and uniform corrosion were detected in coastal railway exposure test. Results from the coastal railway exposure agreed well with electrochemical impedance measurement and cyclic corrosion test. Higher arc current and spraying distance led to a more severe corrosion for all the tests.

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# Corrosion Behaviours and Bonding Strength of Thermally Sprayed Nickel Alloy Coatings for Use as Bond and Top Coatings

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This research investigates the double-layered thermally sprayed nickel alloy coatings (bond and top coatings). Typically, the bond coat is used to compensate the difference in the thermal expansion between top coat and bond coat [1]. However, it can cause difference in corrosion behaviors and affects the adhesive strength [2-3]. Thus, this study focuses on the corrosion behaviors and bonding strength of the thermally sprayed nickel alloy coatings. The Ni-5wt.% Al, Ni-20wt.% Cr, or PMET 866 were used for bond coatings, while highly alloyed Ni-based coatings, Hastelloy C276 or Inconel 625 were used as top coatings. Arc spraying (AS) and high velocity oxygen fuel (HVOF) techniques were used to create bond and top coatings on a 304 stainless steel substrate. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) techniques were used to investigate the microstructure of the coated microstructure, including splats, oxides, and porosities. The corrosion resistance of the coatings was assessed by Potentiostat in a 20 vol% sulfuric acid solution. The result revealed that open porosity between intersplat boundary from electric arc spraying led to a rapid corrosion attack of the bond coat. Thus, the thermal spraying of top coat and bond coat with electric arc technique resulted in lower corrosion resistance compared to those sprayed by HVOF. When bond coating is required in order to achieve the good corrosion property, Ni-20wt.% Cr as bond coating and Hastelloy C276 as top coating by HVOF is recommended as the optimum process. The coating presented the best corrosion resistance, giving mechanical integrity over longer periods. The bond strength of the coatings was examined by adhesion test, following ASTM C633 standard. The results will be discussed in the detail.

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# Phase characterizations of Portland cement-high calcium fly ash-calcined clay pastes by thermogravimetric analysis

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Calcined clay was used with high calcium fly ash to replace Portland cement at 50%. Phase characterizations using thermogravimetric analysis and x-ray diffraction were used for these samples at 7 and 28 days. It is found that at both ages, the use of calcined clay resulted in an increase in the hydration phases. This relates with the increase in compressive strength of the mixes. Using both thermogravimetric analysis and x-ray diffraction, a number of phases were detected such as calcium silicate hydrate (CSH), calcium aluminosilicate hydrate ($C_2ASH_8$) and monocarboaluminate hydrate. A noticeable reduction in $Ca(OH)_2$ was also clear when increasing calcined clay.

# Determination of high calcium fly ash condition after long term storage by thermal analysis

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This work used thermal analysis and x-ray diffraction to characterize fly ash after 5 years storage to determine its condition and usability. Fly ash is of high calcium type obtained from Mae Moh Power plant in Northern Thailand. Single and doubled layers bags were used in the indoor storage. After 5 years storage in tightly sealed double layered bags, the fly ash particles stay in its powder form and did not appear to be hardened. In the single layered bag, some parts of the fly ash particles are visibly hardened. Physical and chemical characteristics of the stored fly ash are reported and discussed. While it is best to avoid long term storage and immediate usage is deemed best for fly ash optimum condition, especially high calcium type, there might be cases where fly ash may not be used or stored after production. In the case where it is unavoidable and stored for a certain time, characterizations such as the use of Thermogravimetric (TG) can help to determine its current condition and its potential for use in cement and concrete mixes to avoid waste. In this case TG help to indicate that the single layered bag sample is affected where carbonation was found to occur while double layered bags sample did not carbonate.

# Microstructure, Wear and Corrosion Behavior of NiCrBSi/WC-Co Thermally Sprayed Coating Before and After Flame Remelting

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This research studies the microstructure, mechanical properties, and corrosion behavior of NiCrBSi coating with an addition of WC-Co powder in various amounts (0, 5, 10, 15, and 20 wt.%) using the High-Velocity Oxygen Fuel (HVOF) process on low carbon steel. Additionally, the coatings were flame remelted at 1100°C for 1 minute. The microstructure of all coatings was examined using Scanning Electron Microscopy (SEM) and X-ray diffractometry (XRD). The mechanical properties of the coatings were assessed through Vickers microhardness tests and ball-on-disk tests. The corrosion behavior of the coatings was evaluated by conducting a potentiodynamic polarization test in a 20 vol.% sulfuric acid solution ($H_2SO_4$). The results demonstrated that an increase in WC-Co enhanceed the hardness and wear resistance of the coatings. Some small clusters of WC-Co were observed, and some cracks were present in the coatings due to heat during spraying and rapid cooling. The presence of porosity directly affected the corrosion behavior of the coatings. Flame remelting process led to better cohesion and distribution of the Ni and WC phases, reducing microdefects such as porosity and cracks in the coatings. The mechanical properties improved with an increase in WC-Co after flame remelting, resulting in the presence of hard intermetallic compounds: FeB, $CoSi_2$, and $Ni_2Si$ along with the WC phase. The flame remelted NiCrBSi/10 wt.% WC-Co coating demonstrated high hardness, low wear rate, and a low corrosion rate of 1072.26 HV, 4.8 $x10^{-6}$ $mm^3/m$, and 0.567 mm/year, respectively. Therefore, an addition of WC-Co and the flame remelting process significantly enhanced the properties of the NiCrBSi coating.

# Determination of the Kinetic Parameters for the Thermal Decomposition of $Al(OH)_3$ and $Mg(OH)_2$ by Invariant-Kinetic Parameters Method from Thermogravimetric Data

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Aluminium hydroxide ($Al(OH)_3$) and magnesium hydroxide ($Mg(OH)_2$) are two of the most common minerals used as flame retardant additives for polymers [1]. The dehydration of $Al(OH)_3$ and $Mg(OH)_2$ (above 200°C and 300°C, respectively) is the fundamental process responsible for their flame retardant activities. The kinetics of dehydration of metal hydroxides was studied by the Invariant Kinetic Parameters (IKP) method in the present study. The IKP method developed earlier by Leskinovich and Levchik [2] allows for the determination of the activation energy ($E_a$) and a pre-exponential factor ($A$) without any assumptions on the kinetic model. A wide range of heating rates (2, 3, 5, 7, 10, 12, 15, 20, 30, 40 ,50 °C/min) was studied and these heating rates were classified: slow, moderate and fast. In the earlier works, Coats-Redfern method was employed to evaluate the temperature integral[3,4], on the other hand, this study makes use of the approximation proposed by Orfão [5].

The values of $E_a$ and $A$ for $Mg(OH)_2$ were calculated as 156kJ/mol and $5.95\text{x}10^{13}\text{s}^{-1}$, respectively when the entire range of heating rates was taken into account. During the decomposition of $Al(OH)_3$, two distinctive stages and multiple reaction zones were investigated. IKP method was employed to the data obtained at slow, moderate and fast heating rates for each decomposition stage. Fast heating rates were found to be rather unreliable for the kinetic calculations of $Al(OH)_3$.

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# Characterisation and thermal study of new sulfonic azoesters

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[2]University of Craiova, Department of Chemistry, Craiova, Romania
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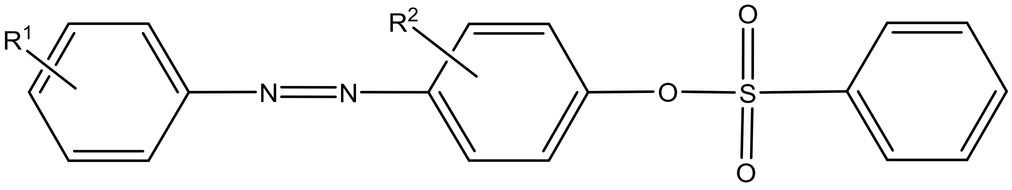
[4]University of Craiova, Department of Biology and Environmental Engineering, Craiova, Romania

In this study we have concentrated our efforts to investigate systematically six azoesters for their stability and biophysical properties. Sulfonic azoesters [1] are azoderivatives obtained from various substituted azophenols by condensation with benzenesulfonyl chloride in the presence of pyridine. The solubility study of these compounds has confirmed that all of them are highly soluble in organic solvents, developing nice & bright colours for the obtained solutions. The physical-chemical characterization of the compounds was made by the following methods: UV-Vis spectroscopy, FTIR spectroscopy and Mass spectrometry. The thermal stability study of the compounds was performed by means of thermogravimetry (TG) and differential scanning calorimetry (DSC), by heating the solid samples in a vertical setup from R.T. to 1000 °C under inert atmosphere (argon flow). The most likely conformations of the azoic dyes structures were optimized in Gaussian03 software using the Density Functional Theory (DFT). In order to probe the biophysical properties, the interaction (molecular docking) between the five azoic compounds and the bovine serum albumin (BSA) was studied with the Autodock Vina software, while the analysis and visualization of the three-dimensional structure of the protein - ligand complex was performed with Python Molecular Viewer of Auto Dock Tools v 1.5.6 and BIOVIA Discovery studio 2019.

$R^1$=$CH_3$, Cl
$R^2$=$CH_3$, Cl



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# Thermoanalytical books on thermophysical research of materials

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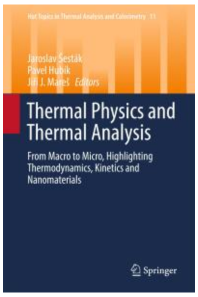
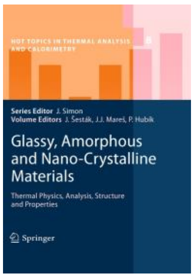
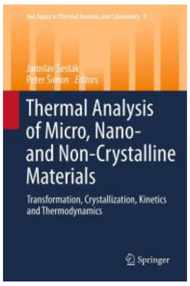
**Thermal Physics and Thermal Analysis:** from Macro to Micro, Highlighting Thermodynamics, Kinetics and Nanomaterials´ was printed by Springer 2017 (with 567 pages and 25 chapters - ISBN 978-3-319-45897-7): https://link.springer.com/book/10.1007/978-3-319-45899-1 as a final book (Vol. 11) of the triptych published within the Springer series „Hot topics of thermal analysis“ (ISSN: 1571-3105, see below). Within two years, this book accredited as many as several thousand downloads. Internet price hard cover 214 Euro.



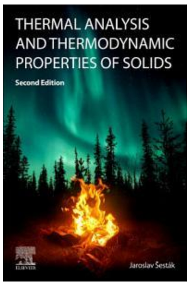
**Glassy, Amorphous and Nano-Crystalline Materials**: Thermal Physics, Analysis, Structure and Properties´ (2011, with 380 pages and 21 chapters - ISBN 978-90-481-2881-5)" see https://link.springer.com/book/10.1007/978-90-481-2882-2, which received 40 thousand downloads, internet price hard cover 236 Euro.



**Thermal Analysis of Micro-, Nano- and Non-Crystalline Materials**: Transformation, Crystallization, Kinetics and Thermodynamics´ (2013, with 484 pages and 22 chapters - ISBN 978-90-481-3149-5) viz: https://link.springer.com/book/10.1007/978-90-481-3150-1, which obtained as many as 50 thousand downloads, internet price hard cover 246 Euro.



**Thermal Analysis and Thermodynamic Properties of Solids,** Second expanded and revised edition (Elsevier 2021 with 570 pages and 20 chapters - ISBN 9780323855372) covers foundational principles and recent updates in the field of thermal science, presenting an authoritative overview of theoretical knowledge and practical applications across several fields concerned with material thermodynamics (https://www.elsevier.com/books/thermal-analysis-and-thermodynamic-properties-of-solids/sestak/978-0-323-85537-2) 220 Euro.



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# Poster Session 3

# Preparing an efficient photocatalyst from $SnO_2$ modified cellulose II highly porous template

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The rapid growth in the population, and the industrialization increase, in combination with limited availability of the water resources are resulting in the increased demand for efficient treatment of urban and industrial wastewater. [1] For that reason, semiconductive materials with efficient organic pollutant removal properties are among the most promising technologies investigated nowadays. Commonly used semiconductors are titania and zincite due to their similar chemical properties, low toxicity and low cost. [2] This work focuses on the investigation of the highly stable, low toxic $SnO_2$ material as the material transparent in the visible, up to the ultraviolet region of the solar spectrum for the wastewater treatment systems.

Specifically, cellulose II aerogel preparation with supercritical $CO_2$ drying was performed followed by the reductive mineralization of cellulose. The post treatment of samples was carried out under different reactive conditions and temperatures. The thin film configuration was prepared via tape casting method utilising powder samples.

Successfully prepared samples were subjected to thorough characterization using grazing incidence X-ray diffraction (GIXRD), which overall showed the degree of chemical homogeneity of studied $C/SnO_2$ composites. Bulk and surface morphologies were studied by scanning electron microscopy (SEM-EDS), pointing to suitable geometries. Finally, the photocatalytic activity was investigated by photocatalytic degradation using a model pollutant. The bandgap values were previously determined using diffuse reflectance spectroscopy (DRS) measurements.

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# The influence of heavy metals on the early hydration processes of Portland cement

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In this study, the effect of Pb and Cr metals on the early hydration and properties of hardened cement paste was investigated. The heavy metal compounds were added to the cement composites in different mass fractions: 0.2-0.7 wt% for Pb salts and 1-5 wt% for Cr salts. Microcalorimetric measurements, conductometric measurements and thermogravimetric measurements were carried out as part of the measurements. These heavy metals alter the hydration rate of the cement at early ages. A particularly strong delay in hydration is observed in the presence of Pb compounds. As a result, the addition of Pb delays the start and end of the setting time, and the content of calcium hydroxide and chemically bound water decreases. With the addition of Cr salt, the heat of hydration and the calcium hydroxide content decrease while the chemically bound water content increases. This indicates that reactions take place between chromium and hydration products.

# Influence of size and concentration of graphene nanoparticles on thermal and electrical conductivity of mineral oil based nanofluids

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Oil fluids are often an essential component of mechanical and engineering operations where they are typically used to improve lubrication/reduce wear, improve heat transfer/dissipation, transfer loads, and others. Their properties can be improved by the addition of nanoparticles, resulting in nanofluids. Nanofluids can be easily prepared by ultrasonic dispersion of nanoparticles in a base fluid, but achieving a long-term stable suspension is challenging because the particles tend to agglomerate and the density differences between nanoparticles and fluid. Stability can be improved by adding surfactants that promote nanoparticle-liquid interactions and lower the agglomeration rate, usually by promoting steric hindrances.

In our research, we used various graphene nanoparticles known for their high thermal and electrical conductivity to improve the properties of mineral oil. The first graphene (A) had a size of less than 10 μm, less than 10 layers (90%), and a carbon content of 98 ± 1%, while the second (B) had a diameter of less than 26.5 μm, less than 10 layers (73%), and a carbon content of 96 ± 3%. We added up to 10 mass % graphene to the oil fluid and archived 102 % higher thermal conductivity by adding graphene A and 67 % higher thermal conductivity by adding graphene B. The volume electrical resistivity of the oil was drastically lowered from about 344 PΩ cm ($10^{15}$) to 3.8 GΩ by adding 1 mass % graphene A, and to 4.4 MΩ for 10 mass % addition . For the same amounts of graphene B, even lower resistivities of 14.2 MΩ and 3.4 MΩ were achieved respectively.

# Low-temperature properties of fatty acid isobutyl, pentyl, and hexyl esters, and their blends with mineral diesel

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In recent decades, a lot of emphasis has been put on finding a renewable, sustainable, and non-toxic alternative to widely used fossil fuels. Biodiesel, as such, consists of fatty acid alkyl esters, that can be obtained from a triglyceride source (vegetable oil or animal fat) and an alcohol (usually, methanol or ethanol) via catalysed transesterification reaction. The use of a waste feedstock, e.g. waste cooking oil, can further contribute to the sustainability of entire process [1]. The downside to its use, however, lies in biodiesel's poor low-temperature properties, which limit its application, especially in cold winter conditions and climates [2].

In general, application properties of biodiesel are highly influenced by the type of a reactant used for its synthesis, i.e. its chemical structure [3]. In this study, biodiesels were synthesized from three different higher alcohols (isobutanol, pentanol, and hexanol), and waste cooking oil, in a presence of potassium hydroxide, as a catalyst. Each biodiesel was blended in two-component and three-component blends with non-additivated mineral diesel and/or a corresponding alcohol. Pour points and cloud points of prepared samples were measured according to the standardized tests, while the crystallization onsets, peaks, alongside with the enthalpy of crystallization, were determined using differential scanning calorimetry.

The DSC results showed that the addition of fatty acid pentyl and hexyl esters in blends with mineral diesel increases the blends' crystallization onsets and peaks, while the presence of branched structures in fatty acid isobutyl esters and isobutanol leads to a decrease in blends' crystallization temperatures. Pour point and cloud point results show that the presence of all types of biodiesels in the diesel blends does not have a negative effect on these low-temperature properties, in some cases even improving them, however all results are within the repeatability of the methods and, therefore, can be considered similar.

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# Investigation of the effect of MgO on the thermal profile of PEO prepared via hot-melt extrusion technique

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Poly (ethylene oxide) (PEO) is one of the most interesting base materials because of its high chemical and thermal stability. PEO is a non-ionic, semi-crystalline, water-soluble and biocompatible polymer of considerable industrial significance, which founds applications in many different field of industry. It is also an organic component in organic–inorganic hybrid material applied in advanced technologies in the field of functional coatings with superior barrier properties [1].

During the past few decades, numerous investigations have been carried out in order to develop water-soluble and biocompatible polymer composites with good thermo-mechanical properties. The compounding of two or more natural additives into polymer matrix is one possible approach for designing material with desired structural, thermal and mechanical properties. One of the interesting natural additive is magnesium oxide (MgO).

Magnesium oxide is a versatile metal oxide and can be used in numerous applications [2-5]. The properties of MgO are highly dependent on the synthesis methods and processing conditions [3,4]. MgO can be obtained by thermal decomposition of magnesium salts, which results in a large crystal size and small surface area and limits its application [4,5]. In this work, seawater bittern was used to obtain magnesium salt by a precipitation method in the presence of a stoichiometric amount of clear limewater ($\gamma$ = 1.54 gL$^{-1}$) as a precipitation agent. To obtain a small crystallite size and a homogeneous morphology of the MgO, a small amount of poly(vinyl alcohol) (PVA) (mass ratio 1:1.5) was used as a surfactant.

Therefore, the main goal of this work is twofold; to investigate the effect of MgO addition on the thermal properties through characteristic melting and crystallization transitions, and on the degradation pattern of PEO by using non-isothermal thermogravimetric analysis (TG). The PEO/MgO composites were prepared via hot melt extrusion. Thermal characteristics of the composites were investigated by means of differential scanning calorimetry (DSC). In order to provide additional insight into effect of the MgO addition on the structural properties of PEO, Fourier transform infrared spectroscopy (FT-IR) was used.

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# Dielectric properties of porous silico-aluminophosphate geopolymeric ceramic-like material

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Phosphate-based geopolymer is a cementitious ceramic-like material usually synthesised from metakaolin in combination with ortho-phosphoric acid. Similar to the conventional alkali-based geopolymer, the phosphate-based one also has a tetrahedral molecular structure consisting of tetrahedrally coordinated $Al^{3+}$, $Si^{4+}$, and $P^{5+}$ atoms connected by oxygen bridges [1-2]. The advantage of the phosphate synthesis route compared to the conventional alkaline route is the use of the $[PO4]^+$ building unit to balance the negative charge on the $[AlO_4]^-$ unit rather than the use of free alkali cations that readily leach. Precisely because of the use of non-alkaline conditions, silico-aluminophosphate geopolymer has reduced efflorescence compared to alkaline analogues and, according to the available literature, provides better mechanical, dielectric, and thermal properties [3]. The reason for the superior properties of phosphate-based geopolymers compared to alkaline geopolymers could be the formation of an isostructural quartz-berlinite composite ($SiO_2$-$AlPO_4$). In contrast to the alkaline synthetic route, where the synthesis of geopolymer is influenced by a larger number of parameters, the main synthetic parameter of the phosphate synthetic route is the Al/P atomic ratio, followed by water content [3-4].

Therefore, in this work, the atomic ratio Al/P is set to 1, and the water-to-binder ratio is set to 0.9 to obtain the appropriate workability of the geopolymer paste. We investigated the feasibility of preparing porous phosphate-based geopolymer from metakaolin, phosphoric acid, and fine quartz sand via replica shaping. The polyurethane template is infiltrated with geopolymer paste, and the whole system represents a green body. The resulting green bodies were dried in closed moulds at 50 °C for several hours to solidify their shape before being subjected to heat treatment. Porous geopolymers were obtained by heat treatment at 600 °C at a speed of 1 °C $min^{-1}$, which enables the combustion of an organic template, after which it was additionally annealed at 1200 °C for 6 h. The samples were broadly characterised by XRD, DTG/DTA, ATR-FTIR, SEM and SS-IS analysis.

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# Influence of LiBOB on the structure, thermal properties and ionic conductivity of poly(ethylene oxide)

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Polymer electrolytes based on poly(ethylene oxide) (PEO) and a lithium bis(oxalato)borate salt (LiBOB) have shown their potential for applications as electrolytes for lithium-ion polymer batteries. In this work the dependence of the addition of the LiBOB salt on the structure, thermal properties and ionic conductivity of PEO was investigated. Solid polymer electrolytes PEO/LiBOB with different EO:Li molar ratios were prepared. Fourier transform infrared spectroscopy (FTIR) analysis showed the dependence of the amount of salt on the structure of PEO, especially on its crystallinity as one of the most important properties affecting the ionic conductivity of PEO-based polymer electrolytes. These results were confirmed by differential scanning calorimetry (DSC) analysis as the degree of crystallinity decreases with the addition of salt. Moreover, DSC analysis revealed the composition of the samples at which crystallinity of PEO completely disappeared. Thermogravimetric analysis (TGA) showed that the addition of salt causes a more complex non-isothermal decomposition of the prepared samples compared to pure PEO. Electrochemical impedance spectroscopy (EIS) revealed that the addition of LiBOB affects the ionic conductivity at room temperature and an optimal EO:Li molar ratio was defined.

# Pre and post processing of the substrates and surfaces for interface stability engineering in perovskite solar cells

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The recent enhancement of performance of optoelectrical devices heavily reposes on the preparing conditions. For example, photovoltaic devices such as perovskite solar cells require ultimate control in preparing and assembly of the constituting films in terms of favourable chemical compositions and advanced nanostructured morphology to yield high efficiencies over extended period. This is not a straightforward case as surface related phenomena influence all of the interfaces, and therefore even the solar cell performance. This is especially obvious in the case of solar cell assembly in the so-called normal configuration, where an electron transfer layer has to be deposited on top of a transparent conductive layer, both on top of glass substrate, before photoactive and other layers. Deriving these in a nanostructured configuration is beneficial, despite the nanostructuring-related higher risk of inducing defects that can diminish both the efficiency and stability of the solar cell.

Here we discuss two compositions: titania and zincite, in several configurations: common planar and advanced nanostructured (titania nanotube arrays and zincite nanorods arrays). We investigate several processing routes to shed more light on the potential strategies to control the interfacing challenges. For example, we treat the surfaces mechanically with nitrogen gas stream and chemically using a sequence of solvents in ultrasonic bath at ambient atmosphere. Alternatively, we applied ozonisation at ambient atmosphere. Finally, we applied several strategies of plasma processing.

This approach offers better understanding of the first and/or last step in the process of producing multi layered thin film samples, the importance of which is mostly overlooked in literature. We try to elaborate on different pre- and post-processing of the samples using chemical, physical and complex methods with respect to the economic, technical and practical aspects to the optoelectrical products.

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# Structural and thermal properties of PEO/NaAlg blend complexed with $NaPF_6$

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As the society develops, the need for different energy sources rises but the awareness of its influence on the environment rises too. To meet this increasing demand for suitable energy sources, that comply with sustainability and much cleaner and efficient energy, researchers turned towards sodium ion battery (SIB) [1]. Development of SIB with solid-state polymer electrolyte (SPE) is challenging, especially in finding a material that meets all the necessary requirements to be considered as SPE in SIB. Poly(ethylene oxide) (PEO) is the promising material for the solid polymer electrolyte usage, but its low ionic conductivity at room temperature needs to be improved. Preparation of PEO blends is one way to improve the ion migration by reducing the crystallinity of PEO. This can be achieved with sodium alginate (NaAlg) [2]. The extension of this previous work is done with the addition of sodium hexafluorophosphate ($NaPF_6$) salt and preparation of SPE as the ternary system.

In this work, the possibility of preparation the flexible and free-standing polymer electrolyte film based on a PEO/NaAlg-$NaPF_6$ composite by solution casting technique is investigated. The objective was to prepare film with good thermal properties and thermal stability for solid-state sodium polymer batteries. The structural and morphological features of the casted polymer composite films have been investigated by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). In addition, the thermal properties and thermal stability were investigated using differential scanning calorimetry (DSC) and thermogravimetry (TG). The structure of PEO/NaAlg blend changes with the incorporation of $NaPF_6$ salt, and the higher the salt concentration, the more it changes. Composites with higher salt concentration goes through the transition from the film state to the gel state. The addition of $NaPF_6$ salt has also a complex effect on PEO the thermal properties in PEO/NaAlg-$NaPF_6$ composites, with a significant reduction in PEO crystallinity. This significant reduction is observed in gel state composites. The glass transition also goes through a major change under the influence of the strong interactions in the ternary system. PEO/NaAlg blend degrades in three degradation stages, while PEO/NaAlg-$NAPF_6$ composites have more complex degradation with up to five degradation stages depending on the composite composition. The main influence of the salt incorporation in PEO/NaAlg blend is the reduction of blend stability with the increase of $NaPF_6$ content, which, however, is still acceptable for the stated purpose.

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# Sol-gel derived calcium phosphates: synthesis and properties

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Nowadays, calcium phosphate (CaP) ceramics are the golden standard of bone engineering materials because of their many useful properties in bone grafting. Their bioactivity can be assigned to their structural similarity to the mineral apatitic part of bone and they exhibit very high osteoconductivity and osteoinductivity.

In this study, we present the sol gel synthesis route to calcium phosphate aerogels via supercritical drying. Calcium and phosphate alkoxides are used as precursors for the aqueous synthesis. The precursors were synthesized by refluxing elemental calcium or phosphorus pentoxide in appropriate alcohols. Aerogels were obtained by drying with supercritical $CO_2$ (100 bar, 50 °C) for 12 h.

General characterization was performed by DTA, FT-IR and XRD, while morphology and porosity specifically were determined by microscopy and adsorption-desorption nitrogen isotherms. Results point to ability to derive calcium phosphates having chemical homogeneity and porous body morphology suitable for bone engineering application.

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# Application of intensive grinding in obtaining metakaolin and zeolite

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Pozzolanic materials with high aluminosilicate content such as metakaolin and fly ash are often used in the synthesis of zeolites as cheap and easily available precursors [1]. The main disadvantage of metakaolin is the need for heat treatment of kaolinitic clays at temperatures around 700 °C [2], while the disadvantage of conventional hydrothermal synthesis of zeolites is the creation of large amounts of waste alkaline solution [3]. The mechanochemical approach represents a greener, cleaner way of processing kaolin-into-metakaolin and, in combination with NaOH, opens up the possibility of obtaining zeolites [3].

In this paper, different conditions for the mechanochemical production of metakaolin and zeolite were examined. The obtained samples were subjected to a different structural, electrical, spectroscopic and morphological characterisation. Results point out to ability to tailor certain via application of the intensive grinding during the synthesis stage.

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# Thermophysical properties of 1-butyl-2-methylpyridinium tetrafluoroborate ionic liquid in water and methanol at different temperatures

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Ionic liquids (ILs) in principle are a diverse group of organic salts which are mostly liquid at ambient temperatures [1]. In this work, three thermophysical properties [2-5], specifically, density, viscosity, and molar conductivity, were determined for 1-butyl-2-methylpyridinium tetrafluoroborate, [b$_2$mpy][BF$_4$] IL in water and methanol in the molality range of IL ($b$ = 0.005 – 0.1 mol kg$^{-1}$), and in temperature range, $T$ = (278.15 – 313.15) K at 5 K intervals. From measured experimental data, the thermal expansion coefficient, $\alpha_p$, apparent molar volume, $V_\Phi$, partial molar volumes for solvent, $\overline{V}_1$, and solute, $\overline{V}_2$, apparent molar volume at infinite dilution, $V_\Phi^o$, Masson's interaction coefficient, $S_V$, Heppler's coefficient, $\left(\frac{\partial^2 V_\Phi^o}{\partial T^2}\right)_p$, limiting apparent molar expansibility, $E_\Phi^o$, viscosity $B$-coefficient, ion association constant, $K_A$, and thermodynamic parameters ($\Delta G^o$, $\Delta H^o$, $\Delta S^o$) of ion-pair formation, were calculated. The ion association process is spontaneous and entropy-driven for [b$_2$mpy][BF$_4$] in investigated solvents.

The obtained thermophysical data were compared with the available values from literature. Finally, from the results obtained, a structure-breaking or making properties for investigated systems are discussed.

Understanding thermophysical properties of pure ILs or their mixtures with different solvents is essential to determine potential applications (*e.g.* electrolytes for Li-ion batteries) [6].

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# Recrystallization of thin Fe-based nanocrystalline films

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Thin films are commonly used in many micro-electromechanical systems (MEMS) which is connected to strict requirements for their mechanical properties. These are firmly connected to their thickness and grain size [1-2]. Recrystallization and grain growth [3] during heat treatment allows for altering the film properties while keeping the thickness.

Fe-based thin nanocrystalline films were prepared by DC magnetron sputtering. Their microstructure and surface morphology were studied by conventional and scanning transmission electron microscopy (TEM, STEM) equipped with Automated phase and orientation mapping (ACOM-TEM) and secondary electron detectors. The prepared films were annealed in-situ in TEM and the distribution of grain size at elevated temperatures was monitored. Moreover, the mechanisms of grain growth were directly observed. The experiment conditions were then reproduced using molecular dynamics (MD) simulations and the effects of grain orientation and geometry on the growth mechanisms were examined.

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# Surface tension in chalcogenide glass-formers

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Surface tension plays an important role in different kinetic processes in amorphous materials. Surface tension is essential for the description of nucleation and crystal growth, as well as for finding physical properties (viscosity, diffusion coefficients) describing the mobility of structural units in the amorphous materials. [1-3]

The prepared contribution focuses on surface tension measurements in chalcogenide glass-forming materials in the melt, undercooled melt, and glass regions. In the melt region, the profile of hanging and sitting droplets is analyzed to calculate the surface tension using OriTas project [4]. Surface tension in the undercooled melt near to glass transition temperature is evaluated using nanoindentation (NI), and flattening of the surface profile (FSP) embossed in the studied material. FSP is based on following the flattening process using atomic force microscopy and light scattering. The measurements reveal the flattening process's rate constant during isothermal annealing. The rate constant depends on near-surface viscosity, surface diffusion coefficient, and surface tension. NI gives an excellent tool for near-surface viscosity estimation in amorphous materials because there is no need for detailed knowledge of material other properties. Therefore, the combination of the NI and FSP allows the evaluation of near-surface viscosity and surface tension in the studied materials.

Combining the surface tension data in the melt region and near the glass-transition temperature can provide a tool to interpolate surface tension data in the undercooled melt region. Such interpolation could be essential for the description of other processes taking place in the studied glass-forming materials.

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# Thermally-activated catalysis on CuNi nanoparticles

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The CuNi nanoparticles (NPs) were prepared by solvothermal synthesis [1]. The nanoparticles were characterized by electron microscopy, X-ray powder diffraction, thermal analysis (DSC), and other methods.

The CuNi NPs were deposited on superfine unreactive silica supports. After purification, the nanostructured mesoporous CuNi(NPs)/$SiO_2$ powder was obtained. The catalyst was compressed into tablets which were activated by hydrogen involving gas (20 vol.% $H_2$ in $N_2$) at 300°C. Tablets containing CuNi NPs with different Cu/Ni ratios were prepared.

The model catalytic reaction of ethanol non-oxidative dehydrogenation to acetaldehyde was studied in the gaseous phase. The reaction feed of absolute ethanol (liquid) was introduced through a syringe pump in a preheated stream on $N_2$ (ethanol vaporization occurs). Catalytic tests were carried out in a fixed-bed stainless steel reactor. The experimental temperature range was 200 - 350°C.

We observe the highest ethanol conversions with acetaldehyde selectivity of about 80% and ethanol conversion of about 10% for catalytic sample involving Cu/Ni molar ratio equal 2.30. The highest conversion was obtained at 220°C but the catalyst deactivation upon a time was observed.

The characterization of the catalyst after the use was done. The electron microscopy confirmed that the catalysts remained mesoporous and free of oxides. Oxide-free structure and nanometer-size particles of CuNi were also confirmed by analysis of X-ray powder diffraction.

The main cause of catalyst deactivation is not due to oxidation. The obtained results were compared with a similar experiment on copper NPs [2].

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# Homogenization of rapidly solidified Al-Li-based ribbons studied by electrical resistivity and in-situ electron microscopy

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Melt-spinning [1] of aluminum alloys improves their chemical homogeneity and refines their grains, which cannot be achieved by conventional alloy casting. The cooling rate of this process could reach $10^3$ -$10^6$ K/s resulting in the formation of a highly supersaturated solid solution. Materials received by this process are in the form of thin ribbons. Ribbons of two Al-Li-Cu-Mg-Zr and Al-Li-Cu-Mg-Zr-Sc alloys were prepared, and their thermal stability was studied by electrical resistivity measurements during linear heating. Subsequently, scanning/transmission electron microscopy (S/TEM) observations during in-situ annealing were performed, and the main features of the microstructure evolution were compared with resistivity measurements. The rapidly solidified microstructure of both ribbons in the intermediate plane consists of fine grains with coarser particles of primary phases containing Cu and Fe (iron is present in the alloy as an impurity) located inside grains and on grain boundaries. These particles dissolve and transform during annealing. The final material after homogenization contains separated grain boundary $Al_5CuLi_3$ phase and $Al_{13}Fe_4$ iron-rich particles. In addition, non-equilibrium $Al_3Zr$ and $Al_3(Sc,Zr)$ (in the Sc-containing alloy) particles evenly distributed in the grains were formed.

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# Characterization of CaP coatings prepared on AZ31 magnesium alloy in the presence of various organic complex substances under hydrothermal conditions

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Magnesium and its alloys are attractive materials due to their specific properties. Their disadvantage is their low corrosion resistance, which can be increased by the use of a calcium phosphate (CaP) coating.

CaP coatings were prepared by hydrothermal method at 120 °C for 2 h at an initial pH of 7 and in the presence of different concentrations of complexing agents including disodium beta-glycerophosphate (BGP), potassium nitrilotriacetic acid (NTA), glycine (Gly) and ethylenediaminetetraacetic acid (EDTA). The prepared coatings were characterized in terms of morphology, chemical composition and thermal stability using scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), X-ray diffraction spectroscopy (XRD), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) coupled with differential thermal analysis (DTA). The corrosion resistance of the coatings was investigated by potentiodynamic polarization in 0.15 M NaCl.

The results showed that the complexing agents influenced the morphology of the CaP coatings and their corrosion resistance increased by two orders of magnitude compared to the AZ31 alloy. The chemical composition and thermal stability of the prepared coatings were similar. The mechanism of action of BGP for the formation of CaP coating compared to other complex substances was different as shown by experiments based on FTIR and TG/DTG analysis.

# The importance of ammonium and potassium precursor cations for the preparation of CaP coatings in terms of impact on microstructure, thermal and corrosion properties

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The effect of a precursor containing a potassium or ammonium cation was studied for the hydrothermal preparation of calcium phosphate (CaP)-based coatings on AZ31 magnesium alloy at pH 5 and 7. This effect was also monitored in the presence of ethylenediaminetetraacetic acid (EDTA). The prepared CaP coatings were evaluated in terms of their morphology and chemical composition using scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), as well as their phase composition using X-ray diffraction spectroscopy (XRD), thermal behavior using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The electrochemical corrosion behavior of the CaP-coated samples was evaluated using the potentiodynamic measurements in 0.15 M NaCl solution. The results showed that the presence of ammonium precursor ions had a negative impact on the quality of the coatings compared to potassium precursor ions.

# Effects of PET microplastics on the soil properties: A thermogravimetric approach

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The problem of microplastics, small plastic particles contaminating the environment, is a highly discussed topic nowadays. Studies monitoring environmental pollution by microplastics have found contamination of the oceans, glaciers, soil, air, fauna, flora, and human food. Thus, plastic pollution is now everywhere, and this fact makes the issue of plastics and microplastics a "major environmental problem" of our time [1].

Many studies demonstrate their negative impact on flora, fauna, and human health [2]. At present, research in the field of microplastics focused mainly on fresh or seawater. However, their effects on soil quality have not been described sufficiently yet. Nevertheless, it became clear that microplastics significantly impact soil properties, particularly soil aggregation, soil nitrogen and carbon content, water retention, or the stability and quality of soil organic matter [3].

In this study, the effects of PET microplastics on selected properties of three soil types were studied. In particular over 1 year, we tested changes in soil organic matter thermal properties, soil respiration, amount of water, water holding capacity, soil aggregation, and nutrient content.

The results revealed specific effects of microplastics on soil properties, already at short incubation times. PET microplastics affected several soil properties including soil texture, water holding capacity, nutrient content, and activity of soil microorganisms represented by respiration. The results showed that the effects of PET microplastics on soil properties were soil-type-dependent and enabled to monitor a gradual incorporation of PET in soil. In addition, thermal analysis revealed the effect of PET on soil quality (priming effect) and also possible partial PET transformation. Nevertheless, further studies are needed to find a connection between these changes in soil properties and soil type and its specific characteristics.

The work was supported by the project FCH-S-23-8297 of the Ministry of Education, Youth and Sports of the Czech Republic.

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# Thermal activity of fresh soil

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Soil as a complex ecosystem is being described by several sophisticated techniques and methods to get information about its type, composition, fertility or contamination. Microorganisms as the most active components in soil are responsible for many biochemical reactions which generate a flow of heat easily detected by a microcalorimeter. Therefore, the isothermal microcalorimeter TAM III was used as a powerful tool to study the microbial activity in soil. The thermodynamic parameters such as enthalpy change, Gibbs free energy change and entropy change can be easily obtained.

The samples of fresh (wet) and dried soil (without any mechanical or chemical modification) with constant small volume of water or nutrient solution were dispensed into measuring ampoules and the heat flow generated by the microorganisms was monitored at constant temperature controlled by the microcalorimeter. For this purpose, the samples of soil were collected in autumn and spring. The nutrient solution contained glucose and ammonium sulphate and the influence of their concentration on the microbial effects was studied.

# Hydration and Thermal properties of hybrid alkaline cements

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This study aimed to prepare hybrid alkaline cements containing flue dust arising from metakaolin production. This material has potential as a suitable source for alkaline activation due to its high proportion of amorphous phase. However, it also contains a non-negligible amount of non-burned clay minerals. The cementitious blends consisted of Portland cement, flue dust and 5% moderately alkaline activators. The specific aim pursued in this research was to determine the effect of different activators on the reactivity of flue dust, hydration kinetic, the development of strength in cement or the reaction products formed. The hydration kinetics of the binder was investigated using isothermal calorimetry. The reaction products were characterized by X-Ray powder diffraction analysis and simultaneous thermal analysis. Heat microscopy and thermal dilatometry were used to study the behaviour of these binders under thermal stress. Other techniques such as scanning electron microscopy were also used to describe the microstructure.

# FT-IR supported thermogravimetric analysis of organic matter decomposition in soil

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Understanding the organic matter (OM) decomposition processes in soil is crucial in many industries. To evaluate a time sequence of decomposition, soil incubations of oven-dried preweighed green tea bags were conducted in soil. Destructive harvests of quadruplicates were taken at 0, 1, 2, 3, 4, 8, 12 and 24 weeks. Tea bags were then oven-dried, adhered soil particles and plant roots were gently removed and the bags were weighed.

For thermogravimetric analysis, samples weighing ~ 7-20 mg were transferred to an alumina sample holder placed into the thermoscale and heated from the initial laboratory temperature (20°C) to a final temperature of 700°C with a heating rate of 10° $C{\cdot}min^{-1}$. The flow rate of reactive gas (air or nitrogen) was 50 $ml{\cdot}min^{-1}$. Ash content and total moisture of the samples were determined. FT-IR spectra of tea organic matter samples were recorded over the range of 4000–400 $cm^{-1}$ with a peak resolution of 4 $cm^{-1}$.

# Thermogravimetric analysis as a supportive method in a study of plasma activated water effect on organic matter decomposition rate in soil

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The recent trend of cold plasma water activation research comprises an increasing number of relevant publications dealing with a variety of devices and applications. Plasma activated water (PAW) contain species responsible for enhancing seed germination, increasing the rooting speed or stimulating plant growth [1]. However, PAW also shows a strong antimicrobial effect [2]. The aim of this work was to find any possible negative effect of PAW on organic matter (OM) decomposition rate in soil.

In this study, PAW prepared by using dielectric barrier discharge for 2, 5 and 10 minutes was applied in a pot experiment to a model plant *Lactuca Sativa* for total of 90 days. As a control, distilled water was used. For OM decomposition rate determination was used tea bag index introduced by Keuskamp [3], which estimates the decomposition constant (k) of an asymptote model of litter decomposition and a stabilized ratio of the hydrolysable fraction (stabilization factor S) using a single measurement of the mass loss ratios of green and rooibos tea. To gain insight on how PAW could affect the process of OM decomposition in soil and its physicochemical properties, thermogravimetric analysis was chosen.

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# Influence of titanium dioxide nanoparticles on soil properties

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Even though synthetic nanoparticles pose potential environmental risk, their impact on the environment is still not well understood. $TiO_2$ nanoparticles are among the most used and widespread nanoparticles, therefore, the contamination of the environment with these nanoparticles is inevitable. One of the properties, due to which are these nanoparticles used, is their photocatalytic effect upon UV irradiation [1]. During this process, especially in the presence of water, highly reactive radicals are formed. They have an oxidative effect on organic compounds, this effect is largely used for the photodegradation of organic pollutants [2]. Therefore, it can be hypothesized that the contamination of soil by $TiO_2$ can lead to the degradation of soil organic matter. On the contrary, some authors suggested that $TiO_2$ polymerization reactions between soil organic matter (SOM) moieties [3]. Thus, the aim of this work is to clarify which processes occur after irradiating soil contaminated with $TiO_2$ nanoparticles.

To assess the impact of $TiO_2$ nanoparticles and UV/vis irradiation on SOM, we caried out experiments during which soil contaminated with $TiO_2$ nanoparticles was irradiated at different water contents. These samples were then analyzed using thermogravimetry and FTIR spectrometry. Surprisingly, using thermogravimetry, it was possible to observe effects of irradiation on soil biomass and also ecotoxic effect of $TiO_2$ nanoparticles. However, no changes caused by photocatalytic activity of $TiO_2$ nanoparticles were detectable using thermogravimetry.

Data acquired using FTIR spectrometry were processed using two different statistical methods – correlation analysis and principal components analysis. Correlation analysis was found t to be not a suitable method of data evaluation for the purpose of this work. Principal components analysis proved, that higher and caused its degradation.

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# Non-isothermal crystallization kinetics of biocomposites based on PLLA/PHBV and spent coffee grounds

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The last decades have been marked by the development of alternative materials to synthetic polymers while maintaining the specified properties. The accent is placed not only on the renewability of resources, but also on the biodegradability of the used materials to prevent accumulation of plastic waste in the environment [1]. To this purpose, many studies have been carried out to utilize agricultural waste as a filler in biocomposite structures [2–4] and it has been found that agricultural waste in the form of particulate filler may not only improve some material properties such as ductility, but may also act as a nucleating agent [5,6]. This study deals with the modification of a predominantly amorphous poly(lactic acid) (PLA) by blending it with a semicrystalline biopolymer, polyhydoxybutyrate-co-valerate (PHBV), which possesses high crystallization ability. The blends with different concentrations of the PLA and PHBV were compounded with a spent coffee grounds (SCG) and processed by injection moulding. The structural, thermal and mechanical properties of the fabricated specimens were investigated. Particular attention was paid to the effect of the presence of SCG and the concentration of PHBV in the blend on the crystallization kinetics and Vicat softening temperature (VST). However, only slight increase of VST (ca. 10 °C) was observed for equimolar blends of PLA/PHBV. The effect of SCG as a nucleating additive and accelerator of primary crystallization was analysed and confirmed by differential scanning calorimetry (DSC) for pure PLA Luminy L130 [6]. The addition of SCG into the matrix of PLA Luminy LX175, characterized by a higher content of D-isomers and higher viscosity in the primary crystallization region, did not affect the heterogeneous nucleation. For the utilized PHBV, SCG caused the growth of nucleation barriers, thus reducing the rate and ability of primary crystallization. Nevertheless, PLA/PHBV/SCG composites provide an attractive possibility in terms of increasing the degree of crystallinity and VST.

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# Insight into soil biochemistry by combining Glomalin-related soil protein (GRSP) and Thermogravimetry/Mass Spectrometry

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Glomalin-related soil protein (GRSP), an essential soil glycoprotein produced by arbuscular mycorrhizal fungi, helps in soil carbon and nitrogen storage, soil aggregation, erosion resistance etc. [1]. This extremely stable and heat resistant protein accounts for a substantial element of organic soil carbon [2]. The presented study aims to combine the GRSP data with the results of thermogravimetry coupled with mass spectrometry (TGA/MS) to understand the soil properties.

A total of 167 soil samples representing erratic soil compositions in the Czech Republic were examined, where GRSP varies from 1.01–17.39 mg/g of soil. TGA weight loss data and GRSP exhibited three pronounced temperature ranges with higher correlation, where each temperature range has different potential reasons to correlate. The most significant temperature range (330—430 °C) is attributed to the co-occurrence of GRSP with other soil organic matter. A strong negative correlation at higher temperatures (>600 °C) indicates an inverse relation between GRSP and soil inorganic components. The results of mass spectrometric analysis of the evolved gases ($CO_2$ and $H_2O$) confirmed these outcomes.

The highest mass loss during thermal analysis is caused either by higher GRSP content or a higher amount of carbonates ($CaCO_3$) in the soil. A strong positive correlation with the humic acid/fulvic acid ratio supports its impact on soil biochemistry. Both positive and negative correlations of GRSP with various soil compounds indicate a comprehensive soil composition scenario influencing GRSP production and storage in the soil.

This study is a novel approach to associate GRSP data with TGA/MS results to evaluate the complex interdependency of soil organic carbon with other soil parameters.

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# Differential Scanning Calorimetry as a Useful Tool in the Study of Phase Change Materials

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Differential Scanning Calorimetry (DSC) is a thermal analysis technique used for examination of thermal effects related to phase transformations in materials. Phase change materials (PCMs) are mostly used for the application of energy storage by latent heat method. They are capable both storing and releasing a large amount of energy during the phase change process. Recently, PCMs were used in many engineering department (e.g. mechanical engineering – heat exchanger, electrical engineering – enhancing efficiency of solar panels, civil engineering – smart construction materials). In general, PCMs are considered as smart materials [1].

This contribution reports on experiments testing one of the important properties, namely long-term chemical stability. The commercially supplied PCMs with phase transition temperatures in the range of 15-25 °C for civil engineering applications were tested. PCMs were analysed using DSC method after defined temperature history, in fact, melting enthalpy of aged samples was measured.

Our work presents unique time study results. For example, the results show that the material commercially labelled Parafol 16-97 is stable even after 2000 cycles. In contrast, the material Parafol 18-97 is likely to show degradation and carbon chain splitting after a short time [2].

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# Analysis of microplastics in sewage sludge

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From the information so far, it is known that microplastics (MPs) at wastewater treatment plants (WWTPs) cause various complications. MPs adversely effect the quality of the treated water by reducing the efficiency of the treatment processes. The presence of MPs also has the effect of inhibiting the production of activated sludge flakes and can inhibit the production of methane in the sludge and effect its key enzymes and metabolic intermediates. In addition, the presence of MPs has been found to reduce the diversity of biological communities and the abundance of essential microorganisms, thereby significantly affecting the efficiency of the biological stage of wastewater treatment [1,2]. Most of the microplastics removed from wastewater accumulate in the sludge which can lead to significant contamination of soil systems with microplastics [3].

The methods published so far for analysis of MPs in sludge are complicated and as there is no standardized procedure for the treatment of WWTPs samples yet, also the analysis already mentioned are very different from each other [2,4].

It is for this reason that the aim of this work is to develop a relatively simple, fast and reliable method for analysis of MPs in sewage sludge. Evolved gas analysis, i.e. a thermogravimeter coupled either with mass spectrometer or with infrared spectroscopy appeared to be a suitable method. Using these methods, we were able to capture characteristic peaks for the analyzed PLA. For MS the signals were *m/z*: 29, 42, 43, 56 and 100. For FTIR it was 1792 $cm^{-1}$ and 1247 $cm^{-1}$. Those signals can be used for both qualitative and quantitative analyses.

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# Properties and microstructure of laser treated WC/CoCr thermally-sprayed coating on AZ91 magnesium alloy

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Magnesium alloys are perspective lightweight materials for aerospace and automotive industry, however, their corrosion and abrasion properties are poor compared to steels or aluminium alloys. One way of improvement are thermally sprayed coatings which can provide both corrosion protection and superior friction surface.

The aim of this work is to study microstructure and properties of thermally-sprayed tungsten carbide-based coating (WC/CoCr) prepared on widely used AZ91 magnesium alloy. To minimize porosity, laser treatment of the coating was performed. The heterogeneous composition of the coating gives rise to many possible phases that can precipitate during either coating preparation or laser treating. Several laser settings were tested in order to obtain the lowest porosity and highest hardness. Phase and microstructure composition were studied with XRD, SEM with EDS and EBSD analysis. In order to fully characterise the influence of the laser technique a TG-DTA and DSC was performed.

The as-sprayed structure was significantly heterogeneous consisting of crystalline, partially crystalline, and amorphous regions formed due to rapid solidification processes and significant plastic deformation of the powder particles during spraying. The laser treatment resulted in recrystallization and removal of microstructural defects in the thermally-sprayed coating.

# Thermal analysis of raw meals doped with Li, Cu and S for the burning Portland cement clinker

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One of the options to reduce $CO_2$ emissions in cement production is to lower the burning temperature of the main intermediate - clinker. $SO_3$ has been shown to have a very positive effect on clinker melt, both in terms of viscosity and surface tension [1].

Both copper and lithium act as strong fluxes and lower the temperature of the clinker melt formation [2]. In addition, sulfur promotes the stabilization of more hydraulically active modification of alite $M_1$ [3].

For the experimental work, a basic raw meal was prepared from common cement raw materials (2 types of limestone, clay shale, iron correction and FGD gypsum). Chemically pure compounds $(NH_4)_2SO_4$, CuO a $Li_2CO_3$ were used like dopants.

The changes occurring in the raw meals with different contents of these dopants were monitored by differential thermal analysis (DTA). In particular, the exotherm of formation of the clinker phase of belite and the temperature of clinker melt formation were monitored.

It was found that lithium decreases the melt formation temperature the most and sulfur the least. Lithium by up to more than 100°C compared to the reference raw meal. In addition, it also lowers the decomposition temperature of limestone, and at higher Li contents, a decarbonation endotherm splitting into two minima occurs.

In practice, the use of these dopants could lead to the intensification of cement production associated with a reduction in energy consumption and $CO_2$ emissions.

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# Influence of salts of simple carboxylic acids on hydration and basic properties of RPC

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This work aims to study whether it would be possible to use compounds of simple carboxylic acids and alkali metals in order to increase the workability of RPC and how these affect the hydration of RPC and its mechanical properties. These substances were added together with superplasticizers. Therefore, paper deals with possibility of increase in workability which would be higher when compared to the sole addition of only the superplasticizers themselves.

The effect of alkali metal formates and propionates on flow, mechanical properties and pH of RPC was studied. The effect of replacing them with calcium formate on the listed properties was also monitored. Furthermore, the influence of potassium formate, potassium acetate and potassium propionate on the hydration of RPC was observed with the help of isothermal calorimetry. The influence of their replacement with calcium formate and with calcium oxide was also monitored.

The results showed that potassium formate, potassium propionate, sodium formate and sodium propionate in combination with calcium formate can increase RPC workability. But it is necessary to add an optimal ratio of alkali metal formate/propionate - calcium formate, because a higher content of calcium formate, on the contrary, leads to a decrease in flow. In calorimetric measurements, it was observed that the addition of potassium formate leads to a decrease in the total amount of heat developed in the induction period. Its replacement with calcium formate has no significant effect on the induction period. In contrast, the addition of potassium acetate or propionate leads to an increase in the total amount of heat developed in the induction period, and their replacement with calcium formate leads to its gradual decrease.

# Viscosity and crystal growth in amorphous samples of $Ge_{25}Se_{75}$

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The presented study deals with crystal growth kinetics in undercooled melts region of $Ge_{25}Se_{75}$ chalcogenide glass. Two types of samples were prepared: bulk samples and thin films. Thin film samples with various thicknesses were prepared using thermal evaporation and spin-coating.

Viscosity measurements were performed using thermomechanical analysis (bulk samples) and nanoindentation measurements (bulk samples and thin films). The obtained data were described using the Mauro-Yue-Ellison-Gupta-Allan (MYEGA) [1] viscosity model, which was further enhanced with the viscosity data of melts.

The crystal growth was observed using an IR microscope. The dual character of crystal shapes was noticeable. X-ray diffraction identified the crystals growing at lower temperatures as $Ge_4Se_9$ composition, with properties similar to $GeSe_2$ [2]. At the temperature of around 380 °C both $Ge_4Se_9$ and $GeSe_2$ crystals were observable. Above the mentioned temperature, only $GeSe_2$ crystals were present, which showed that $Ge_4Se_9$ started to melt and reorganise into a $GeSe_2$ structure, which stayed present up to the melting point. The crystal growth rates were described using the Arrhenius formula, from which the activation energy of growth was calculated. The activation energy values of bulk samples and thermal evaporation thin films are considered equal, while the value for thin films prepared with spin-coating is significantly different [3].

Analysing kinetic growth data, it was determined that the normal growth model was the most accurate to describe the temperature dependence of crystal growth rates. The model was further enhanced using parameter $\xi$, which shows the real relation between viscosity and kinetic growth rate. The chosen crystal growth model describes the measured data well and can be used to predict crystal growth behaviour in broad temperature interval.

Acknowledgement:

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# Dielectric and thermal properties of composites based on low-density polyethylene and NaA zeolite

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The low-density polyethylene/NaA zeolite (LDPE/NaA) composites are recently proposed materials for food packaging. The samples of LDPE/NaA composites are made. Determination of weight fraction and the dispersion degree of zeolite in the LDPE/NaA zeolite composites are done by XRD and FTIR analyses. The obtained data for zeolite's weight fraction are verified using thermogravimetric analyses. Scanning electron microscopy is used to investigate the morphology of composite. It is established that the zeolite particles in the polymer matrix have a cubic shape and that they are well dispersed. Dielectric spectroscopy measurements are performed at room temperature in the frequency range of 20Hz-30MHz. The impact of weight fraction on both, the real and the imaginary, parts of the dielectric constant is investigated. Two relaxation peaks of the imaginary parts of permittivity of LDPE/NaA zeolite composites are detected. The first is due to Maxwell-Wagner-Sillars polarization and shifts to lower frequencies with increasing zeolite mass fraction. The second relaxation peak is due to free sodium ions hopping from one free place to another within the zeolite particles and has a nearly constant frequency. Analysis of the electrical conductivity of LDPE/NaA zeolites showed that it increases with an increase in the weight fraction of zeolite. The thermal diffusivity, by which the thermal conductivity was determined, was investigated using the laser flash method. It is found that thermal conductivity changes in three well-defined intervals. The results are compared with those obtained by the theoretical model reported in the literature. None of the models can describe obtained dependencies in each of the three intervals. Results are discussed from the point of view of the formation of new conductivity pathways formed from zeolite particles.

# Influence of silver introduction on glass transition and crystallization processes in $As_{40}Se_{30}Te_{30}$ glass

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In this paper we have analysed the influence of introduction of silver in wide range of concentration, from 1 to 17 at.% in the $As_{40}Se_{30}Te_{30}$ chalcogenide glass matrix, on the two most important thermally induced processes, glass transition and crystallization. The analysis was applied to data obtained from non-isothermal differential scanning calorimetry at different heating rates. It was shown that the values of the activation energy of the glass transition process range from 160 to 282 kJ mol$^{-1}$. It was found that during the thermal treatment, the structural units of glass matrix as well as the units with silver crystallize. In order to examine the morphology of nucleation and growth, the Johnson-Mehl-Avrami model was applied. Apparent activation energy of crystallization was determined by using different non-isoconversion and isoconversion models. The values of this parameter were between 95 and 127 kJ mol$^{-1}$ and depended on the glass composition in a complex manner. Results have shown that the introduction and increase of Ag content significantly affects the thermal properties and the glass structure not only by forming new structural units but also by changing their extent. These changes have been confirmed by XRD diffraction measurements of annealed samples.

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# Thermal stability and micostructural transformations of Ni-P alloy powders

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Ni-P alloys have been attracting considerable scientific interest due to their catalytic and electrocatalytic activity, magnetic characteristics, anti-corrosion and mechanical properties [1-3]. Their chemical composition and microstructure define their functional properties and possibility of practical application in different fields.

Considering their amorphous structure, Ni-P amorphous alloys are thermodynamically and kinetically metastable, with pronounced tendency to transformations into the structural forms with improved stability. Ni-P powder alloys of different Ni/P ratio and microstructure, prepared by chemical reduction, were studied regarding their thermal stability and mechanism of thermally induced microstructural transformations. Thermal analysis of the Ni-P alloys indicated multi-step processes of crystallization and recrystallization. The analysis of the Ni-P powder alloys thermally treated at different temperatures applying different structural characterization techniques revealed formation of stable and metastable Ni and P -containing crystalline phases. It was confirmed that the starting composition of the Ni-P alloys affect their thermal stability and mechanism of thermally induced microstructural transformations. Further, influence of chemical and phase composition on the properties of the Ni-P alloys is expected, which is illustrated with the example of corrosion performance of the as-prepared and thermally treated Ni-P alloys.

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# The reactivity study of fuels for the metallurgical industry using thermogravimetry

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Pyrometallurgical processing and production of metals by high-temperature methods requires the provision of oxidation-reduction processes, where fuels play an important role [1]. Fuels are generally used for the purpose of obtaining thermal energy and/or reduction work, or perform other functions such as gas permeability or carbonization ability. Due to the nature of the process and the required function of the fuel in it, various requirements are also placed on its properties, and therefore, among other things, on its reaction ability in interaction with the environment [2]. For this reason, assessment of thermal stability and quantification of fuel reactivity in the considered reaction systems is a necessary condition for defining optimal parameters.

Our research is focused on the evaluation of the reactivity of selected fuels that are used in the production processes of ferrous and non-ferrous metals obtained by reduction using thermogravimetric analysis. Thermogravimetry is one of the universal techniques for monitoring the influence of temperature, time and atmosphere on physico-chemical changes in the monitored material. The aim of the work was to use the acquired knowledge for the replacement of fossil fuels and reducing agents in the metallurgical industry and their substitution with hydrogen. The obtained thermogravimetric records provide a comprehensive picture of the thermal stability, reaction kinetics and thermal effects in the temperature range of the tested fuels. The measurement results confirmed the expected differences in mass degradation due to their structural composition. The use of the proposed methodology can be applied to various types of traditional as well as alternative fuels, such as various types of biomass, which are considered to reduce the environmental burden of production processes. From the obtained experimental results, it is evident that thermogravimetry has a great application in the field of investigating the properties of fuels.

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# Study of global warning key parameters in Slovak urban soils via thermal analysis

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Thermal analysis methods were used to investigate the global warning key parameters (mainly soil organic matter (SOM) and its key component - soil organic carbon (SOC)) in five park urban soil samples collected from A horizon around the Slovak lake. The SOM is one of the most important parameter of soil quality, because it largely affects all biological, chemical and physical soil processes [1]. The SOC is an important reservoir of carbon in its bio-geochemical cycle, and therefore attention is also paid to it's, from a research perspective of climate change [2]. The SOC stock reacts sensitively to changes in natural conditions [3]. From this point of view it is important to monitor these parameters not only in agricultural soil but also in urban soils. The SOM determination is possible by application of thermal analysis methods, which can be used to monitor also the other soil properties such as organic C, total N, carbonates and moreover, these methods are relatively cheap, require a small amount of sample, are fast, and provide reproducible results that are strongly correlated with a number of basic soil properties.

In this study thermogravimetry was used to establish mainly SOM by thermal weight losses. It was found that amount of SOM based on the equation: soil organic matter (%) = total organic carbon (%) x 1.72 correlated with the sum of thermogravimetry weight losses in two temperature intervals (200-400°C) and (400-550°C) ($R^2=0.93$). It is known that this interval correspond to labile and stable SOM. Above the 550°C there were found carbonates, which then were remove from soils because of the best description of SOM.

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# Impact of particle size on thermal properties of $Y_2O_3$-$Al_2O_3$ glasses

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The flame synthesis (FS) open possibility of use of difficult-to-melt yttrium- aluminate (YA) glasses not only regarding with the preparation of larger piece samples by hot pressing. This method is also important in development of materials for 3-D printing of ceramic composites. The microspheres obtained by FS are an ideal material due to their shape, but for their successful application it is necessary to achieve a suitable particle size and particle size distribution in the systems. Directed partial grinding appears to be a suitable solution, and therefore it is necessary to investigate the effect of the grinding conditions on the resulting particle size, as well as on the thermal behavior of this way prepared systems.

In this work FS was used for preparation of YA glass microspheres with eutectic composition (76.8 mol % $Al_2O_3$). The size of the microspheres was subsequently adjusted by different types of mills: vibratory mill and ball mill under different conditions of milling. The phase composition of all prepared systems was examined by X-ray powder diffraction (XRD), the size and particle size distribution were determined by particle size analysis (PSA). The prepared systems after FS as well as after milling were studied by differential scanning calorimetry (DSC) and differential thermal analysis (DTA). SEM and SEM-EDX were used for detailed examination of morphology of microspheres after individual steps.

The prepared samples after FS and after milling process were found to be XRD amorphous. The comparison of the results of the PSA measurements after the grinding experiments showed that systems with a smaller average size D [0.9] ~ 25 μm and monomodal particle size distribution were prepared. DSC and DTA analysis in temperature interval 35-1200°C, indicated the presence of 2 exothermic peaks with maxima at 939 °C and 1008 °C, regardless of the method of treatment. The results of the analyses show that the characteristic temperatures of the individual effects did not change and thus the reduction of particle size by grinding does not significantly affect the thermal stability of the glasses. Grinding mainly affected the size (area and height) of individual thermal effects. XRD patterns of samples after DTA shown presence of only YAG phase in all samples. The slight increase of intensities of individual diffractions was observed depending on increasing milling time, which sign different crystallization behavior in ground systems.

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# Porous carbon fibers prepared from cellulose as carriers of particles of active substances

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Due to their large active surface, nano- and microparticulate materials attract notable attention in many areas of human activity [1]. Their direct application runs into several technical problems. Many of them can be overcome when the active substances are applied in the form of composite materials containing a suitable carrier. Porous carbon fibers prepared from cellulose have proven to be a promising carrier that can be used for this purpose. In general, the practical advantage of carbon materials prepared by the carbonization of natural precursors, such as cellulose, is the availability and low price of raw materials. This study deals with the analysis of microstructure and water sorption characteristics of several composites of this type, while oxides of some metals are used as active substances. For this analysis a combination of thermoanalytical and microstructural methods was employed [2]. The study is a part of more comprehensive investigation of the structure and properties of carbon-based particulate porous materials prepared by pyrolysis of natural precursors [2-3].

Microporous carbon fibers were prepared by controlled carbonization of cellulose. Consequently, the particles of substances formed by precipitation of a solution in the presence of fibers are deposited on their outer surface. Composite materials produced by this method were examined by Scanning electron microscopy. Dried composites were filled by water using water vapour saturated desiccator. Amount of adsorbed water was precisely determined by precise sample weighting. The thermal analysis of adsorbed water was performed by differential scanning calorimetry (DSC) using power-compensation calorimeter with automatic intracooler (200 K). Encapsulated samples and dynamic nitrogen atmosphere were used. The free volume cavity sizes of pure carbon particles as well as free volume filled by water were estimated from the positron annihilation lifetime spectra (PALS) at room temperature.

It was shown that, depending on the material used for the active substance, the presence of a mesoporous structure appears in the resulting composite to varying degrees.

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# Thermodilatomery of illite

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Illitic clays, which contain more than 40 mass% of illite, are the second (after kaolin) important mineral resource for the ceramic industry. The illitic clay and water mixture is formed into a ceramic body, which is subsequently dried and thermally treated (fired). The firing process induces various physical and phase changes in the raw ceramic mixture [1-4]. The thermodilatometric curves of illitic clays originating from different sources reflect the differ composition (different amounts of quartz, feldspar, micas, montmorillonite, chlorite, and other mineral) of illitic clays [5-7].

While previous studies have extensively studied the linear expansion of illite crystals using high-temperature X-ray diffraction, the thermodilatometric behavior of illitic clays reflects changes in the crystal lattice and interactions between crystals and their surrounding environment.

The research focuses on illitic samples obtained from a mine located in Füzérradvány, Tokaj region, North-Eastern Hungary. Thermodilatometry (DIL) and simultaneous differential thermal analysis (DTA), and thermogravimetry (TG) were conducted under a static air atmosphere employing linear heating up to 1100 °C. Besides illite, illitic clay from Füzérradvány contains other admixtures, predominantly quartz, feldspar, and smectite. A simplified three-phase solid model was employed to isolate the influence of these admixtures. The results of the study shed light on the thermodilatometric characteristics of illitic clay and provide valuable insights into their behavior during firing. Understanding these changes is crucial for optimizing the manufacturing processes of ceramics utilizing illitic clays, thereby enhancing the quality and performance of ceramic products in the industry.

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# Thermal properties and structure of $Y_2O_3$-$Al_2O_3$-$ZrO_2$ glasses as precursors for preparation of ceramics materials with eutectic microstructure

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Alumina-based ceramic composites with eutectic microstructure have attracted considerable attention as potential candidates for ultrahigh temperature structural applications due to their thermal stability and impressive high temperature mechanical properties. One of the possibilities for preparation of ceramics with eutectic microstructure is densification of glass microspheres with suitable composition via hot-pressing. In the present work, we report on the preparation and characterisation of glasses in the system $Y_2O_3$-$Al_2O_3$-$ZrO_2$ with different content of $ZrO_2$. The compositions of prepared glasses are derived from eutectic composition of the system $Y_2O_3$-$Al_2O_3$ (76.8 mol.% $Al_2O_3$, 23.2 mol% $Y_2O_3$), with addition of $ZrO_2$ (5, 10, 15 and 20 mol. %) in the way that the $Al_2O_3/Y_2O_3$ molar ratio is preserved.

The glasses were prepared in the form of glass microspheres by flame spraying method form precursor powders synthesized via Pechini sol-gel method, which ensured their high homogeneity. The prepared glass microspheres were characterized by differential scanning calorimetry (DSC), X-ray diffraction (XRD) and SEM and SEM/EDX analysis. The high-temperature X-ray diffraction analysis (HT XRD) were used to study phase evolution during thermal treatment of glasses.

The prepared glasses were XRD amorphous except of compositions containing 15 and 20 mol% of $ZrO_2$, where traces of $ZrO_2$ phase were identified in the XRD records. The glass compositions as determined by SEM/EDX analysis correspond well with the proposed theoretical compositions. DSC traces of glasses revealed the presence of two exothermic effects, the first one with peak temperature around 935°C (for all studied glasses), and the second one, which is significantly compositional dependent, with peak temperature in the range of 1000°C (for 5 mol.% $ZrO_2$) up to 1190°C (for 20 mol.% $ZrO_2$), respectively. The temperature gap between two exothermic effects increased with increasing $ZrO_2$ content. The Johnson-Mehl-Avrami-Kolmogorov model (JMAK) was applied to determine the crystallization behaviour of the studied glasses and parameters of JMAK model were obtained. The HT-XRD performed in the temperature interval 820 – 1200°C revealed the crystallization of mainly of YAG ($Y_3Al_5O_{12}$) and $ZrO_2$ phases (moniclinic and tetrahedral) in the measured temperature range, with the onset of $ZrO_2$ phase crystallization detected at lower temperatures than YAG phase for glasses with higher $ZrO_2$ content.

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# The high-temperature crystallizations in a system of illitic clay and wollastonite mixtures

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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 wollastonite mixture. 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.

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# Sensitivity of thermal analysis and calorimetry to assess the impact of forest management on soils

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Forests have a global and essential role in preserving life on Earth. They are responsible for keeping the climatic and environmental balance that maintains living systems. Nevertheless, forests are affected by numerous anthropological factors due to the multiple services that provide to human life. In Galicia, eucalypts are planted for wood and biomass production involving intense exploitation that can be aggressive for soil [1]. For this reason, there is interest in searching for the best management to minimize that impact. The most common criteria are the effect on the carbon sequestration capacity which involves quantitative measurements of the soil carbon content and of the rates at which is lost through microbial respiration [2]. Both are highly variable indices, hence the interest in providing alternatives connecting carbon and soil microbial respiration with the changes in the chemical nature of the soil organic matter. In that sense, thermal analysis and calorimetry can be an option [3].

This work shows the impact of different forest management on soil thermal and calorimetric properties. Soil samples were collected in different eucalypt forests under two different forestry interventions: thinning and clearing of brush. The goal is to settle how they alter the soil thermal properties by simultaneous thermogravimetry and differential scanning calorimetry, and the soil organic matter biodegradability monitored by calorespirometry with a TAM III. The thermal and calorimetric data were analysed together with the soil elemental properties.

Results showed that clearing of brush and thinning alters the soil bio-decomposition given by differences in the heat rate and $CO_2$ rate monitored for soil microbial metabolism among the different soil samples, which affected the soil organic matter content determined by thermogravimetry. The heat of combustion calculated by differential scanning calorimetry did not show up remarkable differences that could be attached to changes in the nature of the soil organic matter. Changes in the soil organic matter content were correlated to those observed in the carbon content and in the bio-decomposition rates given by calorespirometry.

Thermal analysis and calorimetry allowed us to discern the intensity of the management tested on the soil ecosystem.

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# Kinetic analysis of a recyclable thermoplastic for structural applications

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Wind energy is considered a crucial technology for achieving the European climate targets of 2030 and carbon neutrality by 2050 [1]. However, fibre-reinforced wind blades cannot be recycled and are mostly landfilled. The generation of wind turbines installed in the 2000s will reach the end of their useful life between 2020 and 2030. By 2050, 43 million tons of blade waste will accumulate worldwide, 25% of it in Europe. Therefore, there is an urgent need to develop recyclable materials for wind blades [2].

In this contribution, we analyse the polymerization kinetics and degradation of a new 100% recyclable thermoplastic resin, AKELITE that has shown excellent mechanical properties; thus, making it an eco-friendly potential candidate for the manufacture of structural parts in wind turbines. For this purpose, we will use advanced isoconversional analysis. We will demonstrate that kinetic analysis combined with versatile prediction models allows us to determine the manufacturing conditions of composite parts while avoiding thermal degradation. The results will help wind turbine blade manufacturing companies to evaluate the capability of the developed recyclable materials as substitutes for the materials they currently use.

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# Chemical, mechanical and thermal characterization of gypsum samples from quarries in the Tabernas desert (Almería, Spain)

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Calcium Sulphate dihydrate, gypsum ($CaSO_4 \cdot 2H_2O$), and anhydrite ($CaSO_4$), the anhydrous form, are often associated together in nature. Gypsum converts to anhydrite via an intermediate mineral, the hemihydrate or bassanite ($CaSO_4 \cdot 1/2H_2O$). Gypsum is the most important commercially. Moreover, synthetic, chemical or by-product gypsum are increasingly available.

In this investigation, natural gypsum samples from quarries in the Tabernas desert (Almería, Spain) have been examined using several techniques. Thermal behaviour has been investigated using thermal analysis methods (simultaneous Differential Scanning Calorimetry, DSC, and Thermogravimetric Analysis, TGA, up to 1000 °C) and conventional furnace heating in air. X-ray powder diffraction (XRD), X-ray fluorescence (XRF) analysis, Fourier Transform Infra-Red (FT-IR) Spectroscopy and Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDS), have been used to determine the mineralogy, chemical analysis and morphologies of these samples.

Three selected samples (YS, YT and YV) have been studied in detail. The mineralogical analysis of the samples indicated that gypsum is the main crystalline phase, showing additionally a relatively low proportion of (a) calcite and quartz in sample YS; (b) smectite and muscovite/illite mica, besides calcite and quartz, in sample YT and (c) smectite in sample YV. These results were confirmed by FT-IR analysis. Chemical analysis by XRF, and EDS, supported the mineralogical analysis, allowing the determination of trace elements (μg/kg).

The "dehydration" of gypsum in the samples (elimination of 75 % of its water of crystallization) and formation of hemihydrate and anhydrite, was observed by DSC, showing endothermal effects with maxima at 142 °C, 139 °C and 151 °C for YS, YT and YV samples, respectively. These DSC effects were concomitant with mass losses, as assayed by TGA.

The main thermal features are discussed considering the mineralogical composition of each sample. Progressive heating showed small exothermic DSC effects (maxima at 343 °C, 358 °C and 357 °C in samples YS, YT and YV, respectively), associated to the transformation of soluble anhydrite into insoluble anhydrite. A physisorption study of thermal-treated samples was performed, showing important variations in the textural parameters.

# Characterization of crushed brick waste from the Alhabia Ceramic Plant (Almería, Spain)

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Clay-based products, for instance Traditional Ceramics (bricks and tile bodies) and lightweight aggregates, can be obtained using illite-chlorite-kaolinitic, illite-chlorite and illite-kaolinitic clays, with or without carbonates (dolomite and/or calcite). The presence of quartz, feldspars, iron oxide, mixed-layer minerals, smectites and gypsum is very common in these clays. The firing temperatures is between 1050-1150 °C, which are enough to produce bricks and tiles from these raw materials, with potential applications as porous supports for a glaze.

Alhabia clays are important in the province of Almería (Spain). These clays appear as a shallow marine platform with alternating sands, conglomerates, marls and sandstones. Deposits are estimated between 140 and 180 m of a monotonous alternation of sandstones, marls and mainly argillites. They are constituted by illite-chlorite clays (20-25 %) containing calcite (15 %) and quartz (30 %), with minor amounts of gypsum (< 5 %) and hematite (< 10 %). Alhabia clays are being applied as ceramic raw materials in traditional crafts and local industries. A better knowledge of these clays concerning scientific and technological features, including characterization, thermal behaviour and ceramic properties, has been conducted last years, with firing temperatures in the range 900-1200 °C. Cerámica de Alhabia S.L. is a Company, located in Alhabia (Almería, Spain), which uses these clays. This Company is interested in the application of all the fired and ground material generated, as rejected waste, in the Plant.

In this work, it is studied this kind of rejected waste after grinding considered as crushed brick waste. First of all, it was performed a characterization of sieved powders using several techniques: X-ray powder diffraction (XRD), X-ray fluorescence (XRF) analysis, thermal analysis methods (DSC-TGA) and morphology by SEM-EDX. A physisorption study of selected samples was performed to determine textural properties.

The crystalline phases formed by firing have been identified by XRD. They are anorthite and hematite, with relicts of quartz. The main purpose of this investigation was the preparation of innovative mixtures as agricultural substrates using the rejected fired waste, as raw material, with addition of perlite and other materials combined as layers. Thus, the porosity of the fired waste will be of interest to modify the different substrates. Experiments using *Solanum lycopersicum* L. (tomato, Daniella variety) are being studied with promising results following the main productive parameters under controlled greenhouse conditions of the crops.

# High temperature thermochemical energy storage in carbonates: A low-cost high-performance approach

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One of the main drawbacks of renewables is its intermittency. Thus, power is produced only when there is sun or wind. Increasing dispatchability is one of the main objectives in this field. Thus, while a conventional fuel power plant can be switch on or off at will and produce electrical power only when needed, solar power plants depend on the sun. The state-of-the-art technology for energy storage in concentrated solar plant is based on molten salts. Thus, during day time when the sun is shining, the molten salt is heated and stored in a hot salt deposit, while when there is no irradiation at night, the heat from this deposit is used for producing electrical power and the salt is moved into a cold salt deposit. This technology has some drawbacks: high price, corrosion issues, salts should be maintained at relatively high temperatures to prevent solidification, etc. Thus, there is a great interest in improving the technology and new solutions are being sought. Thermochemical energy storage, where the energy of chemical reactions is used for storing thermal energy, is a promising technology that needs to be further explored and developed. Here, we propose a system based on the calcination-carbonation reaction of $CaCO_3$/CaO (also known as Calcium Looping (CaL) process) for storing the heat. This approach uses limestone or other calcium carbonate sources, including residues, which are cheap, abundant and environmentally friendly. In this process, endothermic calcination reaction is produced by the concentrated solar power yielding $CO_2$ and CaO that are stored in separated deposits (long-term storage is possible). When energy is required, the exothermic carbonation reaction between $CO_2$ and CaO is induced and thermal energy is released to produce the electrical power. This technology has been demonstrated in a pilot plant in a relevant environment.

# Microstructural, thermal, and magnetic properties of $(Ni_{50}Mn_{40}In_{10})_{1-x}Co_x$ melt-spun ribbons

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Differential scanning calorimetry, X-rays diffraction, X-ray fluorescence, and scanning electron microscopy were used to investigate the martensitic transformation, microstructural changes and kinetics of the martensitic transformations in the melt-spun $(Ni_{50}Mn_{40}In_{10})_{1-x}Co_x$ (x=0, 1, 2, and 3) Heusler alloys prepared by melt-spinning. The Rietveld refinement of the XRD patterns reveals that the Co-doping affects phase formation from a monoclinic to a modulated 14M structure. Co-doping affects the lattice parameters and crystallite size. The kinetics of the martensitic transformation was studied as a function of the heating/cooling rates. The martensitic temperatures (martensite start, martensite finish, austenite start, and austenite finish) increase with Co-doping. Thus, the controlled addition of Co is a pathway to shift the transition to the temperature interval desired for specific applications. The thermodynamic parameters associated (enthalpy, entropy) to the reversible and hysteretic transition were calculated. Likewise, complementary thermomagnetic measurements are coherent with thermal analysis data. The results are compared with those of Heusler alloys of the Ni-Mn-In system [1-3]. The functional magnetic response is improved by adding 1 or 2 at. % of cobalt.

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# Ns Light Pulses Transmission trough Microcavity in Polaritonic Range

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Exciton–polaritons [1], in thin films can be interpreted as virtual exciton–photon pairs that propagate in the crystal because of a chain of processes of virtual absorption and emission of photons by excitons. In this way a material system consisting of alternating pairs of thin $SiO_2$ and $TiO_2$ layers is proposed to generate polariton lasing at room temperature with organic Dye-Filled material.

Taking into account the polariton (exciton–photon) and elastic polariton–exciton interactions we investigated peculiarities of transmission of 5 ns light pulses in microcavity. We show and predict the appearance of time dependent phase modulation and dynamical red shifts of transmitted pulse. The theory is in remarkable agreement with experimental work made in Moldova see Fig.1

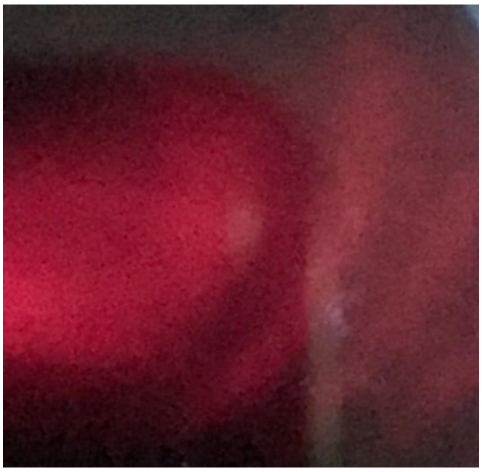

**Fig. 1** The time evolution of the polariton density and amplitude of transmitted 5 ns pulse.

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# Nonlinear Dynamics of an Exciton-Polariton Oscillator in Organic Dye-Filled Microcavity

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The dynamics of optical parametric exciton-polariton oscillations in semiconductor microcavities assembled from two parallel mirrors $TiO_2$-$SiO_2$ thin semiconductor films were studied.

Taking into account the peculiarities of the nonstationary interaction such as the conversion processes of the pump polaritons into signal and idler polaritons [1], the system of nonlinear evolution equations was obtained.

The periodic regimes of the evolution of polariton densities and the amplitude of the polariton density oscillations depend crucially on the initial polaritonic densities, phase difference, and detuning. For the defined relationship between the parameters, the aperiodic evolution of the system is possible by representing the conversion only part of the pump polaritons, which ends the evolution of the system. The significant dependence of the period and amplitude of the polariton oscillations on the initial phase difference is evidence for the possibility of phase control of polariton dynamics. The decoherence of the polaritonic system leads to the oscillatory decay of the polariton density in time, whose rate is defined by the polariton damping constants.

Time evolution of the density of pumps polaritons depending on the initial phase difference for different values of the laser intensities was compared to theoretical computations.

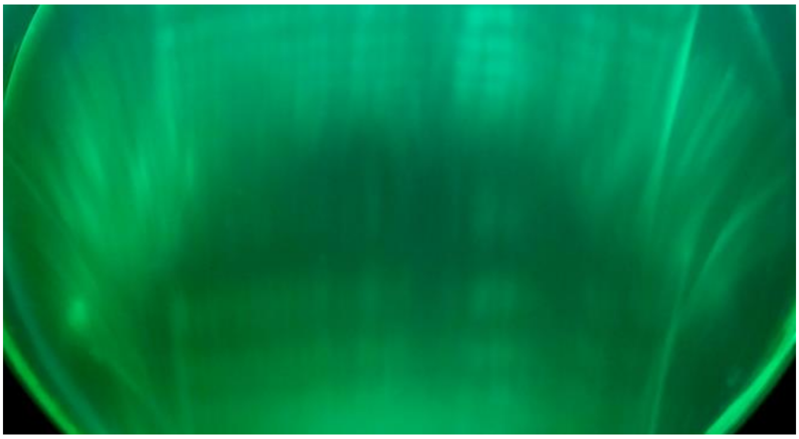

**Fig. 1** Time evolution of the density of pump polaritons in experimental work.

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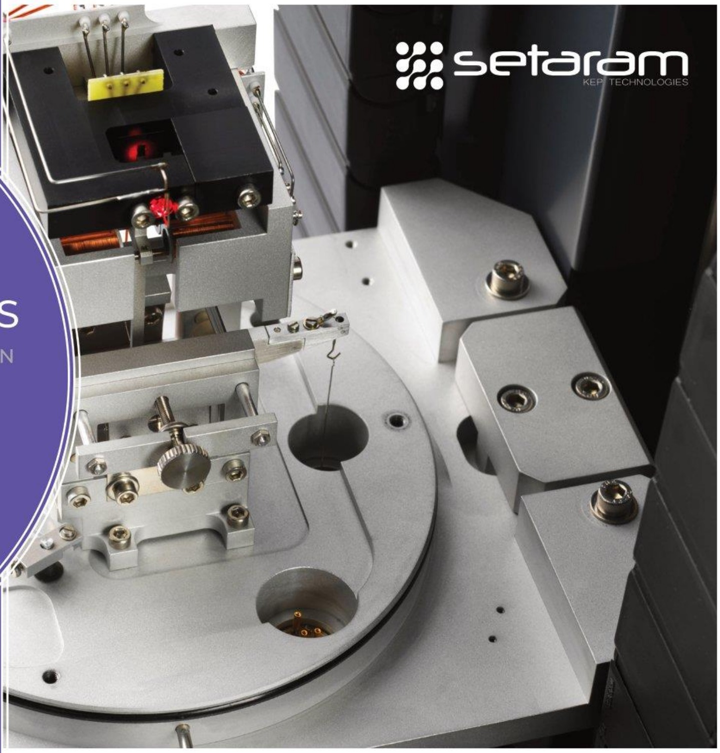
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# Supplementary Poster Session 3

# Soft-templated gels - effect of carbonization heating rate on their mesoporosity

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The porosity of carbonaceous materials can be influenced by several parameters. Carbonization temperature is probably the most investigated parameter. Nevertheless, heating rate during carbonization can have a significant influence too.

The aim of this contribution was to assess the impact of heating rate on the porosity of carbonaceous materials prepared by carbonization of resorcinol-formaldehyde gels containing Pluronic F-127 as a soft-template. Besides, the influence of particle size was investigated.

The experiments were performed by thermal analyser (STA 449 C, Jupiter, Netzsch) under a nitrogen atmosphere (100 ml/min) using heating rates from 1 to 20 K/min with particle sizes ranging from fine powder to particles larger than 2 mm. The porosity was characterized using nitrogen physisorption and thermoporometry.

The results indicated that with increasing heating rate, the size of the mesopores increased from units to tens of nanometers, and simultaneously, the yield of carbon also increased. It is expected that at low heating rates, the decomposition of the soft-template (and the carbonization process) occurs slowly enough for the gaseous products to be continuously released into the surrounding atmosphere, resulting in the development of porosity corresponding to the size of the soft-template micelles. In contrast, at higher heating rates, rapid gas evolution and diffusion limitations within the particles leads to larger mesopores. The effect of particle size was not significant, especially at lower heating rates.

These findings highlight the significance of the heating rate during carbonization in controlling the mesoporosity of carbonaceous materials prepared by the soft-templating method. Understanding the relationship between heating rate, particle size, and mesoporosity is crucial for optimizing carbonization processes to develop tailored carbon materials with specific porosity.

# Thermoporometry of mesoporous carbons: application of octamethylcyclotetrasiloxane as probe liquid for small mesopores

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Porous carbon materials are commonly used for environmental protection (as adsorbents), energy storage (as supercapacitors), or as catalyst supports. From the perspective of application usage, the mesoporosity of these materials plays a crucial role in facilitating efficient diffusion transfer. Typically, mesoporosity can be determined using traditional methods such as gas physisorption or mercury intrusion, as well as alternative techniques like NMR cryoporometry or thermoporometry. These alternative methods focus on determining porosity in the wet state, which can be more predictive, especially for applications involving water treatment.

Thermoporometry (TPM) is a calorimetric method which is based on the depression of the melting/freezing temperature of a liquid entrapped in pores in comparison to the melting of liquid outside the pores (bulk). If water is used as TPM probe liquid, the mesopores larger than 10 nm are hard to evaluate due to the overlapping of the melting peaks of water in pores with bulk water. To overcome this problem, other probe liquids, e.g. cyclohexane, benzene, or octamethylcyclotetrasiloxane (OMCTS), could be used. OMCTS is now the best choice for TPM in the case of large pore characterization, where the water fails. Nevertheless, the usage of such a liquid brings other problems complicating the evaluation. It is proposed that this liquid could be used for determination of pores above 10 nm due to the fact the OMCTS undergoes the solid-solid phase change before it melts/freeze. The solid-solid transition of OMCTS is in the temperature range where the melting of OMCTS in small mesopores occurs. In summary, the analysis of small mesopores could be problematic due to the overlapping with the solid-solid phase transition of OMCTS itself.

The main aim of this contribution is to show applicability of OMCTS as probe liquid for TPM characterization of small mesopores. The separation of melting in small pores from solid-solid transition was analysed by several approaches (heating rate, implementation of prefreezing step, deconvolution of experimental DSC records with the use of basic kinetic equation as underlying functions etc.) to obtain individual record of OMCTS melting in pores, which can be transformed into pore size distribution by standard procedure.

The usefulness of the suggested measurement conditions and deconvolution method is demonstrated using carbonaceous samples with exclusively small mesopores (approximately 6 nm), as well as carbon samples containing both small and large mesopores. The results indicate that this approach enables us to investigate the entire mesoporous range using TPM based on OMCTS as the probe liquid, making OMCTS a more versatile option.

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