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Contents

Keynotes

The role of TG-MS in the characterization of coordination compounds

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The practical applicability of materials strongly depends on their thermal stability, which is commonly investigated using thermoanalytical techniques such as TG, DTG, and DSC, and their combination as well as the coupled techniques such as TG-MS and TG-FTIR. A very important class of compounds present in numerous fields of everyday life and actual research activities is the class of coordination compounds. The high number of coordination compounds are biologically active and show antioxidative, antimicrobial, anti-inflammatory, or even cytostatic effects. There are also coordination compounds used as contrast during MR imaging due to their stability in the living organism, photoluminescent complexes, and coordination polymers with different applicability, as well. Such coordination polymers are planned or yet used as absorbents for different gases. Nowadays high efforts are made to prepare porous materials for CO_2 absorption and storage. In accordance, our main research interests include the synthesis and structural characterization of coordination compounds with the versatile possibility of future application.

Since thermal stability is crucial for the applicability of compounds and materials, it is the most often determined property of new compounds and materials. Even more, thermoanalytical characterization may give much more information about the properties of the compounds, not only their thermal stability. By thermogravimetry, the solvent content of the compounds and the stability of the desolvated form of the same compound or material may be easily determined. These data may give information useful for desolvation/drying the compounds or materials. By heating a compound until a stable state and by analysis of that stable state, its composition can be studied. In the case of inorganic compounds or complex compounds, by heating until a stable oxide, it is possible to determinate the composition of the starting complex. In such an analysis the coupled TG-MS and TG-FTIR measurements can give priceless information about the evolved gases and prove the nature of the solvent or decomposition product. Usually, the supposed lattice solvent is the same as that used during synthesis. But it is not rare that the original lattice solvent molecule has been changed by water, which may be determined by some EGA technique. The lattice solvent exchange may give information about the volume and possible interactions in the pores of the crystal lattice. [1]

The applicability of the thermal methods of analysis is presented in numerous publications like [1-3] and shall be presented including new experimental data in the oral presentation.

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Modeling delayed thermal runaway in nitric acid-soaked cat litter mixed with radioactive waste

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Keywords: thermal hazard, waste behaviour, waste characteristics, safety analysis, cookoff

On February 14, 2014, just before midnight, radioactive waste within a 55-gallon steel drum (designated 68660) thermally ignited 2150 feet underground in a salt formation that is part of a nuclear waste repository located near Carlsbad New Mexico, USA. The waste drum contained nitric acid-soaked organic cat litter mixed with various metal nitrate hydrates, acid neutralizer (triethanolamine), rubber, plastic, a tungsten-lined glove, and transuranic elements (americium-241 and plutonium-239) [1]. Prior to this event, 143 drums with similar reactive contents had been placed in the repository without incident. Following the breach of drum 68660, a technical assessment team from various laboratories reviewed historical drum content data, performed numerous experiments, and attempted to reconstruct the event using computational models. However, no conclusive evidence of the cause of the thermal runaway within drum 68660 was identified. Recently, we were able to simulate thermal ignition in drum 68660 using a pressure-dependent waste decomposition model [2] calibrated with data from full-scale drum experiments [3] and validated with experiments from multiple laboratories [4]. We conclude that a restricted drum vent could have led to the thermal runaway reaction in drum 68660. Here, we address whether the form of the rate equation in [2] is sufficient to extrapolate thermal ignition within aged drums that are over nine years old by investigating four different reaction rate forms for waste decomposition: 1) a zero-order Arrhenius rate, 2) a first-order Arrhenius rate, 3) a Prout-Tompkins rate, and 4) a modified Arrhenius rate using a distributed activation energy. A “critical reaction rate reduction” analysis is performed on each of these models to determine if delayed thermal runaway within vented aged waste can be predicted after nine years.

Acknowledgments

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Comprehensive exploration of critical safety issues in lithium-ion batteries via advanced calorimetry approach technique: thermal runaway and fire behavior

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Keywords: carbon neutrality, green energy, energy storage system, inherently safer design, exothermic process, explosion/flammability limit

In recent years, policies have been implemented to promote sustainable development and address carbon neutrality and net zero emissions. These policies include the transition to green energy, such as solar, wind, and water power, as well as the prohibition of the sale of fossil fuel vehicles. One technology that has gained widespread adoption is the lithium-ion battery (LIB), which is commonly used in electronic devices, electric vehicles, and energy storage systems (EES). However, as the use of LIBs has increased, incidents of LIB failure have also increased in number, severity, and scale. The higher energy density of LIBs can unfortunately exacerbate the severity of such failures, and existing methods for extinguishing LIB fires still need feasible improvement.

Therefore, this effort aimed to investigate the characteristics of LIB fires and thermal runaway reactions based on inherently safer design. Specifically, this study analyzed the exothermic process resulting from multiple interacting reactions among the materials using an improved calorimetry technique. We also explored the gas emissions resulting from unexpected reactions, which can be critical for thermal runaway and pose health risks during emergency response. To this end, we appraised the gas components of several statuses in the elevated temperature step and identified the characteristics of the complex gases, which tend to be toxic and flammable. The relationship between gas composition and the explosion/flammability limit was also discussed and elucidated. The findings of this study will provide a valuable reference for developing emergency response strategies in the event of an EES fire. They will also contribute to the overall understanding of LIB fires and thermal runaway reactions, potentially leading to the development of safer and more reliable LIBs, as an ultimate objective..

Bridge the thermal analysis and fire safety engineering: new insights and challenges

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Keywords: thermal analysis, flame spread model, optimization, kinetic triplet, flame-retardant polymer

Thermal analysis of combustibles plays an important role not only in flame spread modelling in buildings or outdoors but also in the optimization design of flame-retardant products in fire safety engineering. This work will start with the typical schematic of flame spread process over a popular solid combustible, as shown in Figure 1 [1]. The necessary kinetic triplets for the pyrolysis modelling in the solid area and combustion modelling of released gases in the gas area are described respectively. Both the traditional and new methods to calculate the kinetic parameters for pyrolysis and burning behaviours will be summarized. The advantages and disadvantages of thermal analysis based on single-scan and multi-scan ways, the kinetic compensation effect (KCE), as well as some new results about the scale-up for real fire behaviour modelling through the pyrolysis data of micron samples will be presented. For the optimization design of flame-retardant materials, the normal steps of the formula design and fire performance evaluation for flame-retardant products (flame-retardant cable as an example) according to the requirement of fire resistance codes will be introduced, which followed with the role of thermal analysis in those steps. Some new results for the mutual effects between the multi-components pyrolysis when heated will be analysed. The relationship between the morphological evolution (swelling, charring and shrinkage etc.) and the mass loss of samples in the crucible will be introduced for fire safety modelling based on the thermogravimetric analyser with a special “Real View” sample observation option. Finally, the challenges of the reliable application of the thermal analysis for the accurate fire behaviour modelling and optimization design of future flame-retardant products will be talked.

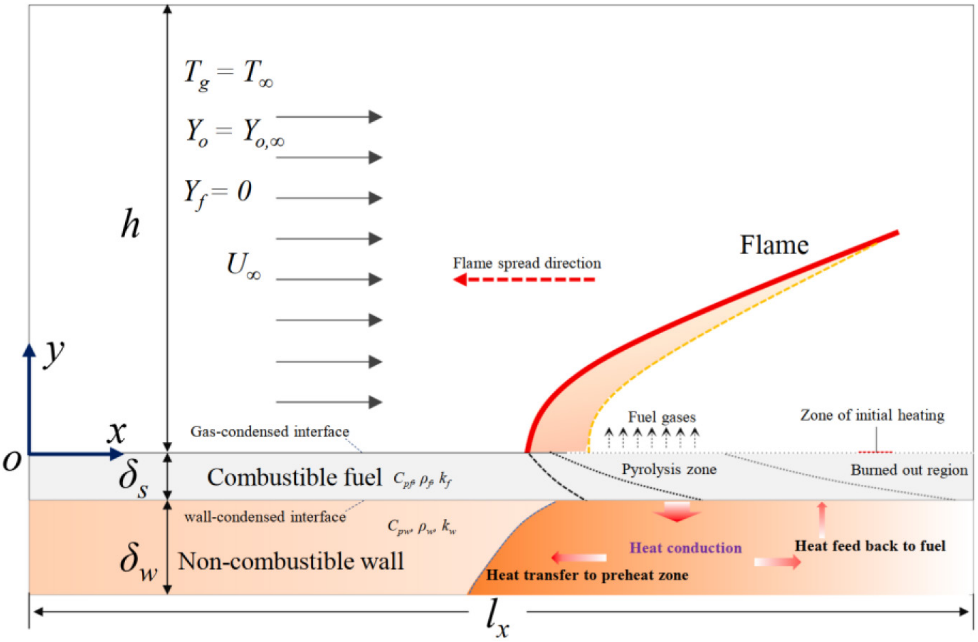

Figure 1 Schematic of flame spread modelling over polymer in fire safety engineering [1]

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Invited

Thermohydraulic performance of water in an inclined circular tube fitted with spring tape inserts in transition flow regime

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Keywords: transitional flow regime, thermal and flow performance, inclined heat exchanger, spring tape inserts

Heat exchangers are usually designed to work in laminar or turbulent flow regime. However, it has been observed that sometimes knowingly or unknowingly, heat exchangers are working in transitional flow regime. Reasons can be roughness on the surface, turbulators, inlet geometries, inclination of heat exchanger, working fluids, obstructions, etc. When the heat exchanger tube is in an inclined position, buoyancy comes into play, and this undoubtedly has an effect on the performance of the heat exchanger in a variety of ways. Inclined heat exchangers experience mixed convection if the Reynolds number is very low. Due to the temperature differential between the fluid near the heated wall and the cooler fluid near the centerline, inclination buoyancy causes mixed convection heat transfer. Hence, it is essential to understand the thermophysical characteristic of fluid flow when heat exchangers are placed at inclination angle. As a consequence of this, the thermal and flow performance of water in an inclined tube that was fitted with spring tape has been experimentally assessed in the current study. The spring tapes that were constructed out of brass and had spring ratios of 3.0, 4.0, and 5.0 as well as a length of 2000 mm were created and manufactured using tape that had a thickness of 1.0 mm and a width of 16.0 mm. All the experiments were performed for three uniform heat fluxes viz. 2.0, 3.0 and 4.0 kW/m2. In order to compare outcomes across all three flow regimes, the Reynolds number was varied from 1000 to 7000. The results obtained from the experimental investigation shows shifting in the transition flow regime. For plain horizontal tube heated using 2.0 kW/m2 of heat flux, the transition begins at Reynolds number 2983 and ends at Reynolds number 3346. At 15o inclination angle, the transition begins at Reynolds number 3012 while ends at Reynolds number 3349. This is due to the buoyancy effect. At inclined position, the effect of buoyancy forces lessen which causes the transition to start at delayed Reynolds number. Along with this enhancement in the heat transfer and pressure drop was also observed when test section was kept horizontal. At inclined position of 150, a slight decrease in the Nusselt number was observed. Correlations were also developed to predict the Nusselt number and friction factor in laminar, transition and turbulent flow regime.

Acknowledgments

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Applicability of model free isothermal prediction procedures based on the Friedman method and three incremental isoconversional methods

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The possibility of using the model free isothermal prediction procedures for complex processes was critical Analyzed. Such procedures based by isoconversional method suggested by Friedman, and three incremental isoconversional methods have been suggested and verified for simulated data corresponding to two first order parallel reactions and two first order consecutive reactions. It has been shown that in order to obtain a satisfactory prediction, these procedures must include the initial stage of determining the range of heating rates at which the thermoanalytical date necessary for the application of these procedures must be recorded, and to consider that the apparent activation parameters depend both on the conversion degree as well as the temperature for the prediction is made.

Thermoanalytical studies of some antioxidants

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Keywords: Antioxidants, Thermal behavior, Thermal stability, polymorphism.

According to the Brazilian healthy regulatory agency (ANVISA) [1], food additives are substances intentionally added to food products without the aim of nutrition, but with the purpose of changing physical, chemical, biologic and sensorial characteristics, during its fabrication, preparation, processing, packing, storage, transportation or handling. They include a variety of compounds that are classified according to their action as flavor enhancers, sweeteners, emulsifying, colorants, enzymes, antioxidants and preservatives. Nowadays they represent a billionaire industry worldwide.

The oxidation of fuels is another issue of high concern, especially regarding those from vegetable oils, that demand the presence of antioxidants for preservation of the properties during the final usage.

Historically naturally occurring substances were used, however with the need for high production and preservation, synthetic products became necessary, thus demanding knowledge of the several characteristics of such substances for safety reasons and to obtain their maximum performance.

Herein our work regarding the thermal behavior of antioxidants tert-butyl hydroquinone, butyl hydroxyanisole, butyl hydroxytoluene and propyl-, octyl- and dodecyl gallates are presented, demonstrating interesting features of these important substances, including thermal stability order, sublimation, polymorphism and volatiles evolved during thermal degradation. Mechanisms describing the thermal behavior of these antioxidants were also proposed [2–5].

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Biocarbons produced under pressurized conditions: characterisation of the volatiles

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Keywords: biocarbon, biomass, VM, TG/MS, Py-GC/MS

The use of renewable energy sources, among them biomass through modern bioenergy applications, should be increased. The solid product of biomass pyrolysis (biocarbon) has various applications, which require different chemical and physical properties of the biocarbon. Changing the carbonization conditions will result in biocarbons with versatile properties, which may open up for renewable alternatives in applications where mainly fossil materials are used today. The amount and composition of the volatile matter (VM) is important for its utilization, while high biocarbon and fixed carbon yields are always desirable. Previous studies have shown that elevated pressure can enhance both the char and fixed carbon yields[1]. The effect of temperature and purging flow at atmospheric pressure on the composition of volatiles was described in our earlier paper[2]. In the present work, the effect of pressure on the volatile composition of the biocarbon formed was investigated.

The aim of this study was to analyze in detail the composition and evolution profile of volatiles from biocarbons produced in reactors at different (constant) pressures and at constant volume in order to compare and understand the carbonization processes taking place under these different reaction conditions.

Biocarbon samples were produced from ground (1-2 mm) birch at 300 °C in a wall-heated tubing bomb reactor[1] under constant pressure (from atmospheric to 10.75 MPa), and of constant volume with different initial pressures (0.55–1.4 MPa). The thermal properties, VM content and the formation rates of volatiles from the biocarbons were characterized by thermogravimetry/mass spectrometry. The composition of volatiles was analyzed in detail by pyrolysis–gas chromatography/mass spectrometry.

The thermogravimetric characterization of the produced biocarbons showed that the VM content of all samples varied from 45 to 50%, while the evolution profile of the volatiles differed significantly. Biocarbons produced at higher pressures released significantly higher amount of volatiles below 350 °C probably due to the enhanced condensation reactions on the biocarbon surface at elevated pressures. The temperature of the maximal rate of decomposition was at around 430°C for all samples, and the maximal rate of decomposition decreased with increasing pressure, indicating developed degradation of the biopolymer components at higher pressures. The detailed analysis of the volatiles indicates that the vast majority of the volatile products were aromatic compounds derived from lignin, while the amount of carbohydrate decomposition products was relatively low. Biocarbons prepared at pressures higher than 6.5 MPa retained significant amount of triterpenoids, i.e., betulin derivatives. The composition of lignin degradation products in the VM of biocarbons produced at elevated pressures also changed slightly, suggesting a modified decomposition mechanism of lignin at high pressures.

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Invited

Development of ultra – high temperature high – entropy ceramics

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Keywords: high entropy ceramics, ultra – high temperature ceramics

The recent development of ultra – high temperature high entropy ceramics – carbides, nitrides, carbo/nitrides, dual – phase systems - in Slovakia is summarized. The applied processing routes are described. The microstructure and fracture characteristics were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM) in combination with electron back scattered diffraction (EBSD) and transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) in conjunction with energy dispersive X-ray spectroscopy (EDS). Depth-sensing nano-indentation of individual grains and grain boundaries of bulk systems has been applied to study the nano-hardness and deformation characteristics. Micro-compression test of micro-pillars prepared by focused ion beam from oriented facets of grains were studied. During micro-cantilever tests in bending deformation and fracture characteristics of individual grains and grain boundaries have been investigated. The high – temperature characteristics were investigated by creep and oxidation tests. A strong influence of the grains orientation on compressive yield stress and rupture stress values was found during the micropillar test. The bending strength of micro-cantilevers prepared from individual grains of HECs or containing grains and grain boundaries was strongly dependent on the character/size of the present fracture origins which were in all cases in nano-metric range. The fracture toughness of the individual grains and grain boundaries of different high entropy ceramics were investigated, too.

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Thermal investigation of hybrid nanoliquid convection across moving surface

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Keywords: boundary layer, convection, hybrid nanoliquid, base fluid, thermal properties.

We analyze the hybrid nanoliquid fluid flow - namely the flow of hybridparticvles added to base liquids namely engine oil, kerosene oil or water over a steady/unsteady sheet in the presence of magnetic field, viscous dissipation and moving parameter wherein the effect of thermal particles interaction parameters on the flow field is emphasized. It is noted that the nanoparticles has a great enhancement effect on hybrid nanoliquid rather than regular fluid. The results are found by converting complicated coupled system of differential equations into non-dimensional form with some suitable scaling variables. We set up the analytical model of the problem employing the similarity transformation to non-dimensionalize the conservation equations they eventually solve numerically by using a Matlab or other function. By means of this model, the Authors analyze several conditions while comparing some of them with literature data. The authors should compare the quantities (such as velocity) in distributions among different grid resolutions to better show its grid convergence. Buongiorno's two-component nanoscale model is deployed and spherical nanoparticles in a dilute nanofluid considered.

Results for the distribution of physical interest like skin friction coefficient, Nusselt number as well as the velocity, temperature, nanoparticle volume fraction are presented for the influence of problem physical parameters. The results indicate that the magnetic field has a substantial effect on the flow properties, and that the addition of nanoparticles increases the heat transfer rate. The study also demonstrates that the heat source and nanoparticle volume percent considerably affect the temperature and concentration profiles and it is anticipated that alternative nanoscale models such as the Tiwari-Das model may also be explored. These findings may have applications in several engineering disciplines, including nanotechnology, materials science, and energy systems. The current investigation has considered non-magnetic hybrid nano-liquids and the numerical computations find industrial applications like manufacturing arena.

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Paradigm-shift in equilibria of nano-materials and some evidence from calorimetry

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Keywords: nano-materials, nano-phases, equilibrium, calorimetry

Nano-materials are materials that contain at least one nano-phase. Nano-phases are phases with at least one of their dimensions below 100 nm. All properties of nano-phases and nano-materials depend on the nano-dimension(s) of their nano-phase(s), its specific surface area and the nature of the surrounding phases. Although according to Kelvin nano-phenomena are due to high curvature of nano-phases, this historical claim (contaminating even today 99 % of nano-related literature in chemistry, materials and biology, but not in physics) will be proven here to be wrong. It is claimed instead that nano-phenomena are due to high specific surface (interface) area of nano-phases: this derivation is an extension of thermodynamics of Gibbs. The heat of dissolution of particles added and dissolved in liquids can be measured by calorimetry. If particles of the same phase and same chemical composition but of different sizes in same amount are added and dissolved in the same liquid at the same temperature, the heat of dissolution can be measured as function of the particle size. It is found that the heat of dissolution is shifted towards more exothermic values with decreasing the particle size, i.e. increasing the specific surface area of the particles. This is because the positive surface energy times surface area of the particles is lost in the process of dissolution, being larger for smaller particles. Based on our recent experimental data it will be shown that the validity of the new paradigm (claiming that nano-phenomena are due to higher specific surface area of nano-phases) is much more probable compared to the previous paradigm in chemistry, materials and biology (claiming that nano-phenomena are due to high curvature of nano-phases).

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Crude oil characterization: simultaneous TGA-DTA, TGA-FTIR and TGA-MS

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Keywords: crude oil, combustion, limestone, thermogravimetry, mass spectrometry, kinetics

In this research, thermal analysis and kinetics of three different crude oil samples (°API range of 21.1–34.1) from different new oil fields of Turkey were studied using thermogravimetry (TG-DTG) coupled with a quadruple mass spectrometer (MS). Mixtures of crude oils and limestone matrix are prepared to give a composition of 15 % wt. crude oil in the matrix and the ramped temperature experiments are performed at different heating rates (10, 20 and 30 °C/min.) under air atmosphere. In TG-DTG analysis three different reaction regions were observed, known as low temperature oxidation (LTO), fuel deposition (FD), high temperature oxidation (HTO) and finally limestone decomposition, respectively. In MS analysis, combustion products of different crude oils on the basis of both relative intensities and relevancy was monitored simultaneously. Finally, two different model free kinetic methods known as Ozawa-Flynn-Wall (OFW) and Kissinger-Akahira-Sunose (KAS) were used to determine the activation energy of the crude oil samples. It was observed that the activation energy values are varied between 189.47–290.41 kJ/mol (OFW method) and 181.75–288.37 kJ/mol (KAS method) in HTO region, respectively.

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Thermal activation of redox-active complexes: solid phase quasi-intramolecular redox reactions as an easy route to prepare nanosized (mixed) metal oxides

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Keywords: solid phase redox reaction, spinel oxides, thermal activation, hydrogen bond

Nanosized oxides, especially mixed oxides with spinel structures have enormous importance in many industrially important catalytic processes including Fischer-Tropsch synthesis, carbon monoxide oxidation, or the reduction of carbon dioxide into hydrocarbons or photodegradation of organic materials in water. Their catalytic activity strongly depends on size, chemical phase composition, valence distributions, surface properties, the presence of structural defects, and other factors. These properties are mainly controlled by the election of a preparation method, however, the temperature is a key factor, due to temperature-dependent chemical transformation and diffusion processes. We have developed a low-temperature (50-200 °C) process to prepare completely amorphous (<2 nm) oxide and mixed oxides with the use of transition metal salts complexes having oxidizing anions and reducing ligands like ammonia, pyridine, or urea. It is a great challenge to decompose these compounds in a smooth way due to the highly exothermic and explosion-like decomposition reaction between the reducing ligand and oxidizing anions. The solid-phase quasi-intramolecular redox reactions initiated by heat are controlled by mixing the solid precursor with an inert solvent, which boiling point is around the decomposition temperatures of the solid precursor (aromatic or chlorinated organic solvents). The evolved reaction heat turns into heating and evaporates the organic solvents, and under reflux conditions, this reaction heat is absorbed by the solvent, and the liberation heat cannot cover the activation energy to initiate the development into an explosion-like reaction. The available data about the structure of the precursors show that the presence of hydrogen bond between the ligands are essential to initiate these quasi-intramolecular redox reactions. The reaction products can be heat treated for a given time and temperature to control the crystallization process of the oxide materials. The heat treatment with and without leaching of each component from the amorphous primary decomposition products gives a possibility to control the chemical composition and reactivity of the prepared oxides. Selecting mixed crystals/solid solutions or various co-anions/cations in the precursor materials resulting in the preparation of mixed oxides with various compositions, e.g. $[Co(NH_3)_6](MnO_4)_3$, $[Co(NH_3)_5Cl](MnO_4)_2$ and $[Co(NH_3)_6]Cl_2MnO_4$ resulting in Co:Mn mixed oxides with $(Co^{II},Mn^{II})^{T\text{-}4}(Co,^{III}Mn^{III})^{OC\text{-}6}O_4$ mixed oxides, with possible intermixing of di and trivalent metal components between the tetrahedral and octahedral spinel sites. Leaching of some Co-containing components from the amorphous intermediate before the annealing leads to higher Mn/Co ratios in the spinel products. The distribution of di- and trivalent metals between the tetrahedral and octahedral spinel sites strongly depends not only on the starting material and synthesis/annealing conditions, but the nature of ligands and anions as well.

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Microwax/halloysite nanotubes composites: a versatile material for conservation of cultural heritage

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Keywords: wax, halloysite, cultural heritage

Nowadays, Pickering emulsions are extensively employed in various applications due to their numerous advantages over surfactant stabilized droplets, such as low or no toxicity, ease of storage, low production costs, etc. In this regard, particles obtained from eco-sustainable sources have been employed for their design in order to satisfy the need for environmentally friendly materials. Among them, halloysite clay nanotubes can act as interfacially active inorganic particles, and we recently proposed a novel protocol for the preparation of wax/halloysite based Pickering emulsions characterizing their stability and structure. Moreover, we designed new green coatings based on biopolymers (chitosan and pectin) [1] and geopolymers filled with wax/halloysite microspheres. Within this, the fillers combined with the aforementioned biopolymers were successfully employed to fabricate composite films with enhanced mechanical properties. A significant hydrophobization of the biopolymeric films was also detected by water contact angle measurements designing novel biocompatible nanocomposite systems that can protect the artwork surface from the aging process caused by environmental conditions. Microwax particles obtained from Pickering emulsions were also embedded in halloysite-based geopolymers developing a new hybrid material with heat storage capacity and enhanced flexural performances [2]. The incorporation of microwax into the geopolymers was confirmed using various techniques, including thermal analyses, spectroscopies, microscopies, and contact angle experiments. The homogeneous dispersion within the geopolymeric network improved again the coating's physico-chemical properties by increasing the hydrophobicity. Furthermore, the Pickering emulsions were employed for the treatment of waterlogged wooden samples [3]. Compared to archaeological woods treated only with wax, the inclusion of nanotubes led to a notable enhancement in mechanical properties such as stiffness and flexural strength, making this method useful for treating larger-sized shipwrecks.

The discussed approaches suggest the development of wax/halloysite Pickering emulsions with versatile functions for both eco-friendly coating and cultural heritage applications.

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Strain and strange small ring organic molecules

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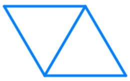
An introduction of strain in organic molecules as a result of bond angle and bond length distortions from ideal strain-free parameters will be discussed. These will include a few examples of the hypothetical and experimental Platonic structures. The determination of strain energies as a model dependant concept will illustrate different results for the same molecule leading to misleading conclusions. The presentation will highlight some recent published and unpublished studies of the strained bicyclobutane **1** along with its heterocyclic analogs **2** and **3** as well as the three centered rings **4** and **5.**



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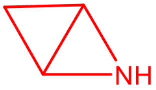

3

4

5

*Blue coded are known molecules

*Red coded are not known to date

In addition to strain a further component associated with antiaromatic destabilization plays a significant role in the increase of overall enthalpies of formation.

Nanoparticles and energy systems

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Keywords: nanoparticles, energy systems, renewable energy systems, storage

Climate change is a complex problem that requires a multifaceted solution, and improving both traditional energy systems and renewable energy systems is necessary to address it. While transitioning to renewable energy is important, it's also important to make traditional energy sources cleaner and more efficient to minimize their impact on the environment. By taking a comprehensive approach to energy, we can reduce greenhouse gas emissions and mitigate the effects of climate change. Nanotechnology offers promising solutions for addressing climate change by enhancing both traditional energy systems and renewable energy systems. For example, nanotechnology can be used to develop more efficient and durable materials for energy production and storage, as well as to improve the performance of solar panels and other renewable energy technologies. By leveraging the unique properties of nanomaterials, we can make significant strides towards achieving a more sustainable and environmentally-friendly energy system. In this presentation, we will discuss the different applications of nanoparticles in energy systems, such as improving energy storage, enhancing solar cells efficiency, and solar desalination. We will also discuss the advantages and challenges of using nanoparticles in energy.

Zinc oxide: thermal analysis, structure, applications

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Keywords: zinc oxide nanomaterials; thermal analysis; infrared spectroscopy

Thermal analysis, with particular reference to thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC), are irreplaceable tools in obtaining and characterizing oxide-based nanomaterials. The design and fabrication of zinc oxide nanomaterials with a variety of shapes and sizes, correlating with novel features and prospective uses, has been the subject of intense research [1–3]. The use of high temperature, high pressure, different chemicals, limits the majority of these techniques.

Nanomaterials are obtained by different chemical methods, but the most used are the sol-gel method [1, 2], the hydrothermal method [3, 4] and precipitation [5]. The transformation of liquid precursors or solid precursors into nanomaterials are complex processes and their description require complementary techniques such as infrared spectroscopy or X-ray diffraction to support the interpretation of the thermal analysis results.

The sol-gel approach has grown in popularity in zinc oxide production due to its high purity and uniformity of final nanomaterials. In addition, it allows the introduction of dopants in order to improve zinc oxide properties.

Hydrothermal synthesis can be defined as a synthesis method to obtain crystalline materials. However, the method is dependent on the solubility of the precursors under high pressure. There are a lot of papers that report the obtaining of pure and doped zinc oxide nanomaterials by hydrothermal method.

In order to obtain nanorod type morphology of zinc oxide, the sol-gel method must be followed by thermal treatment, while the hydrothermal method use lower temperatures [3, 4]. The optimization of energy/ precursors consuming is an issue in the zinc nanomaterials obtaining.

The influence of dopants on the thermal behaviour of doped zinc oxide nanomaterials is discussed. The type and amount of dopant can decrease or increase the thermal treatment temperature to produce zinc oxide nanomaterials. Infrared spectroscopy and X-ray diffraction interpretation are used to examine the structure of gels and nanomaterials and a correlation between their structure and thermal behaviour is presented.

Effect of treatment temperature on the incorporation of doping ions into zinc oxide lattice is established. The evaluation of the thermal properties of zinc oxide nanomaterials in order to use it in applications was carried out.

Acknowledgments

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Crystalline structure and reinforcement in natural fiber reinforced PP composites

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Keywords: polymer composites, natural fibers, functionalized polymers, thermal properties, reinforcement

Natural fiber-reinforced composites were prepared from PP homopolymers and Sugar Palm Fibers (SPF) by twin-screw extrusion and injection molding. Mechanical properties were characterized by tensile and impact testing, while the structure was studied by SEM and optical microscopy. The results showed that SPF has a moderate nucleating effect in the PP used. We selected these grades of polymers to obtain good processability (MFI) for the final product. However, the functionalized polymer may interact with the other component and modify its nucleation effect. The results clearly showed that crystalline structure changes considerably upon the addition of the SPF fibers, with both lamella thickness and crystallinity increasing. However, somewhat contradictorily, the effect of these changes on the mechanical properties of the composites is small. Model calculations have shown that stiffness increases s due to nucleation, while moduli as large as 3 GPa are reached by the addition of SPF fibers. Impact resistance is completely independent of lamella thickness or crystallinity; this property is determined mainly by local deformation processes initiated by the fibers. Dispersed structure and the direct effect of the additive determine properties in the fiber-reinforced composites studied, and the role of the crystalline structure is of secondary importance.

Thermal characteristics of polyurethane/POSS hybrid materials and nanocomposites

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Keywords: polyurethane, NIPU, POSS, hybrid materials, nanocomposites, thermal analysis, thermal properties

Polyurethanes (PU) are an important group of polymers widely used in everyday life and in industrial applications. Polyurethanes are obtained in the polyaddition reaction of diisocyanates and diols, during which a urethane group is formed as a result of the reaction of isocyanate and hydroxyl groups. In thermoplastic polyurethanes, there are flexible segments made of polyol chains, and rigid segments formed as a result of the reaction of isocyanate groups with chain extenders, such as low molecular weight diols. There is a thermodynamic incompatibility between the rigid and flexible segments, resulting in the development of a morphology consisting of microdomains rich in rigid segments and microphases rich in flexible segments. Thermal stability of rigid segments is limited due to thermal dissociation of the urethane bond, hence advanced works are being carried out to improve the thermal stability and flammability of polyurethane materials. One of the promising methods is the synthesis of hybrid systems, among others those utilizing polyhedral oligomeric silsesquioxanes (POSS) which are organo-silicon chemical compounds with the formula (RSiO1,5)n, where n = 6-18, and R is a hydrogen atom or an organofunctional non-reactive or reactive substituent (alkyl or aryl groups). Cubic cage octasilsesquioxanes (R8Si8O12, T8) are widely used; depending on the functionalization applied, they provide interactions with the continuous polymer phase and could be chemically incorporated into the polyurethane structure forming thus organic-inorganic hybrid material, or physically mixed to fabricate nanocomposites [1]. As a result of the works carried out so far, it was found that the incorporation of thermally stable POSS particles into the PU matrix changes polymer thermal properties, affects the value of the glass transition temperature and can lead to the improved thermal stability. Barrier effects and suppression of the molecular mobility of polymer chains by bulky silsesquioxane pendant groups or crystals formed thereof are considered as the reasons for enhancements in the thermal stability of hybrid composite materials [2,3]. These effects are also investigated in non-isocyanate polyurethanes (NIPUs)/POSS systems; NIPUs are obtained in the reaction of diamines with difunctional cyclic carbonates, without the need to use toxic isocyanates [4]. Moreover, effects related to the reduction of flammability and heat release rate during the combustion of hybrid PU/POSS materials were also observed.

In this lecture synthesis, characterization and thermal properties of PU/POSS and NIPU/POSS hybrid materials and nanocomposites, in form of both elastomers and foams, will be presented.

Acknowledgments

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What is a pharmaceutical technologist pharmacist doing among thermoanalysts?

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Keywords: thermal investigation of solid dosage forms, DSC, TG-MS, binary and complex drug systems, development preparation, mucoadhesive polymer films, counterfeiting protection

The main task of the pharmaceutical technologist is to produce the desired pharmaceutical form from a given active ingredient in such a way that the active ingredient is released in the appropriate place, time and quantity for the therapeutic purpose.

The active ingredient is essential for the effect to occur, but in many cases its properties must be changed in accordance with expectations (increasing solubility, increasing permeability), speeding up the development of the effect, or prolonging, retarding it. Of course, all properties must be checked with the appropriate instruments.

There are strict requirements in the pharmaceutical industry for both the manufacturing conditions and the quality of the product, as well as also for the quality of the finished product to be maintained as long as possible during storage.

Since the active ingredients - with a few exceptions - cannot be used and cannot be introduced directly into the body, it is therefore necessary to create appropriate pharmaceutical forms from them.

When dosage forms are planned, the physical properties and the physical-chemical characteristics of the active agents have to be taken as the starting point, and the carrier system which is the most suitable for the application of the active agent has to be created. The thermal investigation of components (active ingredients and excipients) is used for the formulation of dosage forms.

Besides studying individual components, it is equally important to know the thermal behaviour of the intermediate products produced from them, as during drug formulation they are exposed to a heat effect for shorter or longer periods, thus it is essential to be familiar with these.

An extremely promising way of improving the quality of pharmaceutical base materials in terms of physical-chemistry is to choose the right polymorphic form, the transformation of crystalline materials into an amorphous form, the formation of cyclodextrin complexes or API-titanate nanotube composites as new drug carrier systems.

The examination of the thermal behaviour of complex drug systems is a particularly exciting area. Various methods of thermal analysis (DSC, TG-MS) are used for investigating the solid systems (pellets, granules, tablets), although coupled techniques and other investigation methods are often needed, too.

Macromolecules are drug components which are used frequently and for different purposes, e.g., for granulation, as a binder component during the compression of tablets, but one of the major fields of their use in solid dosage forms is the production of film coatings, where, e.g., it is essential to know the interaction between the polymer and the API, too [1].

In the pharmaceutical industry companies try to find new and innovative drug administration routes to deliver the API. The buccal mucosa is considered an innovative route with several advantages. A very fast effect can be achieved both locally and systemically (mucoadhesive polymer films). The examination of the thermal behavior of films also provides information about the structural changes occurring during storage [2].

Another new, innovative solution is the development of 2D identification methods using laser technology (counterfeiting protection, personalized medicines), where thermoanalytical tests can also be used [3-4].

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Two interpretations of isoconversional kinetic parameters

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Keywords: general rate equation, isoconversional methods, Arrhenius equation, kinetic compensation effect, complex processes

Processes in condensed state are widely studied by thermoanalytical techniques. Their mechanisms 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]

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

where α 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. The widely applied isoconversional methods are based on GRE [1-3].

There exist two ways of interpreting the results obtained by the isoconversional methods that are in sharp contradiction and are mutually incompatible, i.e., the concept of variable activation energy and the interpretation of GRE as a mathematical tool for the description of thermoanalytical kinetic data. It is demonstrated here that the concept of variable activation energy is incorrect. When understanding GRE as a formal mathematical tool, the temperature function, $k(T)$, is not the rate constant in general and the conversion function, $f(\alpha)$, does not reflect the mechanism of the complex process. Both, $k(T)$ and $f(\alpha)$, are functions enabling to describe the kinetic hypersurface. The physical meaning of parameters occurring in both functions is unclear for the complex processes. Hence, 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 accessible experimentally. These quantities can be recovered and modelled from the known kinetic parameters. It is proved here that, for a complex process, the right temperature function cannot be the Arrhenius equation. Neglecting the complexity of the process may be the source of the kinetic compensation effect.

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50th anniversary of the foundation of Czech Group for Thermal Analysis

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Keywords: thermal analysis, history, central European region

The Czech Group for Thermal Analysis (CGTA) celebrated its 50th anniversary last year because it has been founded in 1972 being inspired by the foundation of International Confederation for Thermal Analysis in Aberdeen in 1965 (ICTAC from 1992). First chairman was Dr. Karel Habersberger (Inst. Chem. Technol., Prague) followed by Assoc. Prof. Vladimír Balek (Nuclear Res. Inst. Řež). One of the founders and eminent personage professor Jaroslav Šesták served many years as the head of CGTA and national representative at ICTAC. Since 2008 professor Petra Šulcová is the head of CGTA and professor Jiří Málek (University of Pardubice) was national representative at ICTAC (University of Pardubice) from 2010 to 2020. Since 2020, this position has been held by Dr. Jaroslav Barták.

Organization of workshops and meetings focused on theoretical aspects and instrumentation of thermal analysis as well as the methods of evaluation of thermoanalytical data is one of the main activities of CGTA. Among the main achievements of these activities certainly belongs the Czech and Slovak thermal analysis terminology as well as the standardization tests for calibration of thermal analysis instruments that took place in university and Academy of Sciences laboratories and research institutions in Czechia and Slovakia.

The group represents the extensive publications, which also related to an important bibliographic citation response and is associated with the names as Arnošt Bergstein, Antonín Blažek, Vladimír Šatava, Jaroslav Rosický, Rudolf Bárta, Pavel Holba, Jaroslav Šesták, Vladimír Balek, Jiří Brandštetr, Arnošt Hrubý, Jiří Málek, and an array of other celebrities in field of thermal analysis [1].

In 2010 CGTA has organized the session of Thermal Analysis and Calorimetry within the 62nd annual meeting of Czech Chemical Society that has been historically first joint meeting of thermal analyst from Slovakia and Czechia within the framework of annual meetings of chemical societies. According to the participants it has been a successful event that significantly improved mutual exchange of experiences and helped to establish new contacts within the different laboratories.

The section of Thermal Analysis is also part of the program at the Congress every two years (64th in Olomouc, 2012; 66th in Ostrava; 68th in Prague, 2016; 70th in Zlín, 2018; 72nd in Prague, 2020; 74th in Olomouc). This tradition will be maintained in the future. Since 2015, the group has also been organizing Thermoanalytical Seminar (TAS) every two years (2015: Pardubice; 2017: Ostrava; 2019: Brno; 2022: Pardubice).

The CGTA also participated in organization of Joint Czech-Hungarian-Polish-Slovak Conference on Thermal Analysis (the first Joint meeting has been organized by Hungarian Thermal Analysis Group, the second under auspices of Polish Society of Calorimetry and

Thermal Analysis, the third being organized by Slovak Working Group on Thermal Analysis and Calorimetry). The Joint conference in 2013 was organized by CGTA in Pardubice, Czech Republic. This year marks the 9th yar of the Joint conference.

More information about the current and future activities of the Czech Group for Thermal Analysis can be found at: www.thermal-analysis.cz.

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Engineering at the nanoscale: a strategy for developing high performance functional materials from biopolymers

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Keywords: green chemistry, biopolymers, chitosan, starch, biowastes, nano composites

Green chemistry started for the search of benign methods for the development of nanoparticles from nature and their use in the field of antibacterial, antioxidant, and antitumor applications. Bio wastes are eco-friendly starting materials to produce typical nanoparticles with well-defined chemical composition, size, and morphology. Cellulose, starch, chitin and chitosan are the most abundant biopolymers around the world. Cellulose nanoparticles (fibers, crystals and whiskers) can be extracted from agrowaste resources. Chitin is the second most abundant biopolymer after cellulose, it is a characteristic component of the cell walls of fungi, the exoskeletons of arthropods and nanoparticles of chitin (fibers, whiskers) can be extracted from shrimp and crab shells. Starch nano particles can be extracted from tapioca and potato wastes. These nanoparticles can be converted into smart and functional biomaterials by functionalization through chemical modifications due to presence of large amount of hydroxyl group on the surface. The preparation of these nanoparticles includes both series of chemical as well as mechanical treatments; crushing, grinding, alkali, bleaching and acid treatments. Since large quantities of bio wastes are produced annually, further utilization of cellulose, starch and chitins as functionalized materials is very much desired. The cellulose, starch and chitin nano particles are currently obtained as aqueous suspensions which are used as reinforcing additives for high performance environment-friendly biodegradable polymer materials. These nanocomposites are being used as biomedical composites for drug/gene delivery, nano scaffolds in tissue engineering and cosmetic orthodontics. The reinforcing effect of these nanoparticles results from the formation of a percolating network based on hydrogen bonding forces. The incorporation of these nano particles in several bio-based polymers have been discussed. The role of nano particle dispersion, distribution, interfacial adhesion and orientation on the properties of the ecofriendly bio nanocomposites have been carefully evaluated.

Thermogravimetry as a research tool during the beneficiation of diamond mine residues

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Keywords: diamond mine residues, thermochemical treatment, valorisation, magnesium, talc, thermogravimetric analysis

The mining industry plays a vital part in the South African economy. However, its activities are associated with the generation of large quantities of waste mine residues (e.g. tailings, slimes). These residues create major environmental challenges and take up vast amounts of land that could be used for other economic purposes. On the other hand, these same residues may have the potential to be secondary mineral resources that promote sustainability if processed into valuable products [1].

The aim of this study is to develop a process for the valorisation of diamond mine residues. Thermochemical processing using ammonium sulphate, $(NH_4)_2SO_4$, is a promising technology for extracting strategic metals from various mineral-bearing materials [2-4]. The diamond mine residues used in this study were characterised by a complex mineral matrix, with smectite, talc, phlogopite and diopside being the most common minerals. Mg, Fe and Al were determined to be the most abundant metals. The beneficiation potential of these residues could therefore lie in the extraction and conversion of these elements into valuable products. For instance, Mg is frequently listed as a critical element (i.e., a valuable constituent element of a mineral commodity that is subject to risk of disruption in its supply [5]) owing to its importance and versatility in various industrial applications such as automotive, aerospace, electronic, medical or chemical. The relatively high talc content (~30 wt. %) of the residues have furthermore raised the question whether talc should be regarded as a source of Mg or whether it could be purified and recovered as a value-added product.

The degree of conversion of extractable metals from the mine residues into soluble sulphate-bearing minerals, during thermochemical treatment with $(NH_4)_2SO_4$ between 450–550 °C, was monitored using TGA in combination with XRD, FTIR and SEM analyses. Thermochemical treatment of the mine residues with $(NH_4)_2SO_4$ was found to be non-selective at a single temperature, with several metals being co-extracted from the residues. This made the production of pure Mg-containing products difficult, as the removal of the Fe-fraction post thermochemical treatment was challenging. TGA data of the products obtained from thermochemical treatment was used to develop a roasting programme to separate Fe from Mg before leaching. By employing an additional roasting step, the soluble Fe content in Mg-bearing leachates could be reduced by up to 90%. Brucite and Mg/Al layered double hydroxides (LDHs) were successfully synthesised from the leachates, while the talc content of the leach residue could be increased to 56 wt. %.

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"Small dwarfs – high toxic effects"? – Nanoparticles at the workplace and in the environment

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Keywords: nanoparticles, bio-persistence, lung toxicity

Nanotechnology is considered to be the key technology of the 21st century. It is expected that applications will not only be found in many areas of industry, but also in connection with new therapeutic and diagnostic procedures in the medical sector. Nano-sized structures with dimensions entirely or partially smaller than 100 nm can actually generate new functionalities and properties.

Nanoparticles can easily be inhaled into the lungs and can reach even the alveoli, due to their small size. Once deposited there, the particles can no longer be removed by the biomechanics responsible for cleaning the upper and middle respiratory tracts ("mucociliary clearance").

Nanoparticles differ from coarser particles by their increasing tendency to form agglomerates. Agglomerates are macroscopically perceived as one particle and may break down into smaller units in biological material; this dissociation is of toxicological relevance.

Nanoparticles are generally formed by two different processes. Based on coarser particles, the top-down processes leads to smaller particles mainly by mechanical comminution. In bottom-up processes, nano-sized particles are formed by gas-phase or liquid-phase reactions.

The difference between the processes is that the top down method leads to crystalline or polycrystalline samples. This is based on a well-known thermodynamically product, which is described by an ideal crystal structure. The bottom-up procedure results in the formation of nanoparticles from crystalline areas that do not correspond to the ideal lattice (defect structure). These structures, which are difficult to characterize, are typical of kinetic controlled products. An ideal crystal growth is inhibited by bottom-up processes.

Nanoparticles produced by bottom-up processes resulted in modified chemical, physical and toxicological properties.

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Sponsored Speakers

Investigation of Thermal Runaway Reactions by Means Accelerating Rate Calorimetry (ARC)

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Keywords: hydrogen peroxide, ARC, thermal hazard screening, thermal runaway

Calorimetry is the science of measuring heat and heat transfer associated, for instance, with changes of state, chemical reactions or phase transitions under specified conditions. This very general definition implements that calorimeters are adapted and designed to specific measurement conditions according to the particular target of the measurement. This is why nowadays, a huge variety of calorimeters is commercially available such as combustion, reaction, titration, scanning or mixing calorimeters along with many others.

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 work presents results of the thermal decomposition of hydrogen peroxide solutions. It will be shown how to obtain ΔT_{obs}, ΔT_{ad}, T_{D24}, TMR_{24h} and other relevant data for the classification of the thermal hazard potential of samples.

An Advanced Heat Flux DSC Operated in the Power Compensation Mode

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The instrument presented by Boersma in 1955 [1] can be considered the starting point for the development of disk type heat flux differential scanning calorimeters (DSC). In this type of DSC, a single furnace contains thermocouples or heat flow sensors with positions for refence and sample. This type of DSC has been further developed by commercial suppliers and is widely used. One of the advantages of this type of DSC is the high sensitivity and robustness.

The alternative power compensated DSC technique was first developed first by O’Neil in 1964 [2]. In this approach, the power required for compensate for heat is measured. The measurement system consists two small furnaces installed in a cooled metal block. This concept is used for conventional DSC and fast DSC using chip calorimeters (Flash DSC).

An advantage is the relatively short signal time constant, τ, which is given not only by the heat transfer conditions in furnace and sample, but also by the parameter of the controller of the difference temperature.

The new DSC type presented is based on a conventional heat flux DSC, which has been extended with additional heating elements and temperature sensors for power compensation. This new DSC type was developed to combine the robustness of the heat flux DSC with the signal time constant of a power compensated DSC. The new developed instrument has electrical power calibration for outstanding accuracy, small time constant for high resolution, improved sensitivity and excellent baseline stability.

The performance of this device is demonstrated using heat capacity measurements and fast transformations as examples.

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Modern methods in thermal analysis

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The most recent development in thermal analysis will presented with focus on X3 heat flux sensor for DSC increasing the productivity of measurement. Modulated techniques help user to separate complex heat flow curves into specific events and thus are necessary for research and routine analysis of engineered materials. Temperature modulation is also very helpful for thermogravimetric analysis (TGA) and thermomechanical analysis (TMA) and it's importance will be shown. As more and more chemically specific output from thermal analysis in required, DSC and TGA can be connected to spectrometers including NIR, Raman, FTIR and MS. Real time microscope is also a new tool for DSC events observations. In addition separation techniques are going to be a part of modern TGA or simultaneous DSC and TGA. The critical parameters and benefits of TGA-GC-MS technique will be presented with focus on the interface between TGA and GC-MS.

Oral Presentations

Bio sciences, including food, soil, textile, wood

Selected applications of thermal analysis in the research of microplastics in soil

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Keywords: microplasics, DSC, TG, TG-MS, soil, degradation.

Microplastics are small plastic debris that result from both commercial product development and the erosion of larger plastics. Currently, their presence in the environment belongs to the most serious environmental issues. Within soil ecosystems, MPs have the potential to negatively impact the balance of the system, as they can influence a range of physical, chemical, and biological soil properties, including plant growth. The specific effects of plastics on soil properties can vary depending on the type and size of plastic particles present. An alternative to solve the microplastics are bioplastics, which, despite their faster degradation, bring sometimes similar and sometimes different problems [1].

The microplastics-in-soil-research is focused on several areas i) qualitative and quantitative analysis of microplastics in soil, ii) effect of microplastics on soil properties and its productivity, iii) fate of microplastics in soils.

Our group is focused on all three groups of problems and solves related research questions using a combination of many techniques and approaches, including thermal analysis. In this contribution, we would like to demonstrate the usefulness of methods such as differential scanning calorimetry (DSC), thermogravimetry (TG) and evolved gas analysis (TG-mass spectrometry; TG-MS) for solution of specific problems in this field.

DSC method was used to elucidate the effect of microplastics on soil organic matter structure and revealed their effect on the supramolecular structure of soil organic matter and water properties. In particular, it was demonstrated that microplastics cause faster soil desiccation [2]. TG was demonstrated to be a useful quantitative and quantitative method for determination of several microplastics in soil [3] as a tool for elucidation of the effect of biodegradation of plastics on soil organic matter and for the long-term transformation processes of microplastics in soil. Last, TG-MS, based on analysis of pyrolysis products of microplastics, is currently one of the most efficient techniques for the quantitative analysis of microplastics in soil [4,5].

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Thermogravimetry as a tool to discriminate the susceptibility of different components to fibre release from the same fabric

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Keywords: textiles, fibre release, Thermogravimetric Analysis, thermal Analysis, polyester, cotton, elastane, acrylic, wool

The textile industry employs various textile fibres that exhibit different properties, resulting in diverse shedding behaviour [1]. These differences entail a challenge in the study of blended fabrics, whose components might present different susceptibility to be released from the textiles. Moreover, fibres of unequal nature could interact, altering the global fibre loss. In this study, Thermogravimetric Analysis (TGA) is used to compare the susceptibility of different fibres to be released from blended woven fabrics due to physical abrasion of these textile structures [2,3]. The fabrics are subjected to pilling experiments in a standardized machine that produces fibre release and pill formation [4]. Both fabrics and released fibres obtained in the pilling tests will be analysed through TGA. The estimated fibre composition based on these results will then be compared.

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Calorimetry

Adiabatic hydrogenation of Alkyl Levulinates to Gamma-valerolactone

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Keywords: Calorimetry, Adiabatic, Hydrogenation, Kinetic Model

The interest in biomass as a raw material for energy and chemicals production has increased due to environmental concerns, growing global demand and fossil-based raw materials depletion. As such, the use of 2nd generation biomass, specifically lignocellulosic biomass (LCB), has increased due to its availability and no concurrence with the food industry [1,2]. Many useful derivates can be obtained from LCB, among these molecules, gamma-valerolactone (GVL) can be considered one of the most relevant nowadays [3].

It has been shown that the catalytic hydrogenation of levulinic acid (LA) and alkyl levulinates (AL) over Ru/C is one of the most efficient method for GVL production [4]. According to some studies, he risk of thermal runaway must be considered for this system [5]. This study aims to observe the link between the molecular structure of different alkyl levulinates and thermal risk parameters, such as the time for maximum adiabatic rate (TMRad) and highest adiabatic temperature (ΔTad) [6]. While ΔTad would represent the severity of the risk and is linked to the reaction enthalpy, TMRad is used to represent the probability of the risk and is linked to the kinetics of the reaction.

We studied the reaction enthalpies for the hydrogenation of LA, Methyl (ML), Ethyl (EL), and Butyl (BL) levulinates under isothermal conditions [7]. Such measurements were possible with an RC1 and C80 calorimeter. From these measurements, one can notice that LA hydrogenation is the most exothermic reaction system. Since thermal risk also depends on kinetics, and to evaluate this parameter, experiments in adiabatic conditions were carried out (Figure 1). We can observe that for shorter alkyl length substituent of the levulinate, the risk of thermal runaway is increased. We are aiming to develop a kinetic model in adiabatic mode to find a relationship between these thermal risk parameters and the molecule structure. Such study would allow the development of a robust kinetic model.

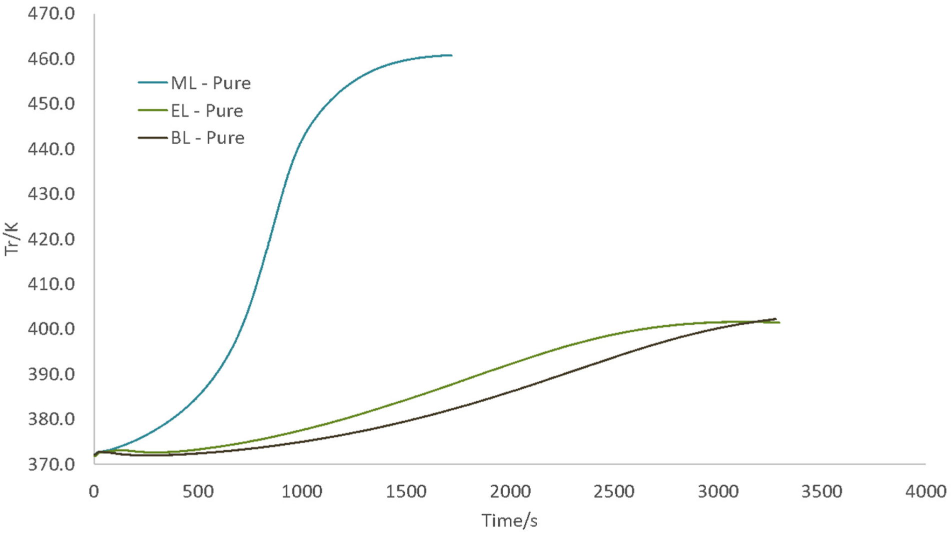

Figure 1 - Temperature evolution for ML, EL and BL in adiabatic conditions

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Self-healing anodes for Li-ion batteries: Enthalpy of mixing in the liquid system Li-Zn, and Li-Sn-Zn

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Keywords: Li-Sn-Zn, enthalpy of mixing, drop-calorimetry, phase equilibria, Li-ion batteries

Tin, a promising anode material for Li-ion batteries, has a high theoretical capacity compared to conventional graphite anodes. However, a major disadvantage is the formation of cracks on repeated charge/discharge cycles due to the large volume changes on lithiation and de-lithiation leading to degradation of the electrode material and hence poor cyclability. The self-healing of cracks based on partially liquid active electrode materials is one idea to overcome this problem. For this purpose, the melting regime of the anode material must be lowered by the addition of further elements (e.g. Bi, Ga, In, Zn) which form eutectic alloys showing lower reaction temperatures [1]. Phase diagram studies, of the intermetallic systems Li-Zn and Li-Sn-Zn, based on X-ray diffraction and thermal analysis were carried out to understand the associated lithiation mechanism of the electrode alloys. In addition, drop calorimetry was applied to determine the mixing enthalpy of liquid alloys. Thermochemical data for the binary Li-Zn were earlier published by Debski et al. [2, 3]. A thermodynamic assessment of the Li-Sn-Zn systems only based on the extrapolation of binary data was published by Turchi [4]. Partial and integral molar enthalpies of mixing of liquid Li-Zn and Li-Sn-Zn alloys have been determined at 550 °C. The binary system was studied up to a total lithium content of $x(Li)= 0.85$. The description with a Redlich-Kister polynomial was in good agreement with literature data. To the best of the authors' knowledge, the enthalpies of mixing of the ternary system Li-Sn-Zn have not been investigated. In the ternary system Li-Sn-Zn nine different concentrational sections were examined and the integral molar enthalpies of mixing were used as input to fit ternary interaction parameters based on the Redlich-Kister-Muggianu model for substitutional solutions. The crossing points of the integral enthalpies of mixing for different experimental sections showed well accuracy. The combination of the obtained ternary interaction parameters with the binary interaction parameters [5, 6] enabled the description of the integral mixing enthalpy of the liquid phase over the entire system.

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Thermally hazardous characteristics of ABS powder: experimental analysis and safety recommendations

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Keywords: thermal accident, thermal calorimetric technique, thermal runaway hazard, combustion and explosion hazard, dust dispersion behaviour

The chemical industry has prioritised process safety production alongside feasible efficiency and quality requirements. To achieve this goal, it is crucial to reduce systemic risks and implement emergency procedures to mitigate the harm caused by thermal accidents. In this study, a flash fire accident involving a storage tank containing acrylonitrile-butadiene-styrene (ABS) powder in a chemical plant in Taiwan was analysed. The accident occurred due to the high temperature of the combustible powder attached to the tank wall, which melted and dripped onto the ABS powder at the bottom of the tank, causing the combustion of styrene and butadiene derivatives and other in flammable gases, leading to a dust explosion. To prevent such thermal accidents, the study used various experimental methods, such as thermal calorimetric technique, Fourier transform infrared spectroscopy, gas chromatography-mass spectrometry, and a 20-L-Apparatus to assess the explosion and thermal runaway hazards of ABS powder in industrial processes proactively. The results showed that ABS powder has potential combustion and explosion hazards due to its particle size, minimum explosive concentration, K_{st} value, and lowest oxygen concentration required for combustion. In addition, ABS powder underwent oxidation reactions upon heating, generating carbon dioxide and releasing various volatile organic compounds. The hazard potential of the ABS powder was also dependent on the dust dispersion behaviour, which could be affected by the equipment configuration. Therefore, it is recommended that nitrogen should be used to replace air during the transportation and handling of ABS powder, and the system should be designed to forestall dust dispersion to minimise the risk of fire and explosion.

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Thermochemical properties of tin disulfide

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Keywords: SnS_2, anode materials, drop calorimetry, enthalpy of formation

Tin disulfide (SnS_2) has been recently investigated as one of the potential lithium-ion batteries anodes to replace the current state-of-the-art anode, graphite, due to its high reversible theoretical capacity of 644 mAh/g and its good cycling stability compared to tin-based anodes. This good cycling stability of SnS_2 likely stems from SnS_2's ability to accommodate volume change by the formation of an active/inactive composite material combination of Sn/Li_2S after the first lithiation of SnS_2. The electrochemical intercalation of lithium ions into the layered SnS_2 structure up to $Li_{1.5}SnS_2$ before its conversion into Li_2S and Sn provides a fine distribution of the metal in the matrix of Li_2S [1]. In the framework of a fundamental thermodynamic investigation, the thermal and thermochemical properties of SnS_2 were investigated and characterized using various techniques. Key thermodynamic properties like heat capacity and decomposition temperatures were determined experimentally. In addition, since crystallite-size and particle-size influence the performance of the materials, investigations on the influence of these features have been done on various SnS_2 sample powders from different syntheses and treatments like, e.g., milling. One of the techniques used was drop calorimetry where 15 drops of tin beakers filled with the SnS_2 powders were dropped into a tin bath. Drop calorimetry was used to accurately investigate the enthalpies of formation of SnS_2. Drop calorimetry was followed by SEM imaging and EDX of the residual of the experiment to verify that the SnS_2 powders were completely dissolved in the tin bath.

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Case study: calorimetry used to support scale-up of the hydrolysis of epichlorohydrin

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Keywords: calorimetry, scale-up, chemical process safety, reaction calorimetry, adiabatic calorimetry

Industry-standard reaction hazard instruments provide effective tools to obtain the data required for safe scale-up of new or altered chemical processes. Collected data can be used to characterize reaction kinetics, properly size process equipment (e.g., cooling systems, relief devices, condensers, knockout drums, etc.), understand decomposition or unwanted side reactions, guide the selection of safe processing conditions, and calculate many important process-related parameters (e.g., heat of reaction, moles of generated gas, etc.). This presentation illustrates several widely used bench-scale techniques that lend themselves to quickly identifying reactive hazards while providing directly scalable data for chemical process or storage facility design. A case study is presented on a hydrolysis of epichlorohydrin process, a type of reaction which remains applicable to several industrial uses. Example data are presented from various instruments (differential scanning calorimetry, reaction calorimetry, and adiabatic calorimetry) with discussion of how the data are analyzed, keeping chemical process safety as a priority throughout the discussion. The conversation also includes selection of the appropriate tool based on the testing goals.

Cements, building materials

Effect of supplementary cementitious materials on the whiteness and hydration heat of white cement

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Keywords: white cement, supplementary cementitious materials, whiteness, hydration heat, mechanical properties

White Portland cement (WC) forms a specific type of cement used for the design of aesthetic and decorative concrete in construction engineering. The production of white Portland cement is highly energy-consuming, using high-quality raw materials for its manufacture at a higher temperature than that of Ordinary Portland clinker. In addition to the engineering properties required for Ordinary Portland Cement, white Portland cement should not contain coloring elements such as Fe, commonly found in OPC. High-quality raw materials and high manufacturing temperatures cause a higher CO_2 emission compared with OPC. Therefore, a systematic study has been undertaken to use Supplementary Cementitious Materials with lower coloring elements to replace a part of clinker. Pure and finely ground limestone (GL) is the most available raw material without Fe content, as well as some Blast Furnace Slags (BFS) and metakaolin (MK). Composite cementitious materials were prepared on models consisting of binary, ternary, and four-component systems with substitution levels from 0 to 35 wt.% of white cement by using BFS, GL, and MK. The whiteness of white Portland cement, hydration heat, and mechanical properties of selected samples were investigated. The addition of some kinds of SCMS at substitution levels non-exceeding 25 % has slightly decreased the whiteness by about 1-2 % compared to WC. The hydration kinetics via conduction calorimeter has revelated that the substitution level decreases the intensity of the first and second peaks but does not change their time-position. The third peak and large shoulders appear at later ager of the hydration. The hydration heat decreases with the substitution level due to the low alkali-activated reaction at the beginning. The heat evolved by alkali-activated reaction and activation energies of each peak were calculated.

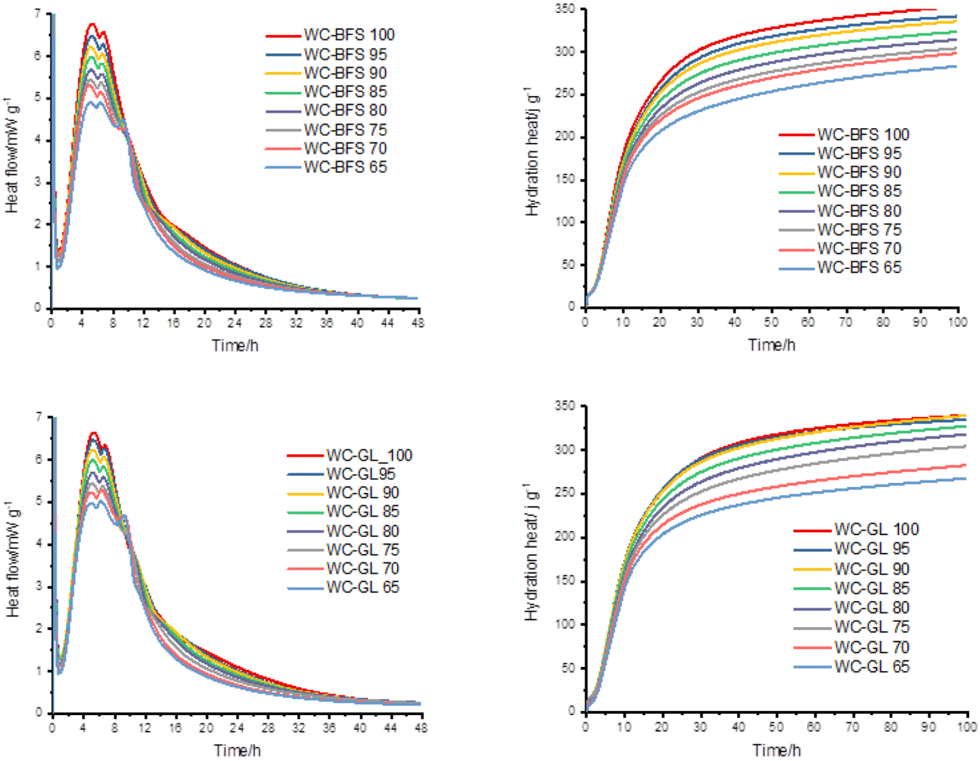

Fig1. An illustration of the influence of substitution levels on heat flow and cumulative hydration heat in binary systems (WC-BFS and WC-GL).

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Effect of four-component binder on strength and microstructure characteristics of fiber-reinforced Self-Compacting Mortars

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Keywords: Self-Compacting Mortars, supplementary cementitious materials, hydration heat, mechanical and physical properties

On recent developments of concrete and construction materials technology, the study on plastering (with different materials) plays a significant role in catering to the issues on crack repairs, damp proofing, and rehabilitation issues of the structures. Self-Compacting Mortar (SCM) is a highly fluid type that tends to pass, fill and flow on the desired form to repair and rehabilitate the structures. As such, the flowability of mortar can be an added advantage when inaccessibility appears, like in the case of congested reinforcement or narrow cracks or fissures [1]. Due to the application easiness and mechanical advantages, Self-Compacting Mortar (SCM) is preferred for repair, especially in reinforced concrete structures[2]. Therefore, cement, as well as the ingredients of the paste, mineral admixtures (pozzolanic or inert nature), and plasticizing chemical admixtures should be carefully chosen in order to obtain a suitable paste composition to enrich the granular composition of the mix. In addition, the self-compactibility of the resulting mortars may provide considerable advantages over conventional mortar, such as reducing construction time and labor costs and enhancing the filling capacity of highly congested structural members[3,4]. The hydration heat of a four-component binder consisting of CEM I 42.5 R, Blast furnace slag, metakaolin, and silica fume was investigated using a conduction calorimeter. Then, the influence of material composition with different substitution levels (SCM100, SCM75, SCM70, and SCM65) on the self-compactibility of the mortars was evaluated. Two mortar compositions comprising SCM75 and sand at 1:1 and 1:2 ratios were used to prepare fiber-reinforced self-compacting mortars in five combinations (0, 0.25, 0.5, 0.75, and 1%) of both fibers (polypropylene-PPF and basalt-BF) at a constant w/c ratio of 0.42. The influence of four component binder fiber-reinforced was investigated with respect to the properties of the mortar in fresh (workability) and hardened state (mechanical properties). Ten Self-Compacting Fiber-Reinforced Mortars (1:1 and 1:2 mixes) SCM75 (0% PPF and 1% BF), SCM75 (0.25% PPF and 0.75% BF), SCM75 (0.5% PPF and 0.5% BF), SCM75 (0.75% PPF and 0.25% BF) and SCM75 (1% PPF and 0% BF) were investigated. Additionally, the microstructure and pore structure of hardened mortar were verified by SEM, MIP, XRD, and TGA analyses.

Acknowledgements

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Measurement of pozzolans reactivity with the Isothermal Calorimetry and other methods

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Keywords: Isothermal Calorimetry, cement, pozzolanic materials, reactivity

With the potential decline in supplies of today's most widely used supplementary cementitious materials (SCMs) such as fly ash and slag, there is a growing interest in the use alternative pozzolans like ground glass pozzolans and calcined clay. The pozzolanic reactivity of these materials is assessed by different methods like ASTM C618 and C311, with the strength activity test being the only real performance indicator. Unfortunately, it is not possible to accurately determine the contribution of the pozzolanic reactivity to the strength in this test. This paper presents the comparisons between the Canadian CSA A3004- E1 method based on compressive strength of lime activated pozzolans (Ground Glass Pozzolan and Calcined Clay) and the Isothermal Calorimetry and Bound Water Measurements (ASTM C1897). The results show that both methods are very good indicators of materials pouzzolanicité, but the Isothermal Calorimetry method shows a lot of sensitivity and variation from one test to another due in particular to the temperature control. The CSA method can easily discriminate between pozzolanic and non-pozzolanic materials.

Ceramics, glasses

Study of thermal behavior and sintering ability of YAG/Al_2O_3 Glasses

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Keywords: crystallization kinetics, YAG-Al_2O_3 glasses, DSC.

In this work, five compositions of yttrium aluminate glasses (glass microspheres) with high alumina content (from 70 to 85 mol.%) were prepared by combining the sol-gel Pechini method and a flame synthesis technique. The crystallization behaviour and sintering ability of the glasses were analysed using differential scanning calorimetry (DSC), X-ray powder diffraction analysis (XRD), high temperature XRD (HT XRD) and scanning electron microscopy (SEM).

Except for the sample with lowest Al_2O_3 content (70 mol.%), which DSC curve showed the presence only one exothermic effect, DSC curves of the remaining samples contained two exothermic effects in the recorded temperature interval 25-1300°C. In the case of the first exothermic effect, the peak maximum was observed in the range of 937-950°C, while for the second effect, the peak maximum was in the interval 958-1102°C. A more detailed evaluation of measured DSC curves showed that the temperature of the maximum of the second effect increased with increasing Al_2O_3 content. The XRD patterns measured after DSC analysis revealed the presence of YAG phase and different forms of Al_2O_3 in the samples. Isothermal crystallization experiments with dwell times ranging from 30 to 240 min and performed at the temperature of the first peak showed gradual decrease of area of second effect in DSC traces, depending on dwell time and glass composition. The HT XRD analysis in temperature interval 25°C-1450°C confirmed the predominant crystallization of the YAG phase in two steps (temperature interval 950°C-1200°C), slow crystallization of θ-Al_2O_3 (1000°C-1200°C) and α-Al_2O_3 at temperatures about 1300°C. To determine the mechanism of crystallization of YAG phase in studied glasses, the JMAK model was applied. The results indicated predominant three-dimensional and two-dimensional crystals growth depending on the crystallization temperature and the glass composition.

To examine the possibility of preparation of bulk ceramics materials via sintering of glass microspheres, hot-press (HP) experiments at 1600°C, pressure 30 MPa and with isothermal dwell time 10 min were performed for all prepared compositions. Fine eutectic microstructures, depending on Al_2O_3 content, were obtained with interesting mechanical properties of bulk ceramic materials, $HV \approx 17$ GPa and $K_{IC} \approx 4$ MPa $m^{1/2}$.

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Effect of melting behavior on the structure of sulfur-bearing glasses for use as a glassy fertilizers

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Keywords: silicate-phosphate glasses, glass batch, sulfur, DSC-TG-EGA (MS), gas emission

The glasses with silicate-phosphate matrix were chosen as a subject of the research, with variable content of glass network formers (Si, P), modified with the addition of sulfur obtained under reducing conditions. Sulfur is a poorly glass-compatible element and the volatilization of SO_2 gas due to the synthesis of sulfate glasses is the largest problem. Therefore, the objective of the investigation was to determine the influence of the melting process on the structure of silicate-phosphate glasses from the SiO_2-P_2O_5-K_2O-MgO-SO_3 system. The actual compositions of the materials were determined with X-ray fluorescence (XRF) analyses. The amorphous nature of the samples was verified using XRD analysis. The structure of the materials was studied with spectroscopic techniques. Changes in the chemical composition were explained by examining the melting processes for selected glass batches with differential scanning calorimetry-thermogravimetry-related gas analysis by mass spectrometry (DSC-TG-EGA (MS)).

Sulfur, apart from being a component needed in growth and development processes of plants, impacts their resistance against different types of pathogens. A progressive process of greening has caused a bigger number of areas poor in sulfur worldwide. Taking the above into consideration, it has been expected that the silicate-phosphate glasses modified with sulfur will act as soil fertilizers fighting against the above mentioned phenomenon which relates to sulfur deficiency in soil. It was found that changes in the chemical composition of the sulfur-bearing glasses were associated with the release of gaseous products. Since these glasses have potential for use as glassy fertilizers, there is no doubt that the present study is important from an environmental point of view.

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Study the influence of Fe, Mo, Mn, and Zn ions on the structure and crystallisation of soil-active glasses

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Keywords: glassy fertilisers, structure, crystallisation, chemical activity

It is known that some special inorganic glasses from SiO_2–P_2O_5–K_2O–MgO–CaO systems have biochemical activity, and they can participate in the biological processes of living organisms. Modifying the glass composition with microelements enables a particular type of glassy fertiliser with the controlled release rate of plant nutrients. All microelements have a significant role in all living organisms. Therefore the subject of the study was silicate-phosphate glasses modified with Fe, Mo, Mn and Zn ions, which participate in almost all the most crucial life processes of plants. Iron ions are essential in metabolic processes such as DNA synthesis, energy transfer, respiration, and photosynthesis. Molybdenum ions transform nitrogen into amino acids in a plant, which is vital to yield. Interestingly, Mo ions become more available for plants in less acidic soils.

In comparison, manganese ions significantly contribute to various biological systems, including photosynthesis, respiration, and nitrogen assimilation. In contrast, manganese ions are used in plants as a significant contributor to different biological systems, including photosynthesis, respiration, and nitrogen assimilation. Zinc ions activate enzymes that are responsible for the synthesis of specific proteins. It is used in the formation of chlorophyll and some carbohydrates and is used in the conversion of starches to sugars. Zinc also helps plant tissue withstand cold temperatures.

Analysed glasses were synthesised by the traditional high-temperature melting of pure materials, i.e. SiO_2, $(NH_4)_2HPO_4$, K_2CO_3, MgO, $CaCO_3$ and MnO_2, Fe_2O_3, MoO_3 and ZnO. The obtained batch was fritted in water and refined to the required grain size. The structural and thermal changes of the silicate-phosphate glasses were followed by XRD, XRF, DSC and spectroscopic MIR and ^{31}P and ^{29}Si MAS-NMR methods. The biochemical activity of glasses was estimated based on their solubility in 2 wt% citric acid solution, indicating plants' assimilative ness of fertiliser components. The leaching of glass components was investigated by the ICP-OES method.

The influence of the increasing content mentioned above ions on the thermal stability and course of crystallisation of glasses was presented. It was found that the growing range of the above modifying ingredients changed the tendency of the glasses to crystallise. At the same time, the type of crystallising phases was related to the dissolution character of the tested glasses. It has been found that the glasses modified with Fe and Mo ions show a decreasing chemical activity, while the presence of Mn and Zn ions causes them to behave differently in the in vitro experiment. Simultaneously spectroscopic studies also showed a decrease or increase in the degree of polymerisation of the glass framework.

The observed regularities linking the peculiarities of the structure of the analysed glasses with their thermal and chemical activity have shown that the strength of the chemical bonds of bond-forming components and modifiers with oxygen atoms in the area of oxygen bridges determines the seemingly different properties of the analysed glasses.

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W–Zr thin-film metallic glasses: thermal behavior and evolution of properties

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Keywords: W-Zr films; metallic glass; thermogravimetry; oxidation behavior

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]. Up to 24 at.% Zr, the structure of W-rich films is characterized by a supersaturated bcc α-W(Zr) solid solution with a highly oriented structure, columnar dense microstructure, enhanced hardness and very low residual stress. In a wide range between 33 and 83 at.% Zr, an amorphous structure with features indicating metallic glass behavior is observed. These films exhibit a very smooth surface, a moderate compressive stress, and a constant electrical resistivity. Above 83 at.% Zr, high-temperature bcc β-Zr(W) and high-pressure hcp ω-Zr(W) phases with an enhanced hardness are observed in Zr-rich films.

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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Energetic materials

FE and Cu spinel based materials as potential oxygen carriers for biomass combustion

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Keywords: CLC, TGA analysis, oxygen carriers

Plant biomass is considered by the European Union an essential renewable energy source that could be a key factor to achieve carbon neutrality. In combination with new clean combustion technologies such chemical looping combustion (CLC) and carbon sequestration units, it is even possible to reach negative emission of carbon dioxide. In CLC technology, oxygen for fuel combustion is provided by a substance called oxygen carrier, whereby the emission of thermal nitrogen oxides is reduced nearly to zero and the whole process of carbon dioxide sequestration is simplified. The oxygen carrier used in such technology should exhibit not only proper resilience for reaction with ashes derived from biomass but also high reactivity with such fuels. In the demonstrated research, selected oxygen carriers synthesized from iron and copper oxides were used for the combustion of plant biomass. Tests were performed with thermogravimetric analyzer coupled with quadrupole mass spectrometer.

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Designation of rare-earth based PVC tube associated with fluorescent and its stabilized properties

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Keywords: mechanical property, mass concentration, thermal stability, thermal decomposition, volatile content

To investigate the effects of fluorescent powder on the mechanical properties and stability of PVC materials, the optimal amount of fluorescent powder is determined. The rare-earth (Eu^{3+} doped LaP_3O_9) based fluorescent powder (REFP) is prepared by the coprecipitation method as filler and photothermal stabilizer, which is mixed into PVC by the thermal processing method. With different mass concentrations (1%, 2%, 3%, 4%, 5%, and 6%) of REFP, the mechanical properties and stability of the PVC tubes is conducted by experimental tests, such as thermogravimetric (TG), X-ray diffraction (XRD), scanning electron microscopy (SEM), and fluorescence spectroscopy (FS). The parameters of thermal stability time, thermal decomposition temperature, and volatile content of PVC raw materials are obtained. The results indicated that the thermal stability of PVC raw materials is significantly improved as mixed with REFP. When the amount reaches 3 mass% REFP, the thermal stability time is increased by 16%, the thermal decomposition temperature reaches a maximum of 158.6 °C. Additionally, the gas HCl generated by the decomposition of PVC raw materials is reduced. Furthermore, after mixing fluorescent powder, the shrinkage rate of PVC fluorescent tubes is reduced, the mechanical properties are remarkably enhanced. When the amount of fluorescent powder is 3 mass%, the elongation at break reaches a maximum of 156%, the vicat softening temperature reached a maximum of 83.6 °C. Moreover, the tensile strength reaches a maximum of 52.1 MPa. As compared with no mixed with REFP, the elongation at break, the vicat softening temperature, and the tensile strength are increased with 20%, 4.1 °C, and 6.6 MPa, respectively. The new designation PVC tube with REFP can absorb and store the energy of UV radiation, and release it in the form of light energy. It can be applied on early warning in-situ industries.

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Energy conversion and storage

Thermogravimetric analysis of oxygen carriers for the application in CLC technology

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Keywords: CLC, TGA analysis, oxygen carriers

Thermogravimetric analysis (TGA) is an analytical technique widely used in material science, in which changes of mass sample are observed as a result of temperature change. TGA also allows to determine properties of the material in the different atmospheres (oxidizing, neutral or reducing).

In the following research, thermogravimetric analysis was used as a method to determine behaviour and properties of mixed metal oxygen carries for their potential application for solid fuel combustion in so called Chemical Looping Combustion technology (CLC).

Oxygen carrier (OC) is a material (usually metal oxide) used as an O_2 donor for combustion process in CLC. OC should be characterized by high oxygen transport capacity and reactivity toward fuels. Ability of spontaneous releasing oxygen due to change of its partial pressure (so called CLOU effect) is also desirable attribute.

Oxygen carriers were tested using TGA method to determine their reactivity toward selected fuels. CLOU properties were measured by heating OC in both neutral (nitrogen), and oxidizing (synthetic air) atmosphere.

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Optimizing working fluids for thermal energy storage systems using open absorption

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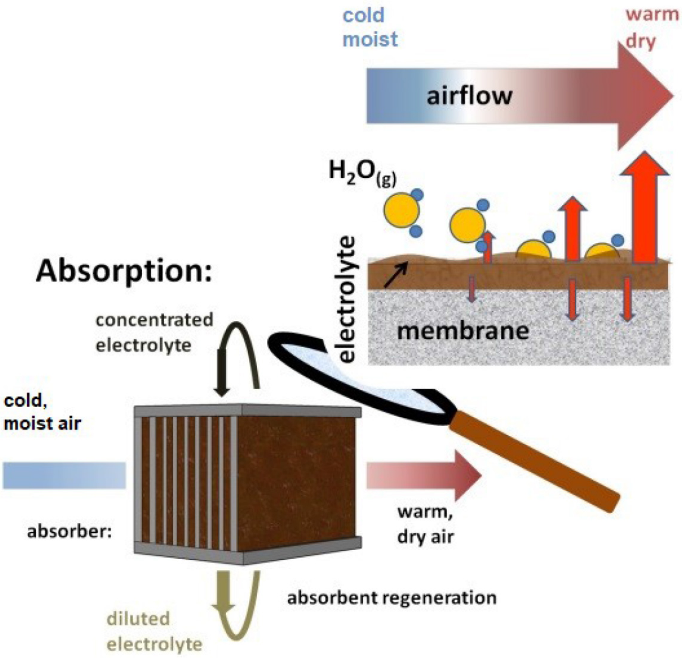
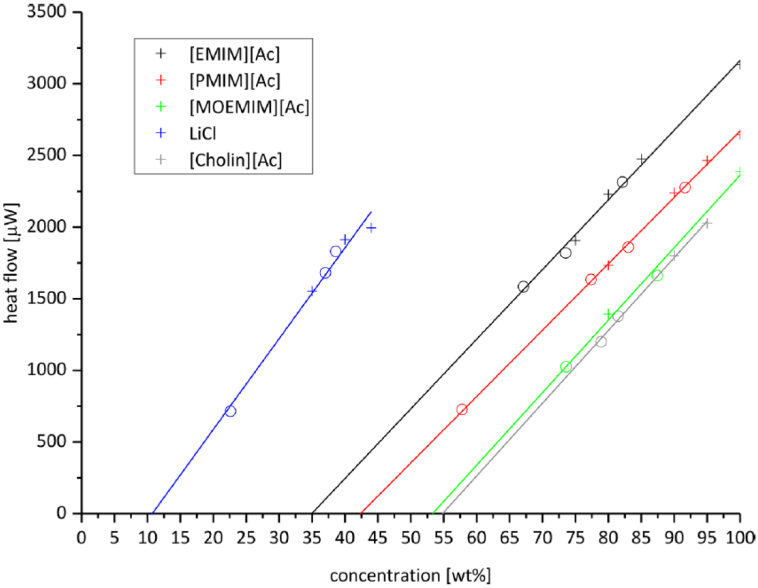
Keywords: **i**onic liquid, isothermal titration calorimetry, water sorption, CO_2 sorption, thermal energy storage, diffusion coefficient

Open absorption storage systems in combination with solar thermal systems are able to contribute reducing high energy consumption in air conditioning. In the absorber, water is absorbed from the air by a concentrated hygroscopic electrolyte. In the process heat is released by the phase transition of gas to liquid and dilution. However, the working fluid pairs currently used in absorption chillers and heat pumps show problems regarding crystallization, corrosion, and storage capacity, which make the development of new systems essential. Ionic Liquids (**IL**) represents a possibility to provide a tunability of properties not only through the variation of cation and anion, but rather by changing the molecular structure. In cooperation with the Department of Thermal Power Engineering of the University of Kassel we modify the properties of the **IL** and explain their thermodynamic characteristics. This means that not only the performance of known systems shall be exceeded, but also especially calorimetric studies shall provide insight into the relationships of structural properties.





For the determination of the heats of dilution, an iso-thermal titration calorimeter is used. This device measures the heat flow versus time, whereby the released amount of heat by the added volume of water can be calculated by integration. With respect to the heat released by dilution, the **IL** supply partially higher values than technically used electrolytes, such as **LiBr** do. As expected, the heats of dilution can be significantly influenced by modification of the molecular structure. Thus, there are clear differences between **IL**s with the same anion and a modified chain length.

Acknowledgments

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Gasification of surgical mask waste and its life cycle assessment

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Keywords: surgical mask waste, updraft gasifier, plasma gasification, syngas, hydrogen, life cycle assessment

Billions of surgical mask waste (MW) have been generated during Corona pandemic. This research aims to study the thermochemical treatment of MW using conventional gasification and plasma gasification. The traditional gasification was carried out using an updraft reactor in air and steam ambient update 900 °C and different air-fuel equivalence ratio and steam-to-carbon molar ratio. While the plasma gasification of MW was performed in steam using reactor with capacity of 1 kg/run. Also, the life cycle assessment (LCA) of conventional gasification of MW was studied based on international environmental standards (ISO, 2006). The results showed that conventional steam gasification can help to increase the amount of hydrogen in the formulated syngas compared to air gasification with (135% improvement). While plasma gasification can reduce tar yield and increase hydrogen amount by 160% compared to conventional gasification treatment. Whereas LCA showed that conversion of MW to hydrogen-rich syngas has high environmental potential, especially in terms of Global Warming item with high significant reduction.

Acknowledgments

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Exergy, Experimental thermodynamics

Thermohydraulic performance and second law efficiency analysis of a heat exchanger tube using a combination of two heat transfer enhancement techniques

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Keywords: thermohydraulic performance, second law efficiency, hybrid nanofluids, coiled wire inserts

In the study, hybrid Graphene-Iron Oxide water-ethylene glycol nanofluid, and modified coiled wire were used to conduct thermohydraulic performance and second law efficiency evaluations for a heat exchanger tube working under continuous heat flux and turbulent flow conditions. It was aimed to enhance the thermal performance and second law efficiency of the heat exchanger tube using hybrid nanofluid with Graphene-Iron oxide nanoparticles in three different weight fractions (0%, 0.5 and 1) and modified coiled wire in two different forms: barrel type and hourglass type. The effects of utilizing two combined passive heat transfer enhancement technique on the dimensionless thermohydraulic performance, entropy generation number, Bejan number and second law efficiency comprehensively discussed for Reynolds numbers ranging from 5000 to 30,000 and modified coiled wire pitch ratios of 0.5 and 1. The experimental findings demonstrated that the overall thermohydraulic performance was relatively improved for configurations with barrel-type helical inserts; however, there were no significant changes in second law efficiency between the barrel and hourglass types due to higher frictional losses. The highest thermohydraulic performance of 1.44 and the lowest entropy generation number of 0.4 was obtained for a Graphene-Iron Oxide water-ethylene glycol nanofluid with the fraction of 1% as a working fluid and barrel type coiled wire insert with pitch ratio of 0.5 at the lowest Reynolds number.

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Low carbon approach with the low-temperature air distribution in air conditioning applications

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Keywords: air conditioning systems, distribution system, low-temperature applications, energy efficiency, sustainability

Today, air management in air conditioning processes stands out with its low displacement preferences independent of energy loads. Especially in low-carbon approaches where thermal control management gains value, the sustainability of energy is shaped together with effective heat management. In the thermal control approaches of air conditioning systems, low-temperature air distribution together with heat mobility can be seen as an approach for an energy-efficient solution. In this study, first of all, the technical characteristics of the low-temperature air distribution system and its effects on the air conditioning systems were examined, and the efficiency effects of the distribution system on the air conditioning potential were evaluated. In the study, especially the energy efficiency effect of refrigerant preferences was evaluated. While the preference for a low-temperature system provides an efficiency improvement of up to 10%, it also directly affects emissions. At the end of the study, thermodynamic and environmental evaluations were made depending on the performance effect of the system.

Energy, exergy, exergoeconomic, exergoenvironmental analysis and optimization of quadruple combined solar, biogas, SRC and ORC cycles with methane system

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Keywords: combined solar cycle, supercritical carbon dioxide, organic rankine cycle, exergy-economic optimization, genetic algorithm, gas turbine, heat exchanger, carbon capture

This speech aims at presenting and reviewing a new configuration of quadruple energy systems. To conduct comprehensive analyses is another objective of this speech to present clear comprehensions into the system. To solve thermodynamic equations of the cycles and the validation of them EES software, and for multi-objective optimization and GA, MATLAB software should be used. Taking into account exergy and energy analysis, efficiency and energy power are generated and the highest beneficial work of energy systems should be assessed. Moreover, the energy systems' side effects on the environment should be evaluated with economic analysis, the costs of generating electricity of the entire system and with environmental analysis. The present work deals with a novel configuration of four cycles such as steam, gas cycles and an organic Rankine cycle and a biogas Brayton cycle and a solar Brayton cycle are introduced for recovering energy from hot exhaust gas and its simulation and optimization are discussed. Also, a carbon-amine adsorption system has been utilized for separating and storing carbon dioxide from hot exhaust gases and convert it to methane. For this new system, exergy, economical exergy, energy, economic and environmental exergy evaluations have been performed. To analyse the different parts, their thermodynamic and economic models, EES and MATLAB software have been used to optimize the exergy-economic cycle in order to reduce costs and increase exergy. In this research, genetic algorithm has been used for optimization. At the optimal point, the values of exergy efficiency are equal to 61.7% and the cost of electricity generation is 6.36 cent per kilowatt hour. The results show that adding Rankine cycles to the gas cycles increments the exergy and energy efficiency to 73.7 and 71.8, respectively. Nevertheless, integrating the carbon capture unit with this system reduced the exergy and energy efficiency to 51.9% and 50.5%, respectively. Based on the economic results for the presented system, it is indicated that the simple return on investment and return on investment are both 1.5 years. In addition, internal rate and net present value of return were 0.68 and 3.13*09 $ respectively. This system can generate 327,160 kW of electricity in addition, the carbon capture system unit can prevent and convert 627,000 tons of carbon dioxide into methane fuel annually.

Fire dynamics (or others for fire safety)

Kinetic parameters and heat of reaction for tropical forest fuels

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Keywords: tropical forest fuels, kinetic mechanism, forest fires, TGA, DSC

Forest fires threatens the environment and population health. Forest fires in tropical ecosystem are also a global concern today. The main goal of this work is to determine the kinetic parameters and heat of reaction for different forest fuels. Three typical tropical forest fuels are investigated: Amazonian leaves, *juncus* and *eichhornia*. TGA and DSC analysis were carried out at 10C/min and 30C/min heating rate under N2 and synthetic air atmospheres. The temperature of maximum pyrolysis, char oxidation as well the heat power profile for each forest fuel are presented. In this work, the proposed pseudo reaction mechanism for pyrolysis and oxidation of the forest fuels contains five steps. The genetic algorithm optimization process compares the instantaneous recorded data of TGA, DTG, and DSC with the calculated ones. The optimized kinetic reactions parameters for the forest fuels are the activation energy, the pre-exponential factor, the global order of reaction, the stoichiometric coefficients, and the heat of reaction. The overall performance of the proposed mechanism is evaluated taking the error or the experimental data into account. This set of reaction kinetics parameters allows for a suitable numerical model for forest fires. To the authors' knowledge, a comprehensive assessment of the above parameters, including the heat of reaction, for tropical forest fuels is lacking.

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The minimum required flammable component renders an aqueous-organic mixture to be flammable

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Keywords: flash point, aqueous-organic mixtures, inertization point, gire and explosion hazard management, wastewater management

The flash point (FP) behaviors of aqueous-organic mixtures are momentous because of their extensive presence in numerous applications. Although plenty of studies have been done on aqueous-organic mixtures [1-3], however, there are still some issues that need to be addressed. The minimum flammable compound required to render an aqueous solution to be flammable is one of the issues in order to achieve both safety and reduce the protection cost in chemical and process industries. In this study, a novel generic model was developed to determine two critical parameters: the minimum amount of flammable components that can make an aqueous-organic mixture to flash (*MinFF*) and the maximum FP that can be measured ($T_{fp,max}$). The model's validity was evaluated by the experimental measurement of some aqueous-organic mixtures with lower volatility. The model showed acceptable results for a wide range of ignitable chemicals when compared with the empirical measurements. The presented model and the results of this study may be particularly effective for fire and explosion hazard management of aqueous–organic processes and operations, improving the safety level of operations, and reducing the costs of ignitable wastewater management.

Acknowledgments

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Fuels, biofuels

The effect of pyrolysis conditions on yield, thermal behaviour and volatile matter composition of biocarbon products

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Keywords: biomass, carbonisation, biocarbon, TG/MS, pyrolysis-GC/MS

In order to reduce the global net emission of carbon dioxide, the fundamental driver of the current climate change, we the have to increase the share of renewable energy sources [1]. Biomass is an important source of renewable energy and the only renewable carbon source. Although raw biomass has a series of disadvantageous properties, the conversion of biomass by pyrolysis produces a carbonised material with improved quality. This solid product has numerous applications like biochar for soil amendment, activated carbon for flue-gas cleaning, renewable biocarbon in metallurgical processes substituting fossil coal, or charcoal, which has the oldest application in history for heating and cooking [2]. However, each application requires large amounts of carbonaceous material with certain properties; therefore, the improvement of yields and fine-tuning of product properties is highly required by selecting the proper feedstock and pyrolysis conditions.

The ground woodchips of a conifer (spruce) and a broadleaf (birch) tree were selected for slow pyrolysis experiments in this work, which were performed in a lab-scale tube furnace [3]. The effects of feedstock, carbonization temperature, heating program, purge gas flow rate and free volume above the sample were studied on the yield of biocarbon, liquid and gaseous products. Increased char yield was observed when staged pyrolysis program, low purge gas flow, or covered sample holder were used at a given final temperature (500 °C). Consequently, the pyrolysis conditions, which increase the residence time of the releasing volatile compounds during pyrolysis, enhance the yield of the biocarbon product.

The thermal behaviour, volatile matter (VM) content and evolution profiles of the compounds devolatilised from the prepared carbonaceous products were characterised by TG/MS. The final carbonisation temperature essentially determined the VM content of the produced biocarbon. Spruce biocarbons pyrolysed at 400 and 500 °C had higher VM content than birch biocarbons. This difference is explained by the higher amount of lignin residue present in spruce biocarbons, which was confirmed by measuring lignin-derived decomposition products. Biocarbons prepared by staged pyrolysis at 700 °C final temperature had lower VM content and released slightly less water above 800 °C during the analysis than biocarbons produced under constant linear heating. We can assume based on this observation that biocarbon samples prepared with staged pyrolysis program retained less hydroxy groups. The composition of the biocarbon VM content was also analysed in detail by pyrolysis-GC/MS.

By increasing the carbonization temperature, the released amounts of mono- and polyaromatic compounds drastically decreased, while the intensity of lower molecular weight gases increased. The aromatic composition of the biocarbon pyrolysates was mainly determined by the final pyrolysis temperature. Therefore, samples prepared at the same temperature have a similar composition of aromatic products, but the measured intensity of acetic acid strongly depended on the carbonisation conditions.

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Energy upgrading of the cocoa pod husk through torrefaction – thermal decomposition and kinetic analyses

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Keywords: combustion, pyrolysis, pyrolysis kinetics, heating value

Cocoa production has a significant impact- not only economic but social- on the rural population of Colombia, and the cocoa pod husk (CPH) is generated in a ratio of 10/1 to cocoa seeds, and is left in plantations to decay [1]. Therefore, this investigation aimed to assess torrefaction for valorising CPH as a solid fuel through thermal decomposition and kinetic analyses. The CPH were solar-dried in the lab facilities for 12 days. Afterwards, the torrefaction was carried out in a muffle furnace, using closed and sealed Petri dishes to simulate a reducing atmosphere. The analysed temperatures were 200, 250, and 300 °C, using 15- and 30-min residence times. Then, ultimate and proximate analyses of the CPH were done, and the heating value by means of a bomb calorimeter. Afterwards, non-isothermal thermogravimetric experiments were carried out in atmospheres of nitrogen and synthetic air at heating rates of 2.5, 5, and 10 °C/min. Also, inert isothermal experiments were performed at 200, 250, and 300 °C with a residence time of one hour. The kinetic analyses were applied using the Friedman and Vyazovkin isoconversional methods. About the CPH proximate analysis, the results in dry mass basis were 70.04% volatile matter, 4.02% ash content, and fixed carbon of 25.93%. Also, through ultimate analysis, the composition was 46.6% carbon, 5.19% hydrogen, 1.14% nitrogen, and 47.05% oxygen. After torrefaction, the result changed to 46.8% volatile matter, 3.85% ash, and 49.35 fixed carbon, increasing 24% the last and improving its thermal performance. The ultimate analysis yielded 56.13% carbon, 4.42% hydrogen, 1.42% nitrogen, and 38.03% oxygen, highlighting the decrease in 10% oxygen, reflected as a 10% increase in carbon. Then, the higher heating values recorded were 16.47, and 16.07 MJ/kg for 200 °C, at 15 and 30 min, respectively; at 250 and 300 °C were 18.81 and 20.26 MJ/kg, and 19.16 and 21.43 MJ/kg, respectively. The heating value of the dry sample was 16.27 MJ/kg. Then, the better energetic condition was achieved at 300 °C and 15 min. The pyrolysis kinetics of the torrefied biomass was characterized by an average activation energy, E, of 199.2 kJ/mol, a reaction model, f(α), of

$$\frac{3}{2}(1-\alpha)^{\frac{2}{3}}\left[1-(1-\alpha)^{\frac{1}{3}}\right]^{-1}$$

and pre-exponential factor, A, of 6.38×10^{14} s^{-1}. In the combustion analysis, activation energy presents a variation higher than 30% from the average [2]. Therefore, these results are unreliable, and a more complex reaction mechanism is necessary to represent the data [2]. The isothermal kinetic analysis provided an E=16.96 kJ/mol, A= 0.02 s^{-1}, and

$$f(\propto) = \frac{2}{3}\propto^{\frac{1}{2}}$$

The error involved in the model prediction was lower than 3%. Finally, it was concluded that torrefaction is an excellent way to improve the thermal properties of the cocoa pod and could be a good and cheap raw material for energetic purposes.

Acknowledgments

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Analysis of potassium release from paper sludge under oxygen rich combustion conditions

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Keywords: combustion, paper sludge, biomass fuel, oxygen enriched combustion, alkalis metal

Paper sludge can be used as a biomass fuel, which contains a certain amount of potassium element (0.38%). It is valuable to investigate the release characteristics of potassium during paper sludge combustion process. On the one hand, it benefits to explore the storage forms of potassium for utilization, and on the other hand, it can also obtain the optimal combustion conditions by comparing and analyzing potassium release data.

This study prepared three types of experimental materials: raw paper sludge, washed paper sludge, and paper sludge coke. The release of potassium in paper sludge treated differently during combustion in different oxygen rich atmospheres was detected by using a metal wire mesh heating table and emission spectroscopy technology. The experimental conditions are divided into six groups, including five groups of oxygen rich atmosphere (with oxygen content of 20%, 25%, 30%, 35%, and 50% respectively), and one group of air atmosphere for comparison. The obtained results suggest that the release of potassium from paper sludge is positively correlated with oxygen content at a certain range. When the oxygen content is below 30%, the total amount and rate of potassium release increase with the increase of oxygen concentration. However, when the oxygen concentration exceeds 30%, the release of potassium has little relationship with the oxygen concentration, as the release of potassium has reached saturation. Therefore, when the content of oxygen is 30%, paper sludge can achieve the most economical combustion condition.

By comparing the release of potassium element with that of air atmosphere combustion, it can be seen that carbon dioxide has a certain inhibitory effect on the release of potassium. The release of potassium in the washed paper sludge is similar to that of the raw paper sludge, indicating that there is almost no water-soluble potassium in the paper sludge. In addition, the potassium release from paper sludge coke is relatively low, only released when the oxygen ratio is higher than 25%. The release rate of potassium from paper sludge is about 0.26%, and the majority of potassium will remain in the ash, making it easier to recover potassium.

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Optical observation and combustion properties during paper sludge fast heating

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Keywords: combustion, biomass fuel, CH* radical, paper sludge, optical observation, fast heating

The challenge of paper sludge disposal has become an important environmental issue, therefore there is a need to study the combustion characteristics of paper sludge. In this paper, the combustion of paper sludge particle compacts under different atmospheres was analysed and investigated using a flat flame burner and optical observation techniques under fast temperature rise conditions. The fast heating conditions are provided by a flat flame burner, which allows us to better simulate the operating conditions of sludge particles in the actual combustion process.

The flame morphological characteristics, such as flame size, intensity, free radical distribution and burning time, were analysed and discussed in terms of time-series images of its combustion on the burner. A narrow bandpass filter at 430 nm is added in front of the camera lens so that it picks up the optical signal of CH* chemiluminescence. The final conclusion is that the increase in oxygen content has no significant impact on the ignition time of sludge particles, and volatile flames can be observed around the 16th second. However, the flame brightness will significantly increase with the increase in oxygen content. The CH * free radical appears in the most intense stage of combustion and is depleted before the volatile flame disappears. The higher the oxygen content, the faster the CH * depletion.

The influence of oxygen content on the combustion rate and burnout degree of sludge particles was investigated by comparing weight loss data and heating data: under low oxygen content (oxygen content accounts for 4% -8%) conditions, the highest temperature and heating rate increase with the increase of oxygen content. The reduced oxygen concentration cannot fully penetrate the ash layer on the surface of the particles and react with the interior sludge, resulting in a lesser degree of sludge particle burnout.

Acknowledgments

Key Project of the National Natural Science Foundation of China: The Migration Behavior of Alkali Metals in High Alkali Solid Fuel Combustion and Its Microregulation on Pollutant Generation

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Geosciences and minerals

Experimental investigations on the thermo-mechanical characterization of Jalore granitic rocks for India's HLW disposal

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Keywords: TGA, DSC, XRD, Thermal Expansion, XRF, SEM, Nuclear Waste Repository

Deep underground disposal of high-level radioactive waste (HLW) is one of the most challenging research topics in engineering structures. Crystalline rocks may be used to host high-level radioactive waste (HLW) repositories. A better understanding of the thermomechanical properties of rocks is fundamental for the safety evaluation and operational optimization of an intense HLW disposal system. In India, Jalore granite is usually chosen as the host rock for the construction of the HLW repository. Many researchers have experimentally conducted the thermomechanical properties of various kinds of granitic rocks at elevated high temperatures up to 1000°C at a constant heating rate. However, its thermomechanical performance at 300°C temperatures at different heating rates remains unknown. As a result, this study is focused primarily on experimentally investigation on the thermomechanical characteristics for use in nuclear waste disposal. To evaluate the feasibility of using two different kinds of Jalore granitoid rocks in this investigation (red and white granites). The main objective of this research is to investigate thermomechanical characteristics when determining a potential host rock, since little work has been done in the domain of rock mechanics, particularly in the context of nuclear waste disposal. The rock specimens were heated to 300°C for 12 h, with different heating rates (3, 5, 10, and 15°C/min) and constant slow cooling inside the tube-type high-temperature furnace rate was 0.57°C/min. The results show that the load-displacement curve under tension (line loading) for Jalore granitoid rocks after different heating rates treatments. Additionally, we investigated and analyzed the process of internal degradation using microscopic observation (thin section), mineral characterization (XRD), and surface morphology (SEM), elemental compositions (EDX), and chemical compositions (XRF) at various heating rates addressed. Thermal and kinetic behaviour alterations have also been identified using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). DSC-TGA was found to differentiate between endothermic and exothermic events which do not result in weight loss (e.g., melting and crystallization) but those that do lead to weight loss (e.g., degradation). It has been observed that increasing the heating rate causes the growth of stresses and an increase in rock strength. According to our results the thermal damage to the rock, in the form of mass loss and elastic modulus, occurred on the surface owing to thermal cracks and nonuniform expansion of grains along the grain bound-

ary. However, the cracking within the rock is more intense after being subjected to heating rates below 15°C/min, compared to 10°C/min after being subjected to above 3°C/min. The rock strength and elastic modulus of the Jalore granitoid improved when heated at a rate of 15°C/min. It's worth noting that the thermal damage and stability of the granitoid stayed substantially unchanged while thermally treated at 15°C/min.

Heat transfer

Thermal performance analysis of a heat pump assisted regenerative solar still

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Keywords: solar still, heat pump, roll-bond evaporator, desalination, mathematical calculation

Research and developments in the field of seawater desalination using a solar still is mainly developed in hot climate countries with tropical and subtropical areas and high solar irradiation. There is a lot of research work to improve the performance of a solar still by combining it with other renewable energy technologies. Among them, there are few studies on the integration of vapor compression heat pumps. The use of a heat pump evaporator in the cabin of a solar still allows not only to increase freshwater productivity (condensation rate) and is also justified for use in continental climate conditions such as the Caspian region (Kazakhstan) for preheating salt water before being fed into the solar still. For example, the shortage of drinking water in the Mangistau (Caspian) region of Kazakhstan is 70,000 m^3 per day. At the same time, this region has many sunny days and relatively mild winter weather conditions. The authors have now started a project to test the performance of a heat pump assisted regenerative solar still for water desalination and hot water production in this region.

In this paper, the authors present calculations of the thermal performance of the system, as well as a thermodynamic analysis. A calculation algorithm has been developed based on mathematical models available in the literature, heat transfer mechanisms and heat transfer coefficients. Based on the thermodynamic model, calculations of the efficiency of a vapor-compression heat pump part on the R134a refrigerant and its environmentally friendly alternatives were carried out. Based on the developed algorithm and a computer program, various modes of the system operation in local climate conditions were investigated.

To date, the created calculation algorithm is being validated by comparison with experimental data available in the literature. In addition, the sizing of the system components is being calculated for further assembly of the experimental prototype.

Acknowledgments

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Using a GPU-based lattice Boltzmann method to investigate the heat convection of a lithium battery pack

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Keywords: Lattice Boltzmann Method, Large Eddy Simulation, Battery cooling, LG Chem INR18650MJ1

Thermal management of lithium batteries has become a critical issue due to their high energy density and tight packaging. Lithium-ion batteries are highly employed in electric vehicles due to their high energy density, power output, and longevity. During a high discharge operation, poor cooling conditions will lead to structural damage considering the optimal operating temperature of lithium batteries is limited to 60 °C. This study extended the investigation of the thermal flow field surrounding a 18650-battery pack [1] utilizing the two-dimensional (2D) Thermal Lattice Boltzmann Method based on the Large Eddy Simulation [2] (TLBM-LES) model. However, the sensitivity to high temperatures threatens their reliability.

A new heat generation model is proposed for LG Chem INR18650 MJ1 [3], which was previously adopted in the experimental design of battery packs. The present experiments measuring battery resistance and voltage relevant to battery temperature and state of charge (SOC) will verify the proposed heat generation model [4, 5]. Establishing the heat generation model of LG Chem INR18650 MJ1 brings advantages in predicting battery temperature during operation time to achieve thermal management. Computational operations were significantly accelerated with the conversion from Central Processing Units (CPU) to Graphics Processing Units (GPU).

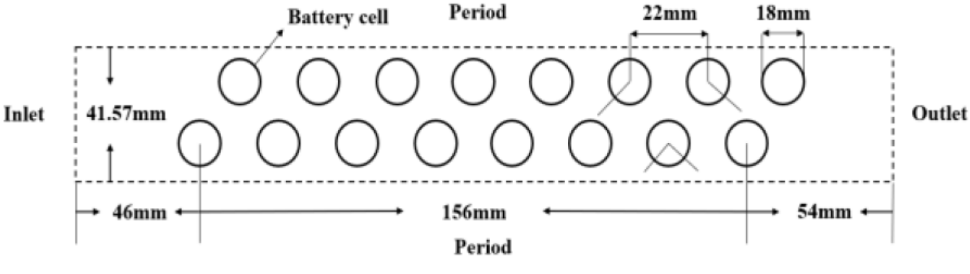

Figure 1. Specification of the battery pack arranged in cross structure.

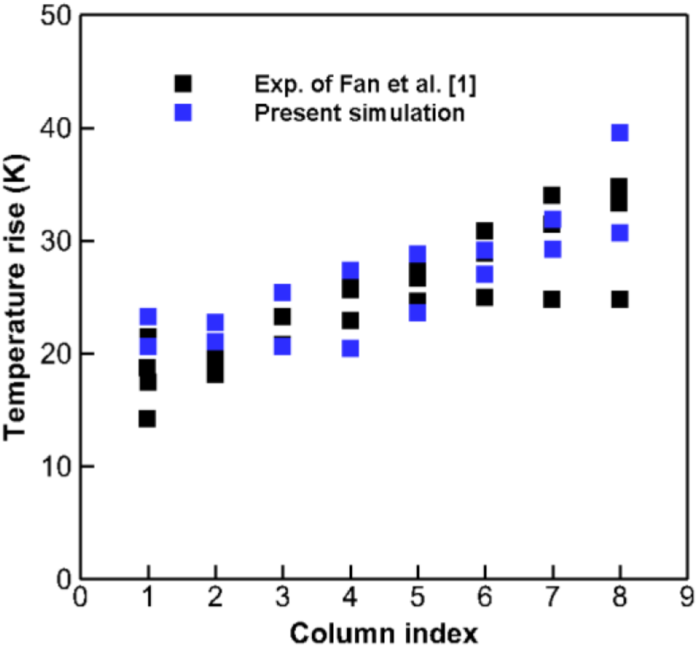

Figure 2. Comparison between measured and computed temperature rise of cross battery cells at the 2C discharge rate (1800 s), inlet velocity of 0.6 m/sec, and 20°C ambient temperature.

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Evaluation of mechanical vapor recompression system based on twisted oval tube evaporator for treatment of high salinity wastewater

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Keywords: mechanical vapor recompression, heat transfer enchantment, evaporator, twisted oval tube

Mechanical vapor recompression (MVR) evaporation is an energy-efficient heat pump evaporation technology. To further reduce the investment and energy consumption, a novel set of MVR evaporation crystallization system based on a twisted oval tube evaporator is developed and applied to a high salinity wastewater zero discharge engineering project of 10,000 tons/a cellulose ether. The evaporation requirement is 14.3t/h. Compared with the conventional evaporator, the heat transfer area and the volume of the twisted oval tube MVR evaporator is reduced by 32.5% and 41.2%, and can save the cost of 72.5 thousand dollars. The performance of the novel MVR system are tested and analyzed. The results show that the novel MVR evaporation crystallization system runs stably with the parameters meeting and better than the design requirements. Due to the heat transfer enhancement of the twisted oval tube MVR evaporator, the compression ration of the vapor compressor reduces, thus greatly decreases the operation energy consumption. The average specific energy consumption and COP of the system is 32.9 kWh•t-1 and 19.0, which is 45.2% lower and 86.3% higher than the conventional MVR system. Compared with the traditional three-effect and four-effect evaporation systems, it saves about 76.6% and 68.8% of standard coal, respectively. Results from current research indicate that considerable benefits in terms of energy and cost savings can be realized through the application of this novel set of MVR evaporation system in high salinity wastewater treatment.

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ZnO@GO/DW based binary composite nanofluid for improved energy transmission

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Keywords: composite, nanofluids, heat transfer, Nusselt numbers, thermal conductivity

Nanofluids have expanded a substantial approbation in the renewable and sustainable energy field. The heat transfer efficiency of these nanofluids has a great influence on the efficiency of renewable energy systems as compared to conventional fluids. A small number of solid nanoparticles with higher thermal conductivity added into conventional fluid could develop a bigger improvement in heat transfer. The current study is focused on the preparation of metal oxide (ZnO) and Graphene oxide (GO) based composite nanofluids to achieve the higher thermal properties of composite as a potential nanofluid. The advanced hummer method and sonochemical techniques were used to synthesize ZnO, GO, and ZnO@GO composites. Further 2-step preparation methods were used to prepare ZnO@GO/DW based well stable nanofluids at changing 0.1, 0.075, 0.05, and 0.025 wt.% concentrations. All the materials were confirmed by different characterizations like XRD, RAMAN, FESEM, EDX, and UV-Vis analysis. At 0.1 wt.% all the nanofluids showed a higher thermal conductivity, viscosity, and density which is 0.821 W/m.K, 2.85 kg.m^{-1}s$^{-1,}$ and 1.0018 g/cm^{3}. All the wt.% were tested for stability analysis using the sedimentation photograph method and found remarkable stability up to 5 weeks after the day of preparation without using any surfactant. Similarly, all the nanofluids were tested for hydrodynamic characteristics like friction coefficient (ff), pressure drop(ΔP), and pumping power(PP) where a notable value of friction was 0.057, a 12000 m.Pa pressure drop and 1.45MPa pumping power were achieved at 0.1 wt.% against the higher value of Reynold numbers (5849 to 24544). Finally, the greater development in average heat transfer/Nusselt numbers was achieved which is 3010/70 W/m^{2}.K, 2490/42 W/m^{2}.K, 2133/32 W/m^{2}.K 2000/29 W/m^{2}.K and 1000/W/m^{2}.K for all wt.% and base fluid (DW) at a higher rate of Reynolds. This all happened due to the use of ZnO and GO composite together.

Is thermal-guided mobile air supply unit a practical measure in burn isolation wards? Pontential future applications

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Keywords: airborne infection, isolation ward, operating room, burn patient, ventilation strategies

A validated Computational Fluid Dynamics (CFD) model that represents a burn patient ward was used to evaluate the combined effects of a mobile air supply (MAS) unit, an air curtain jet, and localised exhaust grilles in controlling particle dispersion. Since burn patients are highly sensitive to air temperature changes, which could impair their bodies' ability to regulate temperature and maintain fluid balance, this study integrated an air temperature control function using a MAS unit. The findings revealed that the MAS unit can provide a clean and sterile environment (0 BCP/m^3) within the region of laminar airflow in a burn patient ward ventilated by an air curtain jet. Likewise, the MAS unit effectively reduced the particle penetration distance into the patient protective zone by 82%. The MAS unit also effectively regulated the ambient air temperature (i.e., 21 °C – 24 °C) within the recommended range in the burn patient recovery zone. However, the temperature distribution around the Healthcare Workers (HCW) did not achieve satisfactory conditions. In addition, the particle dispersion outside the protective zone was exacerbated when the MAS unit was activated, which demonstrated its contradictory effect. In clinical practice, professional healthcare teams select the optimum operating temperature applied in the burn isolation ward. In actual applications, the clinical testing and comprehensive verification of the MAS device are conducted by varying the room configurations, ventilation arrangements, and pollutant sources.

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Research on safe vibration-free modular energy saving technology of high efficiency heat exchanger

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Keywords: tubular heat exchanger, heat transfer enchantment, three-dimensional variable space, modular design

In this paper, the green design of tubular heat exchanger is realized by using the technology of three-dimensional variable space, variable flow field and high efficiency heat transfer without vibration. Based on the high efficiency heat transfer mechanism of three-dimensional variable space and variable flow field, the design method of axial multi-channel, longitudinal full space and variable space, controllable turbulence heat transfer and energy saving heat exchanger is developed, and a new generation of safe and vibration free modular heat exchanger with high energy saving is developed. The modular design and the optimized design of the three-dimensional variable space self-supporting structure can not only improve the anti-vibration and safety reliability of the tube heat exchanger, but also improve the product life and quality. At the same time, the material can be saved by 30-70% and the volume can be reduced by 40-60%, so as to save costs and improve the competitiveness of the product. The three-dimensional variable space, variable flow field and modular standardized design of tube heat exchanger create conditions for the programmed and standardized intelligent manufacturing process of products, and provide guarantee for the large-scale production of green intelligent manufacturing of tubular heat exchanger.

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Inorganic materials

Phase equilibrium and phase analysis of molten lanthanide systems

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Keywords: molten salts, lanthanides, phase analysis

Molten fluoride systems are already investigated over decades and still catch the attraction of the researchers. They are investigated for applications covering nuclear industry, where molten fluoride salts are considered as coolants or fuel salts; nuclear reprocessing, electrochemical recovery/deposition of rare-earth elements. They are used for preparation of materials with excellent luminescence properties or preparation of magnetic materials [1-3]. A huge part of the research is devoted to corrosion of different materials in molten fluorides. For any of these applications, the knowledge of basic physicochemical properties is crucial. These properties determine the above mentioned applications. For examples temperatures of melting define the working temperatures.

In our recent works we have focused on a systematic research of selected molten lanthanides systems such as $(LiF\text{-}CaF_2)_{eut} – LnF_3$, $(LiF\text{-}MgF_2)_{eut} – LnF_3$ or $(LiF\text{-}NaF)_{eut} – LnF_3$ and among several physicochemical properties also phase equilibria of these systems were investigated by means of thermal analysis and STA analysis. Based on the obtained experimental data we were able to draw corresponding phase diagrams consisting of several crystallization fields. Solidified samples were analysed by means of XRD powder diffraction analysis.

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Thermal and spectroscopical analysis of platinum (ii) complexes with glyoximes, Schiff bases and thiosemicarbazones

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Keywords: azomethines, platinum complexes, thermo-gravimetric study, spectroscopic study, biological activity

After the discovery of anticancer activity of cisplatin by Barnett Rosenberg, platinum coordination complexes became a very important class of drugs [1]. In recent years other platinum-based drugs have entered in clinical trials, and high efforts have been made to find more active and less toxic agents for cancer treatment in humans. Many pathogenic bacteria show resistance toward antibiotics, therefore it is necessary to find new compounds to control the multidrug-resistant microorganisms [2]. Other platinum coordination and organometallic complexes have demonstrated applications in homogeneous catalysis, such as the oxidation of ethanol to acetic acid or acetaldehyde, the oxidation of sulfur dioxide to sulfuric acid and, furthermore, in catalytic combustion, hydrogenation reactions [3].

In our research project new Pt(II) complexes were synthesized from the reaction between azomethine derivatives (glyoximes, Schiff bases and thiosemicarbazones) and $PtCl_2$ salt, in suitable solvent. After presenting a short historical survey, classification, and possible application fields of these compounds, we report the study of their thermoanalytical behaviour (TG-DTG-DTA), spectroscopic features (such as FTIR, NMR, UV-VIS, Raman spectroscopy, mass spectrometry) as well as their powder XRD and AFM or SEM investigations. The biological activity of complexes, especially their antibacterial activity, will also be discussed. A few representative examples for their thermal decomposition are shown in Figure 1.

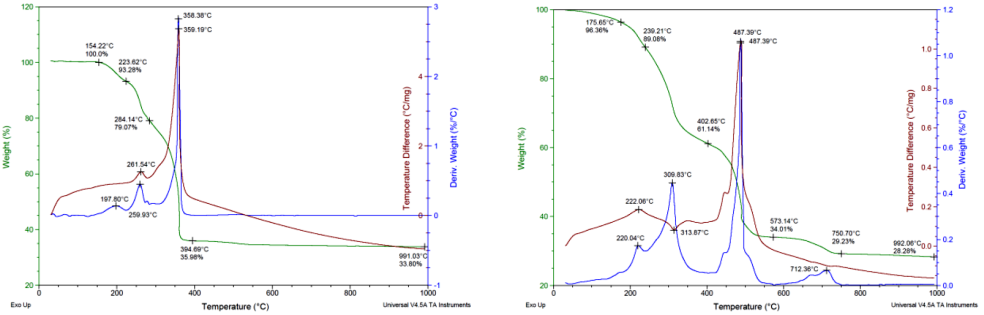

Fig. 1. Thermal decomposition of [Pt(Et-Pr-DioxH)$_2$(3-amino-1-propanol)$_2$] and [Pt(2-heptanone-TSC)$_2$].

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Kinetics and catalysis

Assessing the performance of various incremental isoconversional methods

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Keywords: activation energy, non-linear regression, kinetic analysis

Incremental isoconversional methods represent a practical compromise between differential and integral methods. They still possess the ability of differential methods to correctly deal with conversion-dependent kinetic parameters while partially inheriting the robustness of integral methods [1]. Over the last two decades a number of novel incremental methods have been proposed. The main difference between them resides in the way of approximating the temperature integral, which perhaps was also the main motivation for developing many of said methods. Based on the analysis of results from datasets simulated with reasonable levels of noise, the conclusions can be summarized as follows:

1. In real applications, even the most basic linear method with trapezoidal integration yields good results with negligible bias.
2. The methods differ more due to data transformations being applied than due to the temperature integral approximations.
3. Differences between the parameters estimated using various methods are usually well below the uncertainty of kinetic parameters.

A question remains which (if any) transformations should be applied to experimental $\alpha(T)$ curves in order to get data suitable for ordinary least-squares fitting, i.e., with approximately normal distribution and constant variance in the response variable. Moreover, as there is barely any improvement beyond the simplest conceivable linear incremental method, another question is whether differences between the kinetic parameters obtained using various methods have any practical consequences, especially when applied for calculating a directly measurable quantity such as rate constant, isoconversional time or isoconversional temperature.

Acknowledgments

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Thermal decomposition kinetics of ammonium nitrate – the issue that is yet to be fully resolved

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Keywords: ammonium nitrate, thermal decomposition, multi-step kinetics, safety assessment

Ammonium nitrate (AN) is a well-known chemical compound due to its worldwide use as a component of explosives, fertilizers and chloride-free, promising rocket propellants. The uncontrolled thermal decomposition of AN has caused multiple horrendous disasters throughout the past century. Its thermal stability is heavily influenced by multiple factors, such as the presence of impurities in the system, elevated temperature or pressure accumulation. Various types of thermal analysis methodology are among the most popular methods for assessing the safety of systems containing ammonium nitrate [1, 2]. Thermal decomposition of ammonium nitrate has been defined, described and evaluated in detail by multiple research groups in the past. Plenty of studies have been conducted to define kinetics of this dangerous process to provide governments, manufacturers and scientists with better tools to deal with hazards accompanied by its unavoidable use [3-5]. As kinetic studies become more popular among the scientific community, several experts in the field have voiced their concerns regarding wrong methodologies, erroneous experiment design and lackluster conclusions drawn from obtained data. Although sets of recommendations are available in form of manuscripts that should be followed when thermal analysis is employed to define kinetics of studied processes, a wrong methodology is still commonly used in many published studies [6-9]. The ammonium nitrate case, similarly to other hazardous substances, should be treated with special caution to avoid the occurrence of future disasters. As the observed decomposition mechanism is strongly dependent on mass transfer conditions, there are multiple cases where research groups obtain kinetic data for the endothermic decomposition reaction and draw wrong conclusions about the safety of studied systems. There are several cases in which the decomposition mechanism is defined as a single-step reaction that is later used to simulate and extrapolate the thermal behavior of other ammonium-nitrate systems, especially those stored in large amounts. The study mentions common misconceptions regarding the AN decomposition process, addresses previous work of other research groups and proposes methodology to obtain the multi-step kinetic model that allows to simulate the process over wide range of mass transfer conditions and could be further developed to include the presence of other substances in studied systems.

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Kinetic analysis using isoconversional methods and fitting model of fire retardant coated on banana biocomposite reinforced by silicon carbide

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Keywords: biocomposite, kinetic analysis, silicon carbide, model-free, thermal decomposition

The thermal performance of natural-based composites remains a significant challenge in their industrial applications, especially in thermal energy storage (TES). This study aims to address this challenge by developing a bio-composite material using Green-epoxy biodegradable resin reinforced with banana fiber (BnGBC) and micro silicon carbide (SiC) as a filler, with the goal of improving its thermal conductivity and for TES applications. The study explores the effects of adding 2 wt.% and 8 wt.% SiC to the BnGBC material, based on promising results from prior research [1]. To enhance the thermal stability of the composite, an intumescent fire retardant (IFR) coating consisting of 29wt.% ammonium polyphosphate (APP) and 1wt.% boric acid was applied to the BnGBC/SiC samples. The manufacturing process involved the use of vacuum-assisted resin transfer moulding (VARTM) technique to control the amount of banana fibre and sample thickness. The purpose of this work was to investigate the effects of SiC weight variation and the application of fire-retardant coating on the thermal decomposition of BnGBC/SiC. The kinetic mechanism in the material was examined by calculating the kinetic parameters. The study conducted Thermogravimetric analysis (TGA) tests under an O2 atmosphere, with processing parameters such as temperature and variation in heating rates set at 30 – 900 °C and 5, 10, and 15 °C/min, respectively. The activation energy (Ea) was evaluated using model-free (Isoconversional method) and model-based (fitting model) approaches such as the Friedman, Flynn Wall Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) methods, and the Expanded Prout-Tompkins (Bna) fitting model. Results indicated that the use of 8wt.% SiC improved the thermal stability of the composite compared to 2wt.% SiC. Additionally, the application of a 16 wt.% IFR (29APP/1BA) coating helped maintain the thermal stability of BnGBC/SiC. Moreover, the fire-retardant coating revealed that the Ea value of BnGBC/SiC increased by approximately 10 – 14% (Friedman approach), which is consistent with previous research [2,3]. The BnGBC/2SiC sample showed a smaller value of the kinetic parameter m compared to the other samples studied, implying a lower level of autocatalytic effect in the BnGBC/2SiC sample [4].

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Modelling the regeneration process in soot filters using iterative lattice Boltzmann method

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Keywords: surface-reactive flow, regeneration process, Lattice Boltzmann method, conjugate heat transfer, heterogeneous reaction

Modelling chemical reactions at pore-scale is important to understand the complex physics that take place inside reactive filters to achieve successful operation, on the other hand the Lattice Boltzmann method showed higher capabilities in simulating multi-phase pore-scale phenomena than conventional CFD lately. In this research, surface chemical reaction and conjugate heat transfer are modeled in porous media using the Lattice Boltzmann Method. Flow, thermal and species concentration fields are coupled to study surface combustion accompanied by species mass transfer and solid consumption. The conjugate heat transfer is modeled through thermal counter-slip method [1] while surface chemical reaction and species transfer is modeled through Kang et al wet node scheme [2] and the update of solid phase is modeled through volme of pixel method (VOP) [3].

The reactive gas transfer simulation is applied to investigate the combustion dynamics in a simplified 2D channel with four square-shaped obstacles (Figure 1). In this study, the inlet conditions for temperature, species concentrations and flow fields were given as $T_{(f,inlet)} = 773\ K, C_{O2,inlet} = 0.22,\ C_{CO2,inlet} = 0, u = 6y(1-y)$ respectively, while no-slip condition for the flow field on the top and bottom surfaces of the domain were applied and zero gradient for all fields at the outlet, also zero gradient for the temperature and species fields at the top and bottom surfaces. The chemical reaction was defined at the obstacle's surfaces to model the heterogeneous combustion process and it was solved through an iterative method as a boundary condition where the consumption and creation of species and heat generation were calculated in this iterative step.

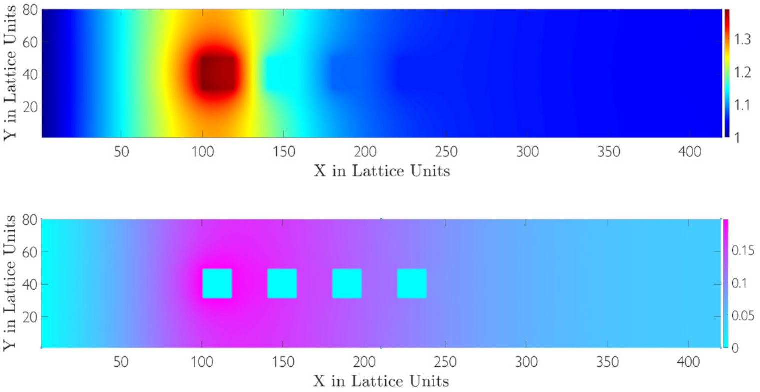

Figure 1: The reactive gas transfer simulation shows the (top) Temperature contour in fluid and solid domains and (bottom) Carbon dioxide contour in fluid and solid domain

After validation of our model with the result of Xu et al., we test different numerical and operational parameters such as Péclet and Damköhler numbers and porosity and investigate their influence on the coupled processes. We identify different combustion regimes through parametric studies and deduce the role of chemical reaction rate and different transport phenomena like diffusion and convection in each of the combustion regimes.

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The kinetics analyses of non-isothermal dehydration of poly(methacrylic acid) hydrogel by application of nucleation model

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The poly(methacrylic acid) (PMAA) hydrogel is synthesized. The non-isothermal thermogravimetric curves of PMAA hydrogel dehydration are recorded at the heating rate in the temperature range from 300 K to 600 K. The dependence of apparent activation energy on the dehydration degree is determined by Vyazovkin's isoconversional method. Commonly-used equations for the processes with nucleation-limited step is used to fit the conversion curves. The Gompertz function can describe all conversion curves. The dependencies of model equation parameters (*a* and *b*) on heating rate, the rate constant on temperature, and kinetics parameters on both temperature and dehydration degree are determined. Distribution functions of activation energies are obtained. The obtained results are confirmed by quantum chemistry calculations. During the 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 a decrease in the activation energy.

Can varying activation energy be determined reliably from thermoanalytical experiments?

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Keywords: non-isothermal kinetics, uncertainties, fit quality, isoconversional.

Hundreds of papers are published each year in which the activation energy (E) is determined as function of the reacted fraction (α) by a popular isoconversional method. The isoconversional methods are based on a kinetic equation of type

$$d\alpha/dt = A(\alpha)\, f(\alpha)\, \exp(-E/(RT)) \qquad (1)$$

where $A(\alpha)$ is the preexponential factor and $f(\alpha)$ is a model function. Usually $A(\alpha)$ and $f(\alpha)$ cannot be determined separately, only their product, $A(\alpha)f(\alpha)$ can be obtained [1].

It is well known that there is a considerable compensation effect between the E and A values even if E and A do not vary with α. One can expect that this compensation effect is much higher when E and A are functions of α. This is the topic of the present lecture. It will be show that markedly different $E(\alpha)$ functions can provide equally good fit quality on series of experiments due to this compensation effect. Here the term “fit quality” means the closeness of the measured data to the data calculated from the numerical solution of Eq. (1) at the given $E(\alpha)$, $A(\alpha)$ and $f(\alpha)$. Results of earlier works will be checked in this way and simulated experiments will also be presented to assess this phenomenon more exactly.

The techniques of the kinetic evaluation will not be discussed. According to the opinion of the author the method of least squares should be employed as it was outlined earlier [2,3].

Conclusions: (i) The $E(\alpha)$ functions reported in the literature should be regarded skeptically; (ii) Further work is needed to analyze how to plan experimental series with suitable temperature programs when we wish to obtain sufficient experimental information for the estimation of a unique, reliable $E(\alpha)$.

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Life sciences

Improved deep neural network-driven automatic segmentation of skin's thermal radiation in moving posterior legs during cardiopulmonary exercise testing for time series data analysis

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Keywords: artificial neural networks, biotechnology, semantic segmentation, thermal imaging

Background: Infrared Thermography is promising considering the non-invasive and contact-free quantification of individual thermoregulatory needs, acute physiological adaptation to exercise. Current applied methods to analyze the skin's thermal radiation during exercise are limited regarding the objectivity, reproducibility, and time-efficiency. Hence, we developed a deep neural network approach to measure thermal radiation automatically during treadmill running [1] and examined its current performance after implementing new features.

Method: Thirty-one participants performed a step-wise incremental running test on a treadmill. The skin's thermal radiation of the posterior extremities was captured with a high-resolution infrared thermal camera. In comparison to the previous version of the automatic analysis approach, we added i: a greater data set of manual annotated images (636); ii: a segmentation network with state of the art deep neural network architecture (DeepLabv3+ [2]) for multiple leg regions (left vs. right; regio femoris, genus, cruralis posterior); iii: use of recent optimization algorithms and loss functions for neural network training. We measured the Jaccard similarity coefficient to test the performance of the network in processing the calves' skin thermal radiation automatically and exclusively against a distinct test set of 200 manually segmented images.

Result: The current deep neural network approach reaches a very good Jaccard similarity coefficient of 0.94 (best possible value 1.0) for the left and the right calf, which measures the intersection area of a manually and automatically regions of the calves divided by their union.

Conclusion: The DNN is now capable of distinguishing between different anatomical regions and to generate reproducible time series data of a specific region of interest objectively during running. In a highly time-efficient way, it is now possible to analyze millions of thermograms (one exercise test of 17.000 thermal images). This is an important precursor to enable a detection and classification of pathophysiological functions during exercise.

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Materials science

Analysis of thermo-physical and mechanical properties of the 3D printing materials applicable for superconducting tort cables

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Keywords: 3D printing materials, thermo-mechanical loading, high-temperature superconducting tape, TORT cables, AC losses

A high-temperature superconducting TORT (Tapes on Round Tube) cables are based on a centrally located cylindrical support, a so-called former. Until now, the copper tube was used as a former material [1-2]. However, in AC (alternating current) mode operation, electricity conducting copper can contribute to AC losses through eddy current losses [3]. Thus, it is necessary to replace the conductive copper former with nonelectricity conducting material, i. e. 3D printing polymer materials PETG (polyethylene terephthalate glycol-modified), PETG CF (polyethylene terephthalate glycol-modified reinforced with carbon fibers), PC (polycarbonate) and PC CF (polycarbonate reinforced with carbon fibers). Due to the lower thermal conductivity of polymers compared to the copper, former must be perforated to improve cooling of HTS tapes wound on a former, which could decrease the toughness of the cable. Thus, thermal deformation of the former as a result of the cooling from room temperature to liquid nitrogen temperature could damage HTS tapes. For that reason, mechanical properties in the temperature range from 373 K to 77 K were measured. In addition, CTE measurements in the range from 108 K to 531 K were performed and were supplemented by heat capacity measurements. Post-processing heat treatment of 3D printing materials can improve the mechanical properties and lower the CTE [4-5]. Thus, some samples were annealed, and temperature dependence of mechanical properties and CTE were measured. These material properties served as input data in structural and thermal FE (finite-element) analysis carried out using the FEM SW (finite element modeling software) ANSYS, in prototyping of the former.

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Thermal analysis and Oxidation behavior of Al-Co-Fe-Ni-Cu multiprincipal element alloys at high temperature

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Keywords: thermogravimetric analysis, oxidation kinetics, parabolic rate law, MPEAs, HEAs

Multiprincipal element alloys (MPEAs) are a new class of materials that are composed of two or more major elements. MPEAs combine a simple structure [1] with unique mechanical and physical properties [2]. As such, they have a new application potential. In this study, a series of five AlCoFeNiCu$_x$ MPEAs (x = 0.6, 1.0, 1.5, 2.0 and 2.5) have been studied. The basis for this study was our previous research [3], in which we investigated the oxidation behavior of binary Al-Co alloys. Now, the system has expanded for additional elements (Fe, Ni, and Cu), and the concentration (ratio) of Cu in the alloys was gradually increased.

The AlCoFeNiCu$_x$ alloys were prepared from pure elements by vacuum arc smelter under an argon atmosphere. Small, round-shaped ingots (with a mass of 5 g) were produced in this way. All ingots were re-melted five times to ensure homogeneity of the alloy.

X-Ray diffraction patterns confirmed the presence of solid solutions with body-centered cubic (FCC) and face-centered cubic (FCC) crystal lattices in the alloys. The microstructural analysis indicated that the FCC to BCC ratio was increasing with increasing Cu content.

Dilatometry and differential thermal analysis (DTA) measurements were performed to determine the coefficient of thermal expansion (CTE) and melting temperature of the alloys. DTA showed that the melting temperature (solidus) decreased substantially with increasing amount of Cu in the alloy.

To study the oxidation behavior, the as-cast alloys were exposed in synthetic air (mixture of N_2/O_2 at 80/20 vol.%) at 1000 °C for 70 hours. The mass increase was recorded continuously by thermogravimetry. It has been found that the specific mass increase of the alloys was found to follow a parabolic rate law. The parabolic rate constants were determined. The rate constants increased with increasing Cu concentration. The oxide scale was found to be predominantly composed of aluminum oxide. At higher Cu concentrations, copper oxide was detected. The oxidation mechanism of the alloys is discussed. Implications for possible applications of the alloys at high temperatures are provided.

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Combining ZnO inverse opal and ZnO nanorods using ALD and hydrothermal growth

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Keywords: inverse opal, atomic layer deposition, hydrothermal growth, nanorods

Inverse opal structured materials are known and researched for their optical properties; the photonic band gap, which prevent the propagation of light at certain frequencies and the "slow" photon effect, what can cause an absorbance enhancement at the borders of the photonic band gap [1,2]. These unique properties can be utilized in various fields, like photocatalysis [3] or optical devices [4] to name a few. The bottom-up preparation of inverse opals is possible using vertical deposition to form a colloid crystal and atomic layer deposition to fill up the opal with the desired material [5]. It is possible to combine inverse opals with various other nanostructures like nanoparticles [6] or nanorods [7]

In this paper we combine the atomic layer deposition (ALD) synthesis method of inverse opal with the hydrothermal growth of nanorods. From 460 nm polystyrene nanospheres opal crystals were produced using vertical deposition on Si wafers. The opal templates were covered with ZnO by atomic layer deposition. High temperature annealing was used to remove the polystyrene nanospheres to obtain the inverse opal structure. For the hydrothermal growth of ZnO nanorods two production routes were analysed: hydrothermal reaction before and after the removal of the templates. The two paths produced two distinct structures, one with plate like formations and one with nanorods, respectively. Also, the sample modified by the hydrothermal growth after the annealing showed differences in optical properties compared to the regular inverse opal. Morphology, composition and structure of the samples were explored using SEM-EDX and XRD. Optical properties were investigated with reflectance UV-Vis spectroscopy. Thermal stability of the polystyrene opal was determined using TG.

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Reactivity of precursors for geopolymerization studied by isothermal calorimetry

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Keywords: type your, keywords here, separated, with commas

Alkali activated materials (AAM) are studied mostly (but not only) as a more sustainable alternative to Portland cement [1]. The expected smaller environmental impact lies in lower energy consumption of the production process and in the possibility to use broad range of raw materials originating as wastes or by-products in industry or agriculture. Each AAM consists of two fundamental raw materials: precursor and activator. Precursor is every time an aluminosilicate solid with certain amount of amorphous/glassy phase and the activator is liquid or solid alkaline matter – usually an alkaline silicate or hydroxide. While the range of wastes useable as alkaline activator is rather limited [2], the number of potential precursors is much higher. So far the highest attention has been paid to alkaline activation of calcined kaolin (metakaolin), coal fly ash (FA) and ground granulated blast furnace slag (GGBFS). These materials are characterized by very high (ca 90 %) content of amorphous matter, providing them high reactivity [3]. On the other hand some of another potential precursor may contain higher amount of crystalline minerals which are not taking part in the alkaline activation, i.e. the precursor contains lower amount of active matter. Typical example of such kind of precursor is ceramic waste, e.g. from demolition of old structures. It contains certain amount of amorphous matter coming from thermal decomposition of clay and the rest are crystalline minerals, especially quartz. This must be taken into consideration when the geopolymer concrete is designed [4]. The present paper deals with reactivity assessment of four types of geopolymer precursor: two types of ceramic waste (differing in the composition, specifically in the CaO content) and two conventional precursors: slag and metakaolin. The reactivity in geopolymerization was primarily monitored by isothermal calorimetry; this method enables to compare the reaction course and mechanism of individual precursors [5]. The results of calorimetry were complemented by thermogravimetry, SEM and XRD of activated precursors in order to determine and quantify the reaction products.

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Structural, morphological and thermal properties of kenaf microcrystalline cellulose/PBAT films for packaging applications

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Keywords: poly (butylene adipate-co-terephthalate), microcrystalline cellulose, kenaf, tensile properties

The awareness of the environment is becoming more widespread in society today. As a result, more research on the use of biodegradable polymer as a substitute for non-biodegradable polymers have been published. Poly (butylene adipate-co-terephthalate) (PBAT) biopolymer that has attracted the most attention among various biopolymers since it can be processed using the majority of conventional polymer processing methods. The aim of this study to utilizing microcrystalline cellulose (MCC) extracted from kenaf fibres during extraction of lignin by eutectic green solvents as filler to PBAT to fabricate compostable packaging films. In this work, MCC extracted from kenaf biomass reinforced PBAT blend composites via melt-mixing followed by hot pressing at 180 °C. PBAT and MCC were prepared in various formulations (0.5, 1, 1.5 wt%) to improve and strengthen the properties of the PBAT/MCC films. The structural, morphological, thermal, and tensile of PBAT/MCC film was investigated by using XRD, SEM, TGA and Universal testing machine. Thermal stability of prepared blend improved on addition of MCC due to homogenous dispersion of MCC within the polymer matrix. However, good compatibility was achieved using MCC with PBAT which is clear from Scanning electron microscopy. Tensile properties increased on the addition of MCC above 0.5 wt% and it will decrease brittleness. Obtained PBAT/MCC film can be potential compostable film for food packaging applications.

The effect of magnetic particles on the selected thermal properties of polyurethane-based biomaterials

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Keywords: polyurethanes, biomaterials, thermal properties, phase transition, thermal stability

Polyurethanes (PU) are promising materials in biomedical field as they can be obtained from a different monomers and chain extenders/crosslinkers that enables formation of materials with abroad range of the thermal and mechanical properties, biodegradability, bioactivity and porosity [1, 2] and allow to obtain PU with desired properties for different biomedical applications. Polysaccharides can be used as cross-linkers to improve biocompatibility and stiffness. On the other hand, magnetic particles (such as magnetite) can be used for tissue regeneration and tumor hyperthermia [4,5]. The results show that externally applied magnetic fields strengthen bone-implant integration, increase bone density and accelerate bone fracture healing [6].

In this study, polyurethane scaffolds were synthesized, crosslinked with gellan gum and modified with magnetite. Polyurethane was synthesized in in polyaddition reaction using a single step method. PU synthesis was performed using poly(ε-caprolactone) 2000 as a soft segment and 4,4'-methylenediphenyl diisocyanate (MDI). Various molar ratios of gellan gum and 1,5-pentanediol (PDO) as crosslinker/chain extender were applied, and the effects of incorporating different amounts of magnetite, as well as the role of PDO to gellan gum ratio, were investigated. The use of the additive - magnetite particles – makes it possible to consider the polyurethane materials in hyperthermia treatment. The prepared polyurethanes were investigated using spectroscopic methods, differential scanning calorimetry (DSC), thermogravimetry (TG), and dynamic mechanical analysis (DMA). Degradation kinetics of PUs modified with magnetite was studied. Scanning electron microscopy (SEM)/energy-dispersive X-ray spectroscopy (EDX) analysis and preliminary bioactivity assessment were also performed. The obtained PUs have vast potential in orthopaedics combined with an effective hyperthermia treatment.

Acknowledgments

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Thermal and spectroscopic characterization of manganese oxides prepared by different synthesis routes

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Keywords: manganese oxides, XRD, spectroscopy, magnetic property

Nanocrystalline metal oxides with tunable oxidation states are crucial for controlling their catalytic, electronic, and optical properties. Manganese oxides nanoparticles have large number of potential applications in the field of sensors, catalysis, pharmaceutical industries, piezoelectric crystals and electrodes of fuel cells.The properties of manganese oxide nanomaterials are dictated by the structure and morphology of the particular phases they can adopt. Manganese oxides crystallize in several different structures with varied proportions of Mn in different oxidation states (+2, +3 and +4). Several reports are available on the preparation of manganeses oxides such as using template method, precipitation method, self reacting microemulsion, sonochemical, hydrothermal method etc.

In this work, manganese oxides were prepared by using diffferent synthetic strategies by using reactants such as Potassium permangnate, manganese acetate manganese nitrate and complexing them with sodium dodecyl sulphate, Citric acid, sodium citrate, ethylene glycol. Thermogravimetry(TG), Differential thermal analysis (DTA), UV visible spectroscopy, X- ray diffraction (XRD) methods were used to investigate the thermal behaviour and structure of the manganese oxides. Thermogravimetry and DTA reveals that manganese oxides are formed below 500°C. The infra red spectrum shows the characteristic peaks for Mn-O. X-ray diffraction pattern confirms the phase purity for nanocrystalline Mn_3O_4 and MnO_2 formation. Surface morphology was monitored by SEM/EDAX. Effects of synthesis conditions on the evolution of structural morphology and phase transformation of Manganese oxides nanostructures were investigated. Magnetic behaviour of nanostructured manganese oxides were studied using were studied using a combination of superconducting quantum interference device (SQUID) magnetometer.

Acknowledgments

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Metals, alloys, intermetallics

What if the protection against oxidation of chromia-forming alloys was not always due to the chromia layer? Example of Inconel®625 oxidation in CO_2

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Keywords: oxidation, kinetics, chromia-forming alloys, diffusion, protection

When chromia-forming alloys are heated at high temperature in oxidizing gases, they first develop a chromia layer at their surfaces. It is generally admitted that these chromia layers protect the underlying alloys and allow the use of these alloys up to temperatures of 800°C and more. The involved mechanism implies that the chromia layers act as a barrier that slows down oxidation via a kinetically limiting step of diffusion of cations Cr^{3+} or anions O^{2-} through the Cr_2O_3 surface layer. This mechanism was widely studied according to the nature of the alloys, the temperature and the nature of the semi-conduction in chromia.

Now, a very recent study [1] devoted to the behaviour of Inconel®625 in CO_2 demonstrated that, in this case and at least at the beginning of the oxidation, the limiting step was not any diffusion process inside the chromia layer but the chromium diffusion inside the alloy. It was shown that the chromia layer did not play any kinetic role and, consequently that it was not at the origin of the protection of the alloy against oxidation.

The key experiment simply consisted in removing the chromia layer after a 10h oxidation in CO_2 at 950°C. The samples were small thin disks of Inconel® 625 (φ= 12 mm, e= 2 mm) that were initially covered by a about 4 µm-thick chromia layer after oxidation. Then both faces of the disks were etched with the GATAN Model 682 precision etching and coating system (PECS), using argon, for 4 hours, with the current of 350 µA, the accelerating voltage of 6 keV and the rotation rate of 10 rpm. With these conditions, the oxide layer was entirely removed, and then, the samples were oxidized again in the same conditions than previously during 5 h more. The result is given in the Fig.1a below that compares a 15h-direct kinetic with that obtained with the removing of the Cr_2O_3 surface layer at time= 10h. The superimposition of these two curves shows that there was no significant change of the reaction rate before and after the removing of the chromia layer, the kinetics being parabolic as well before than after removing this layer (see Fig. 1b). This very simple experiment proves that the chromia layer was not responsible for the diffusion mechanism that slows down the reaction rate.

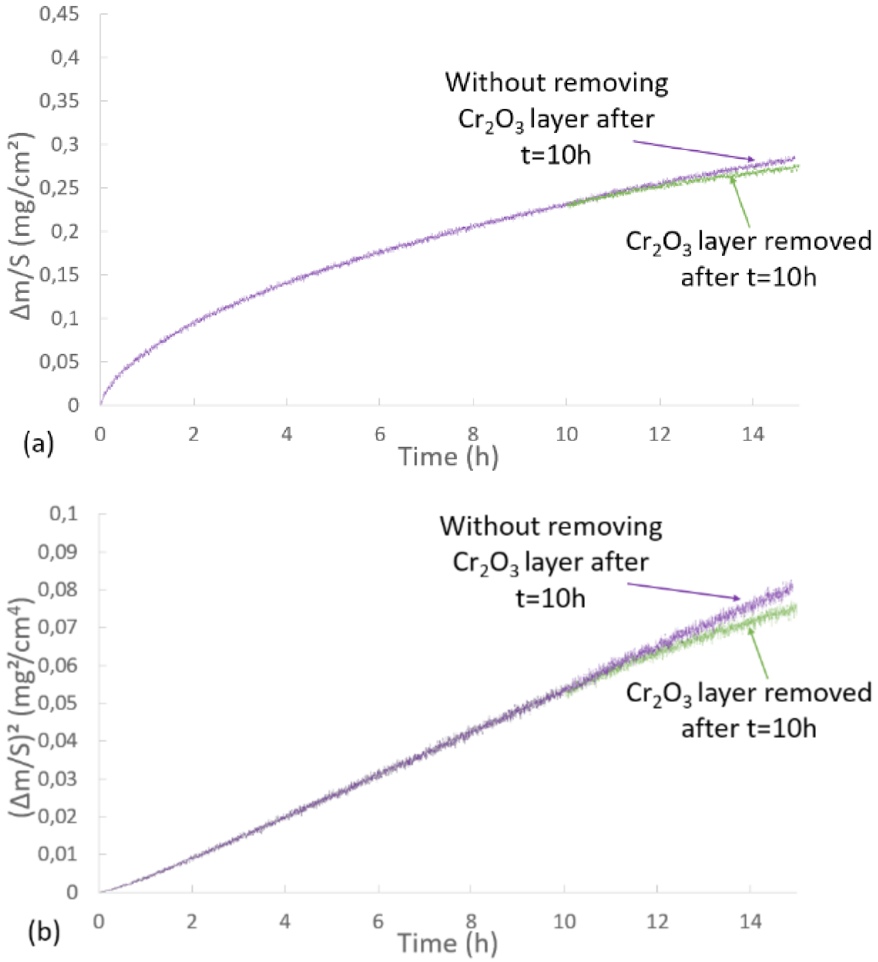

Fig.1 Kinetics with and without removing the Cr_2O_3layer**(a)** and the same curves in the coordinates $[(\Delta m/S)^2,t]$**(b)**

Factually, a chromium-depleted zone was created by oxidation, inside the alloy, just beneath the oxide layer, and the limiting step of the overall reaction was the outward diffusion of chromium through this Cr-impoverish zone of the alloy.

Such a behaviour has never been described before, and it would be interesting to test this kind of experiment with other alloys and other oxidizing gases in order to see whether the same behaviour could be observed in other systems than Inconel®625 / CO_2.

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Self-healing anodes for Li-ion batteries: phase relations in the systems Li-Zn and Li-Sn-Zn

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Keywords: Li-Sn-Zn, phase diagrams, phase relations, Li-ion batteries

Tin, a promising anode material for Li-ion batteries, has a high theoretical capacity compared to conventional graphite anodes. However, a major disadvantage is the formation of cracks on repeated charge/discharge cycles due to the large volume changes on lithiation and de-lithiation leading to degradation of the electrode material and hence poor cyclability. The self-healing of cracks based on partially liquid active electrode materials is one idea to overcome this problem. For this purpose, the melting regime of the anode material must be lowered by the addition of further elements (e.g. Bi, Ga, In, Zn) which form eutectic alloys showing lower reaction temperatures [1]. In a first approach, phase diagram studies of the Li-Zn and Li-Sn-Zn systems, based on X-ray diffraction and thermal analysis, were carried out to understand the associated lithiation mechanism of the electrode alloys. The phase relations in Li-Zn have been described in various compilations and assessments and all date back to comprehensive thermal analysis of Grube and Vosskühler [2]. The existence of most of the postulated intermetallic phases was later proved and their crystal structures could be clarified. We reinvestigated this phase diagram by means of XRD and thermal analysis to verify the phase relations and the compound formation. The existence of $LiZn_2$ was ruled out and slightly different phase transition temperatures were established. For the ternary system Li-Sn-Zn no experimental information to the phase relation is published. Two ternary phases, Li_2SnZn [3] and $Li_3Sn_4Zn_2$ [4] have been reported earlier. Turchi [5] published an thermodynamic assessment of Li-Sn-Zn which is only based on the extrapolation of binary data. The known ternary compounds were not considered. Our experimental investigations hitherto showed the existence of at least one further ternary compound. Furthermore, Li_2SnZn was found to deviate from the ideal cubic symmetry and can be described based on an orthorhombic unit cell. DTA analysis was performed on a larger number of ternary alloys. Several invariant reactions, a partial liquidus surface projections and liquidus temperature plots could be established. Our new results together with an investigation of the mixing enthalpies of liquid ternary alloys along 9 concentrational sections form the basis for an improved thermodynamic assessment of the ternary system Li-Sn-Zn.

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Identification of a new phase transformation of C36 → C14 for $NbCr_2$ alloy: An experimental and First Principle calculation study

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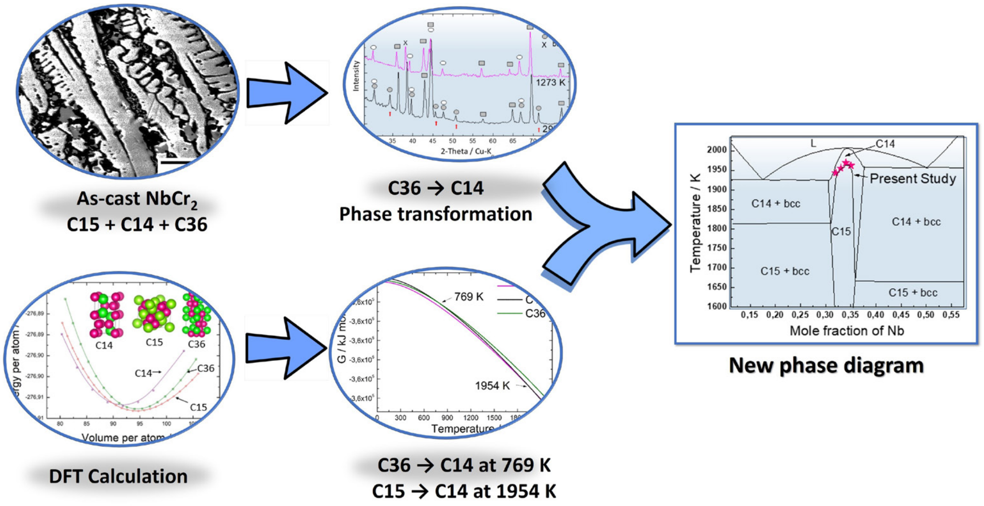
Keywords: laves phase, first principle calculation, HTXRD, DSC, Gibbs2

The high temperature phase stability and phase transformation of $NbCr_2$ laves phase has not been established beyond speculation in literature[1–3]. The previously accepted C14 phase field of the $NbCr_2$ alloy has been excluded from the Nb-Cr phase diagram. This study aims to address this controversy by investigating the high temperature phase stability and phase transformation characteristics of the $NbCr_2$ alloy through both experimental and First Principle calculation methods. The as-cast alloy was found to exhibit all three structures of C14, C15, and C36. The DSC thermogram of the as-cast alloy indicated a transformation of the eutectic mixture of bcc + $NbCr_2$ to a single phase $NbCr_2$ at 1338 K. Additionally, in-situ XRD studies at 1273 K revealed the C36 → C14 transformation occurring below 1273 K. First principle calculations were performed for the C14, C15, and C36 structures using density function theory (DFT) with pseudopotential, augmented plane wave formalism, as implemented in Quantum Espresso. The ground state energies for all three structures were calculated, with full relaxation allowed to minimize the force per atom to < 0.01 eV/Å. The pseudo-wave functions were expanded using a plane wave basis set with cut off energies of 250, 180, and 180 eV for C14, C15, and C36 structures, respectively. The Monkhorst-Pack scheme, with a K-points mesh of 12x12x12, 10x10x10, and 8x8x8, was used for C14, C15, and C36 structures, respectively. Formation enthalpies for C14, C15, and C36 structures were calculated as -4.5, -6.1, and -5.5 kJ/mole, respectively, indicating that C15 is the ground state structure. The present calculations also confirmed two phase transformations: (a) a metastable transformation of C36 → C14 at 769 K and (b) an equilibrium transformation of C15 → C14 at 1954 K. These results suggest the presence of a C14 phase field in the phase diagram prior to melting for the $NbCr_2$ alloy. Furthermore, extended DFT calculations for three non-stoichiometric compositions of $NbCr_{1.9}$, $NbCr_{2.1}$, and $NbCr_{2.2}$ also confirmed the presence of the C14 phase and conclusively modified the Nb-Cr phase diagram.



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An investigation of phase behavior in the Co-Se-Sn ternary system using experiments and thermodynamic modeling

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Keywords: Co-Se-Sn system, phase equilibria, CALPHAD, thermodynamic modelling, scanning electron microscopy, X-ray diffraction, thermal analysis

The ternary Co-Se-Sn system has been investigated experimentally to determine the phase equilibria and the microstructure of the alloys formed at different temperatures (400, 700, 1000 °C). Samples of various compositions were prepared by melting, annealing, and quenching techniques and characterized using scanning electron microscopy, X-ray diffraction and thermal analysis. The combined experimental results confirmed the presence of several binary phases in this system, including Co_3Sn_2[1], $CoSn_2$[1], CoSe[2], Co_9Se_8[2], $CoSe_2$[2], SeSn[3] and one ternary phase $Co_2(SnSe)_3$[4].

Furthermore, a new thermodynamic description of this system was introduced using the CALPHAD (CALculation of PHAse Diagrams) approach to predict and describe the phase equilibria, including the development of new models for phases CoSe Co_9Se_8 and $CoSe_2$. The models and thermodynamic description were verified by comparing the predicted phase diagrams with the experimental data obtained in this study.

The experimental and modelling results obtained in this study provide new insights into the behaviour of the Co-Se-Sn system and can be applied in the design and optimization of Co-based alloys for various industrial applications, such as magnetic storage media, high-temperature materials, and thermoelectric devices.

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Nanofluids

Experimental study of the rheological behavior of nanofluids containing palmitic acid/silica nanocapsules synthesized by the sol-gel method

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Keywords: nanoencapsulated phase change materials, rheological behaviour, nanofluids

Assessing the performance of a thermofluid is primarily done by characterizing its thermal conductivity, shear viscosity, heat capacity, and density. The addition of nanoparticles is well-known to enhance the thermal conductivity of the base fluid, while simultaneously giving the base fluid a non-Newtonian rheological behavior in response to shear inputs. Due to the homogeneous characteristics of the added nanoparticles, the effect of nanoparticles on the heat capacity and density tend to follow the rule of mixtures. However, the development of nanoencapsulated phase change materials can be designed to enhance the heat capacities of the base fluids and vary the local density depending on the phase of the nanoencapsulated materials. In this present study, the effect of using nanoencapsulated phase change materials as the nanoparticle suspension in a mineral oil base fluid is investigated. Rheological experiments are performed to determine how the particle concentration, nanoparticle composition, and temperature affect the overall viscosity and the rheological characteristics of nanofluids containing palmitic acid/silica nanocapsules. The nanoparticles used were synthesized using the sol gel method and the silicon dioxide nanocapsule shells contained palmitic acid (PA) as the phase change material core. Core-to-shell mass ratios were investigated for their shell structural stability, encapsulation ratio (R), encapsulation efficiency (E) and energy density storage during phase transformation of the PCM core. Differential scanning calorimetry is used to determine the effect of the fixed volume nanocapsule shell on the latent heat of fusion, melting temperature and heat capacity for the PA core. Surface, subsurface, and microstructural characteristics of the nanocapsule are investigated using SEM, TEM and XRD. Nanofluids containing 0.2 – 1.0 % volumetric concentrations are prepared using two-step method, and viscosity is measured using a Brookfield Dv2T rotational viscometer with a cone (CPA-40Z) and plate apparatus.

Nanomaterials and composites

The effect of mono, di and trivalent transition metals doping on the thermal behavior, structure and morphology of $NiFe_2O_4@SiO_2$

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Keywords: thermal decomposition, nickel ferrite; nanocomposite; metal doping, silica embedding

The influence of doping with monovalent (Ag^+, Na^+), divalent (Ca^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}) and trivalent (La^{3+}) ions on the structure, morphology and thermal properties of $CoFe_2O_4$ nanoparticles synthetized via the sol-gel method, followed by calcination at 500, 800 and 1200 °C, was investigated. The ability to tailor the structure, chemical, optical, magnetic, and electrical properties by selecting the synthesis parameters and doping ion allows the widespread use of ferrites. The thermal behavior of reactants during the synthesis process indicated the formation of metallic carboxylate precursors up to 200 °C and their decomposition up to 500 °C into metal oxides that further reacts to form the ferrites. The rate constants and activation energy of carboxylates decomposition into ferrites, computed using the isotherms at 150, 200, 250 and 300 °C are influenced by the doping cation. The functional groups identified by Fourier-transform infrared spectroscopy confirmed the decomposition of metal nitrates, the formation and decomposition of precursors and the formation of the SiO_2 matrix. The crystallite sizes depended on the calcination temperature and type of doping ion. This study is of particular interest due to the lack of data on the effect of dopant nature (Ag^+, Na^+, Ca^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, La^{3+}) on the properties of $NiFe_2O_4$ embedded in SiO_2 matrix. As the oxidic phases at low temperatures are poorly crystalline or even amorphous, the surface properties and crystallinity can be obtained by calcination at high temperatures. By calcination at low temperatures, single-phase ferrites with low crystallinity were observed, while at 1200 °C the well-crystallized ferrites are accompanied by crystalline phases of the SiO_2 matrix (cristobalite, tridymite and quartz). The AFM images expose spherical ferrite particles covered by an amorphous phase, the particle size and coating thickness depend on the doping element and calcination temperature. The particle size increases with calcination temperature and is contingent on the doping metal. The produced ferrites display good magnetic (high coercivity, anisotropy, Curie temperature, moderate saturation magnetization), electrical (high electrical resistance, low eddy current losses), mechanical (good mechanical hardness) and chemical (chemical stability) properties that make them capable candidates for various applications in industry (magnetic recording media, photoelectric devices, sensors, magnetic pigments, photocatalysts for dye degradation, controlled signal transformation, storage devices, batteries, solar cells) and biomedicine (controlled drug delivery, tumor treatment, magnetic resonance imaging, biomagnetic separation, cellular therapy, tissue repair, cell separation and biosensing) [1-5].

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Effect of kenaf fibre loading on thermal and dynamic mechanical properties of bioepoxy composites

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Keywords: kenaf fibres, bioepoxy, composites, thermal properties, dynamic mechanical properties, thermomechanical properties.

The aim of this study to investigate the thermal stability of kenaf fibres (KF)/bio epoxy composites by studying thermal gravimetric, dynamic mechanical and thermomechanical analysis. In this work green bio epoxy composites reinforced with KF by pulverization and sieving to accomplish a range of size (0.8mm to 1mm). Biocomposite samples fabricated by loading of KF between 30wt.% to 60wt.% by using compression moulding technique. Obtained results indicated that thermal stability of KF/bioepoxy composites were improved at KF-30 and KF40 as compared to the highest loading of KF (KF-50 and kF-60). From the dynamic-mechanical analysis (DMA) results, its indicated that storage modulus (E') exhibited the greatest value for KF-50 biocomposite as compared to other composites, while the loss modulus(E'') exhibited the highest value (349.5 MPa). On the other hand, the results of thermomechanical analysis (TMA), showed that the dimensional changes improved with biocomposites (KF-40) compared to other composites. We concluded that obtained KF green bio-composites have potential to utilize for manufacturing of components for various industries such as aerospace, automobiles, and construction and building materials.

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Thermogravimetry analysis of free and gelatin hydrogel formulated nanocellulose extracted from non-native *Arundo donax* plant

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Arundo donax or Giant Reed is a perennial plant native to the Asian continent and is considered a non-native (invasive) plant in Europe, especially in Madeira island, Portugal. This invasive plant has been identified to possess the ability to form a large population, monopolize soil moisture, and increase the risk of fire during summer in Western Europe [1, 2]. Thus, the present study focused on reducing these plants by reusing them for biomedical applications via extraction of nanocellulose from their leaves, which were identified to contain 31% of cellulose. Organosolv process to form acidic cellulose complex, bleaching process to form neutral cellulose complex [3], calcination approach to eliminate hemicellulose and lignin from cellulose complex, fractional centrifugation [4], and freeze-drying methods were used for the extraction and formation of nanocellulose. The calcination is a significant step in this extraction process, where thermogravimetry analysis (TGA) is utilized to select the calcination temperature. The study showed that the first degradation (30-130°C) indicating endothermic reaction via differential thermal analysis (DTA) was due to the elimination of water molecules in all the samples. A second intermediate thermal degradation (100-200°C) is observed only in neutral cellulose complex samples, which was identified to be due to the elimination of carbon present in the phytochemicals, lignin, and hemicellulose [5]. The third thermal degradation (130-350°C) of the samples was due to the degradation of lignin and hemicellulose [5], whereas the final degradation (350-500°C) was due to the decomposition of cellulose. The variations in the temperature and the degradation percentage are due to the interaction of chemicals in each extraction approach. Further, the resultant nanocellulose was formulated in gelatin ballistic hydrogel, and their thermal stability was evaluated. The TGA results showed that the gelatin-nanocellulose formulation has two decomposition stages: water is eliminated at 30-100°C, and the carbon is removed at 100-145°C from the sample. It can be noted that the gelatin-nanocellulose formulation possesses better thermal stability until 200°C compared to pure gelatin hydrogel. These thermally stable nanocellulose formulated in ballistic gelatin hydrogels were proposed to be beneficial as medical gummies as a potential antidiabetic agent.

Acknowledgement
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Nanocomposite polyfenilenoxide with amino-functionalized silica: structural characterization based on thermal analysis

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Keywords: thermal analysis, nanocomposite ionomer, amino-silica, sulfonated polyphenylene oxide

Nanocomposite polymer based on sulfonated polyphenylene oxide with amino-silica or amino-functionalized mesoporous silica was designed for proton exchange membrane (PEM) production. The structure and properties were analysed by Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Broadband Dielectric Spectroscopy (BDS). Also, the thermal analysis was used as important tool for structural characterization, as well as to assess thermal stability of the nanocomposite compounds (Fig. 1). The thermal degradation of the three samples (mesoporous amino-silica compound with the template, MS-NH2 I, mesoporous amino-silica after the template removal, MS-NH2 II and nanocomposite ionomer sPPO-MS-NH2) shows the mass loss up to 600 °C due to organic contents. Thermal degradation of nanocomposite ionomer occurs in two stages, the first, up to 300 °C, when the organic functionalities, amino ($-NH_2$) and sulfonyl acid ($-SO_3H$) are broken, and the second, up to 600 °C, when the main polymer backbone is degraded. The final residue is lower for the nanocomposite ionomer (25.13 %) due to degradation of the high amount of organic and more or less higher for the two mesoporous silica, depending on the presence or absence of the organic template.

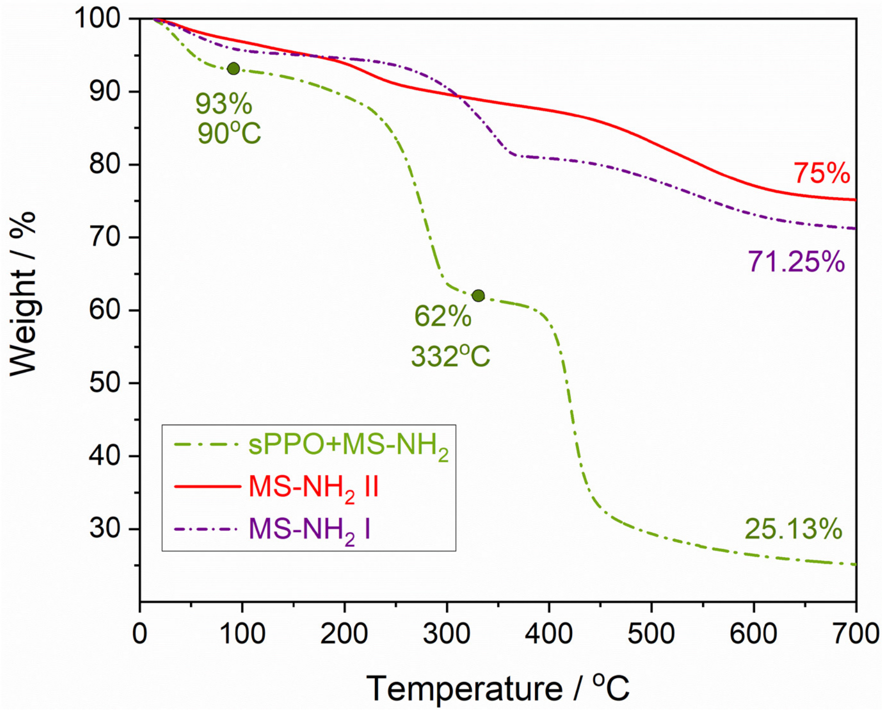

Fig. 1 Overlapped graph of thermal degradation for mesoporous-silica compound before CTAB template removal (MS-NH_2 I) and after template removal (MS-NH_2 II) and the thermal degradation curve for nanocomposite ionomer sPPO-MS-NH_2

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Halloysite – Zn-cu/Zn-Cu/ti-Ni oxide composite systems as potential photocatalysts

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Keywords: oxide nanocomposite, clay mineral, photocatalytic activity

Discovery of separate photocatalytic properties of clay minerals, such as kaolinite and halloysite, has given new impact to application as adsorbent or catalyst carrier [1, 2]. This property highly depends on the nature of the active sites and the morphology (pore structure, specific surface area). The photocatalytic efficiency can be improved with modification of the surface or with in-situ preparation of metal-oxide onto the surface [3, 4]. The synthesized composite could be implemented in environmental technologies (e.g. wastewater or gas purification).

In this study a morphological advantageous and mineral impurity free halloysite was modified with different metal-oxides having photocatalytic property of their own. In order to have better surface dispersion and physical-chemical bonding the oxides were prepared directly to the clay surface from precursor salts (zinc, nickel and copper nitrate, titanium-isopropoxide) by means of sol-gel method and thermal treatment. The evolution of Zn-Ni-oxide – halloysite, Zn-Cu-oxide – halloysite and Ti-Ni-oxide – halloysite mixed oxide composites was followed by thermoanalytical (TGA-DSC), X-ray diffractometric (XRD), infrared (FTIR-ATR) spectroscopic methods. The porosity were determined by N_2 adsorption (N_2-BET) while the morphology was investigated by TEM-EDX. The photocatalytic activity was determined through degradation of different test molecules, such as 4-nitrophenol, oxalic acid or the transformation of coumarin under UV irradiation. Coumarin as radical scavenger provides an opportunity to determine the generated ·OH radicals. Concentration of 7-hydroxycoumarin as degradation product was observed by emission spectrometry. Knowing the photocatalytic and surface properties of the composites, the optimal halloysite-metal-oxide and Ni-Zn, Zn-Cu and Ti-Ni ratio and the preparation parameters (e. g. temperature of treatment) can be evaluated.

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Pharmaceuticals

2-cycloalkylsulfanyl-[1,3,4]thiadiazole-5-thiol or 5-cyclopentylsulfanyl-3h-[1,3,4]thiadiazole-2-thione? Synthesis and spectroscopic characterization, and single crystal xrd of new monocycloalkyl sustituted bismuthiol and study of its ftir vibrations and thermal behavior compared with bismuthiol and the corresponding 2,5-bis-cyclopentylsulfanyl-[1,3,4]thiadiazole

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Keywords: Structure elucidation; X-ray diffraction; IR spectroscopy; Thermal behaivor; Biological activity

In continuation of our sulfur compound interest [1-3], we encourage synthesizing a new derivative of 2-cycloalkylsulfanyl-[1,3,4]thiadiazole-5-thiol. It was synthesized via a one-pot two-step procedure through the nucleophilic substitution of the potassium salt of 1,3,4-thiadiazole-2,5-dithiolate with chlorocyclopentane in a mole ratio of 1:1 in ethanol under reflux conditions. The pure product was characterized by physical and spectroscopic techniques. The long colorless needle-like crystals of pure product were obtained from a mix solvent n-hexane and ethyl acetate (volume ratio of 8:2), which was studied by single-crystal X-ray diffraction. The vibrational frequencies of bismuthiol, 2,5-bis-cyclopentylsulfanyl-[1,3,4] thiadiazole and its corresponding mono substituted 1,3,4-thiadiazole were studied to define the characteristic wavenumbers to differentiate 2-cycloalkylsulfanyl-[1,3,4]thiadiazole-5-thiol or 5-cyclopentylsulfanyl-3H-[1,3,4]thiadiazole-2-thione through IR spectra analysis (4000–500 cm^{-1}). A possible hyperconjugative interaction was considered between S–H and π bond of C=N. the single crystal XRD demonstrated the exisrtence of C=S and C–NH for new product, which could be predicted regarding comparative study of IR spectra. Finally, the influence of chemical structure on the transition phases and thermal stability of bismuthiol, bis-cyclopentyl substituted and mono-cyclopentyl substituted of bismuthiol were investigated by TGA/DTA and DSC. In addition, the biological activity of bismuthiol and bis- and mono-cycloalkyl substituted derivatives were screened in vitro against the gram-negative (Escherichia coli ATCC 25922) and gram-positive (Staphylococcus aureus ATCC 25923) bacterial species by the disk diffusion method.

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In-depth investigation of thermal behaviour of pharmaceutical amorphous solid dispersions

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Keywords: amorphous solid dispersions, pharmaceutics, thermal analysis, molecular mobility, relaxations

Pharmaceutical amorphous solid dispersions (ASDs) consisting of one or more active pharmaceutical ingredients (APIs) and usually polymers are extensively researched formulations [1]. Thanks to the amorphous structure the dissolution of the poorly water soluble APIs is increasing, resulting in better bioavailability in the most cases. Although several ASD-loaded medicines can be found on the market ensuring the physical stability of the amorphous forms is always a crucial part of the developments [2]. To tackle this challenge, understanding the thermal behaviour of the ASDs can help as there are correlations between the relaxation temperatures characteristic of amorphous materials and the physical stability [3].

In this work, the glass transition temperature and the relaxation below the glass transition were investigated with different methods for getting insights to the temperature dependent molecular behaviour of ASDs. Two APIs, namely naproxen and spironolactone, and one polymer (poly(vinylpyrrolidone-*co*-vinyl acetate)) were selected to the experiments. In this way, the effect of hydrogen bonds was possible to be examined since naproxen can form such secondary interactions with the polymer while spironolactone not.

The measured glass transition temperatures confirmed the plasticizing effect of the naproxen; with increasing API content the glass transition temperatures were decreased. This tendency proved to be well measurable with differential scanning calorimetry, micro-thermal analysis, and thermally stimulated depolarization current as well. Furthermore, the ASD containing 50% API and 50% polymer, having the lowest glass transition temperature, was characterized with poor physical stability, indicating a clear correlation between the glass transition temperature and physical stability of this interacting API-polymer system. The plasticizing effect of the API was observed in the case of the spironolactone-loaded ASDs too. However, investigation of the relaxations below the glass transition did not result in differences according to the results of the thermally stimulated depolarization current measurements. While the relaxation temperatures below the glass transition increased in the function of naproxen-loading, it did not change significantly in the function of spironolactone-loading.

The study demonstrated that measuring the glass transition temperatures does not always give an explanation to the physical instability of ASDs. Investigation of relaxations below the glass transition with sensitive thermoanalytical methods such as thermally stimulated depolarization current analysis is also suggested to perform if instabilities that is required to be filtered in the early stage of pharmaceutical ASD developments.

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Polymers

Hybrid mesoporous silica with Antioxidants as a feasible approach for improving thermal protection of recycled polyolefins

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Keywords: recycling, antioxidants, nanocomposites, MCM-41.

The deficient management of plastic waste has caused a serious environmental problem once their useful life has ended. Especially in the case of the widespread use of polyolefins, materials that are used in a multitude of single-use applications. Giving a second life to this waste is one of the main challenges of the industry in the plastics sector. Its reuse supposes the preservation of resources and an important economic benefit by taking advantage of these still useful materials. The greater social sensitivity in sustainability together with more rigorous government regulations have promoted the policy on recycling. Degradation of polymers is a common consequence that occurs throughout their useful life in a given application. Therefore, it is a key factor that will be essential for its subsequent recycling process. This unwanted effect can be caused by a number of factors including exposure to sunlight, heat, chemicals, oxidation and mechanical requirements. Degradation can cause the loss of important physical and chemical properties, such as mechanical resistance, transparency, elasticity and appearance of corrosion, among others. Obviously, this degradation will be transferred to products manufactured from recycled material.

To avoid the degradation of polymers, the incorporation of additives can be used, known as antioxidants, whose function is to prevent or delay the degradation of polymers, thus protecting their physical and chemical properties. In the case of recycled materials, the selection of these antioxidants requires special attention [1]. Different studies have dealt with the use of hybrid materials to improve protection against degradation. Loading of organic compounds with antioxidant activity into a mesoporous silica matrix has been proved to be an effective method to control the release of these active compounds, [2,3]. Concerning the latest, MCM-41 particles have been impregnated with different types of antioxidants to be studied in protection systems against the degradation of polymers due to their well-defined porous structure with a high specific surface area and uniform pore distribution. These characteristics provide them capability of neutralizing the free radicals generated during degradation of the material.

Thus, the aim of this research consists in the preparation of recycled polypropylene based materials with different antioxidant systems by melt extrusion. Differences between the single incorporation of common antioxidants for polyolefins and the addition of hybrid MCM-41 particles loaded with the distinct antioxidants are tested focussing the attention in the effect in the thermal stability of the resultant polypropylene materials. A promising behaviour was observed, showing a synergistic effect between antioxidants and MCM-41 as a function of their combination strategy.

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Morphological evolution of long-chain branched polypropylene under various processing conditions

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Keywords: long-chain branched polypropylene, polymorphism, injection moulding

Polymorphism of polymers is a fascinating phenomenon that predicts the end-use properties of products. Therefore, to achieve the required characteristics, the thorough control of specific nucleation and processing parameters is necessary, e.g. flow induced crystallization is fundamental for injection moulding. One of the most commonly used polymorphic polymer is isotactic polypropylene (iPP) and its modifications, e.g. long-chain branched polypropylene (LCB-PP), owing to its flexibility in term of property function and processability. LCB-PP usually consists of monoclinic α-phase and orthorhombic γ-phase. However, using of processes where shear field is dominant, such as injection moulding, can promote the formation of trigonal β-crystalline structure, that modified mechanical properties of iPP toward better toughness at worse stiffness and heat resistance [1, 2]. In this work, the influence of important processing parameters of injection moulding on the morphology evolution and the β- and/or γ- crystals distribution in “skin–core” structure and Charpy impact strength was studied. Four sets of processing parameters were applied. In the P-set holding pressure varied within a range of 30–70 MPa by 10 MPa, in T-set mould temperature raised from 40 to 120 °C in 20 °C step, while in S-set1 and S-set2, injection speed increased from 20 to 140 mm/s in 30 mm/s step and mould temperature were 40 or 120 °C, respectively. Data derived from the wide-angle X-ray scattering demonstrated distinct ability of injection speed, mould temperature and holding pressure to affect the polymorphic composition of LCB-PP specimens (Figure 1). The joint effect of higher injection speed (140 mm/s) and mould temperature (120 °C) promoted the formation of trigonal β-phase in the skin layer. Under shear flow, an oriented centre can be easily initiated, which provides nucleation sites for β-crystal growth. Prolonged relaxation times of LCBs after deformation contribute to the incorporation of loosely coined linear chains on the surface by orientation of the induced nuclei and crystallize into β-crystals. On the contrary, a significant effect of growing holding pressure on the γ-phase is manifested predominantly in the core of specimens. The higher content of γ-phase is promoted by higher mould temperature and holding pressure. The polymorphic composition of the individual specimens is reflected in their impact strength. Co-existence of β-phase and γ-phase has a favourable impact on the enhancement of impact strength.

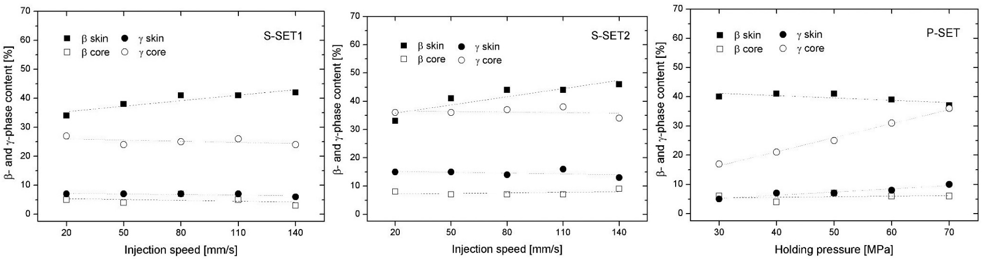

Figure 1: Dependence of β- and γ- phases content on the mould speeds and holding pressure

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Fully recyclable vitrimers based on ternary thiol-isocyanate-epoxy dual-curing systems

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Keywords: stress-relaxation, epoxy, thiol, isocyanate, trans-thiocarbamoylation, transesterification

Poly(thiourethane)s-poly(thiol-epoxy) hybrid materials were prepared from ternary thiol-isocyanate-epoxy formulations. Trimethylolpropane tris(3-mercaptopropionate) (S3) was used as crosslinking agent, in stoichiometric ratio with respect to a mixture containing a diisocyanate (hexamethylene diisocyanate, HDI, or isophorone diisocyanate, IPDI) and an epoxy (bisphenol A diglycidyl ether, DG). 1-methylimidazole (MI) was used as initiator or the curing reaction. Different ratios of isocyanate:thiol (or conversely epoxy:thiol) were used A tetraphenylborate salt derived from 1,5,7 triazabicyclo [4,4,0]dec-5-ene (TBD) was used for the activation of bond exchange reactions at elevated temperature. The curing process followed a well-defined dual-curing sequence, in which the thiol-isocyanate took place first. The T_g of the materials containing IPDI system ranged from 37 (neat thiol-epoxy) to 112 ºC (neat thiol-isocyanate); in contrast, that of materials containing HDI ranged from 37 to 41.5 ºC. Thermal stability of the samples was tested using thermogravimetric analysis (TGA) where no significant change was observed up to a temperature of 200 ºC. All the materials containing epoxy and isocyanate in their formula showed a vitrimer-like behavior. Stress-relaxation experiments of the fully-cured materials revealed that, in general, the higher the epoxy content, the slower the stress-relaxation of the material (Figure 1, left and right). The presence of a small fraction of epoxy seemed to have a positive interaction with the bond exchange catalyst, leading to faster relaxation than the pure thiol-isocyanate material (Figure 1 left). When the ratio of epoxy groups was higher than 50%, stress relaxation was incomplete (Figure 1, left and right), leading to further fraction of unrelaxed stress with increasing epoxy. However, stress relaxation of the pure thiol-epoxy material was also possible but at much slower rate. At lower temperatures, the trans-thiocarbamoylation was the dominant bond exchange mechanism. Increasing the temperature led to the activation of the transesterification bond exchange reaction, making it possible to relax completely the stress in samples with higher epoxy content Recycling ability of the materials was tested by hot pressing of chopped samples at different temperatures. As a means of example, samples containing 50% of isocyanate and epoxy could be recycled completely at 140 °C within 5 hours under a pressure of 10 MPa (Figure 2).

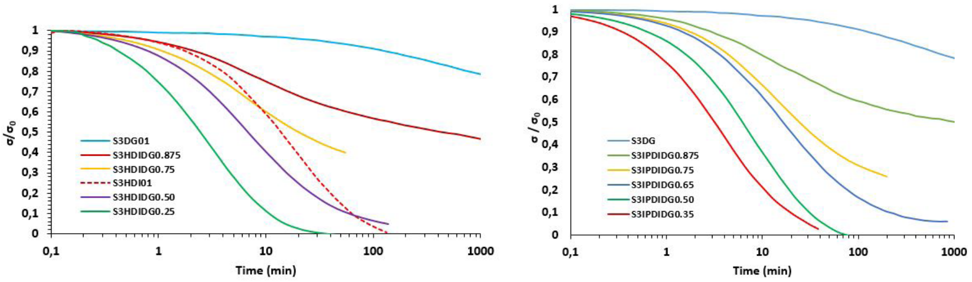

Figure1. Stress-relaxation of S3HDI$_x$DG$_y$ system (left) and S3IPDI$_x$DG$_y$ system (right) in which x and y indicate the proportions.

Figure 2. Recycling of S3HDI$_{0.5}$DG$_{0.5}$ at 140 ºC within 5 hours under a pressure of 10 MPa.

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Crystallization of long-chain branched polypropylene with nucleating agents

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Keywords: long chain branched polypropylene, isothermal crystallization, nucleation

Isotactic polypropylene (PP) is a versatile material which can crystallize into several crystal modifications according to molecular structure and crystallization conditions. Common linear polypropylene (L-PP) usually crystallizes into monoclinic α-phase. To increase rate of crystallization, heterogeneous nucleating agents are often added which affect also morphology decreasing size of spherulites. Special α-nucleating agents serve as clarifying agent improving transparency of the material. Specific nucleators can induce crystallization into trigonal β-phase showing significantly higher impact strength. The introduction of long branches onto polypropylene chain significantly changes the crystallization behaviour. As long-chain branched polypropylene (LCB-PP) processes self-seeding effect, the overall crystallization is faster with higher crystallization temperature [1, 2]. In this work, isothermal crystallization of LCB-PP without/with two types of nucleating agents is studied and compared with that of linear PP. Crystallization half-time of linear and branched PP with/without commercial α-nucleating/clarifying agent Millad 3988 (1,3;2,4-bis(3,4-dimethylbenzylidene)sorbitol)) (α-PP and α-LCB-PP) or β-nucleating agent NJ Star NU 100 (N,N´-dicyclohexylnapthalene-2,6-dicarboxamide) (β-PP and β-LCB-PP) crystallized at several temperatures (135, 140, 142, 144, 146, 148 and 150 °C) is shown in Figure 1. While L-PP crystallized in a given time of 180 min only at low temperatures of 130 and 135 °C, branched polypropylene and all nucleated ones could not be evaluated at these temperatures: they crystallized already when cooled to the crystallization temperature and the exotherm was not complete. LCB-PP samples showed the lowest crystallization half-life independent on the presence of nucleating agent. Figure 2 shows melting temperatures of isothermally crystallized samples. Several melting temperatures (peak of melting endotherm) in L-PP indicate the polymorphic composition, especially in the β-nucleated PP. On the other hand, all LCB-PP samples show only one melting temperature corresponding to α-phase.

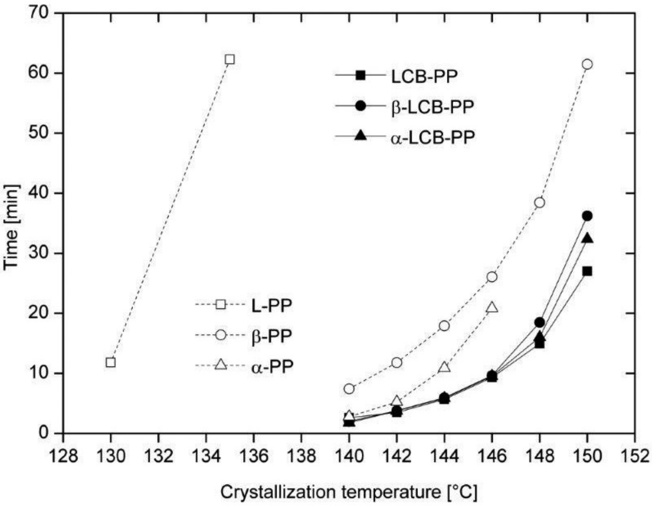

Figure 1: Crystallization half-time of isothermally crystallized samples.

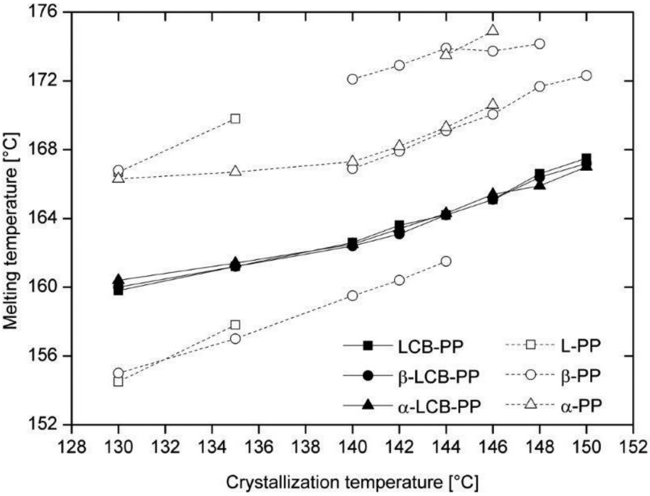

Figure 2. Melting temperature of isothermally crystallized samples.

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Thermal decomposition of pvc and leather mixtures

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Keywords: leather, PVC, thermogravimetry, pyrolysis

Artificial leathers are widely used as clothing and shoes fabrics, furniture upholstery and automotive interiors, several times in combination with real leather material. The tanned leathers and the synthetic leather wastes are not easy and economically not beneficial to separate, therefore need to recycle together. Slow and fast pyrolysis are a promising tool to produce value added products from waste materials. The most widely used polymers for artificial leather production are polyvinyl chloride (PVC) and polyurethane (PU).

Thermal decomposition of PVC is a well-known process. PVC decompose in two well separated step under gradual heating. The first thermal decomposition step with mass loss can be found between 220 and 380 °C where the chlorine content of the PVC eliminates in the form of HCl, along with the release of aromatic volatiles, mainly benzene. At higher temperatures, between 390 and 530 °C the second weight loss step can be detected which corresponds to the cracking of the remaining polyene chain and release of various aromatic and polyaromatic compounds. The main thermal decomposition step of the tanned leather samples takes place between 220 and 530 °C. Both the vegetable tanning agents and the protein chains are decompose in this temperature range [1]. It is known, that HCl releasing from PVC during thermal degradation has effect on the decomposition mechanism of various PVC containing mixtures, among them woody biomass or polyamides [2]. As a result of the interaction between the components, decreased thermal stability and modified composition of pyrolysate was observed.

In this work the thermal decomposition of untanned parchment and several types of tanned leathers (vegetable, chromium and mixed tanned) were studied in the presence of PVC. The thermal stability and evolution profile of the degradation products were studied by thermogravimetry/mass spectrometry (TG/MS). The changes in the composition of the pyrolysis oil were determined by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The results clearly indicate that the PVC and the leather components interact with each other during the thermal decomposition of their mixtures. Mixtures of various leather – PVC samples were prepared and studied.

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Research on the carbonization process of hybrid polymer microspheres using the TGA-EGA method - evaluation of the influence of sulphanilic acid on the process

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Keywords: TGA, EGA, FTIR, hybrid polymers, hybrid carbons, carbonization process

Hybrid polymer materials are of great interest nowadays. In their structure, they combine polymer chains with inorganic molecules, allowing to obtain new products with unique properties. Such modern materials can be used, for example, in the form of porous microspheres as adsorbents in purification and separation techniques. They can also be a substrate for the synthesis of hybrid porous carbons, which have a much higher chemical and thermal resistance than their polymer precursors. Sometimes the thermal treatment process is further enhanced by the use of activating substances to give the final carbonization product even more desirable properties. In this work, we present the application of thermogravimetry with the analysis of evolved gases (TGA-EGA) to study the course of the carbonization process of porous hybrid polymer microspheres. The polymeric precursors were synthesized using methacrylamide (MA) as the primary monomer, divinylbenzene (DVB) as cross-linking monomer and trimethoxyvinylsilane (TMVS) as a source of inorganic fragments in hybrid polymer. The obtained materials differed in the content of the monomers molar ratio: P1 - MA-DVB-TMVS (2:1:0), P3 - MA-DVB- TMVS (1.33:1:0.67), P4 - MA-DVB- TMVS (1.5:1:0.5), P6 - DVB-TMVS (1:1). Details regarding the syntheses of precursors were described in previous work [1]. The resulting polymers were impregnated with sulfanilic acid (SA) to obtain a more homogeneous porous structure. The impregnation was carried out with the use of saturated solution of SA (10ml/1g polymer). Next, the samples were dried and carbonized at 600°C under N_2 atmosphere to obtain hybrid carbons. For a detailed evaluation of the SA activator effect on the precursor under heat treatment conditions, TGA-EGA was used. The measurements of the samples both with and without the activator were carried out under helium atmosphere (40 mL/min) in the range of 30-1100°C with the heating rate set on 10°C /min. The released gaseous products were analysed by the FTIR spectrometer (in the range 4000 - 600 cm^{-1} at a resolution 4 cm^{-1}). TG analyses revealed that thermal decomposition of the polymers not impregnated started in the range of 240-350°C with higher values being achieved by samples with higher TMVS content. The impregnated precursors were much less thermally stable, as their decomposition started in the range of 177-211°C, also with higher values for samples richer in inorganic phase. However, the course of the decomposition was significantly different. In case of the former, it was a fast one-stage process (peak around 447°C), while for the latter in two slower steps (334 and 449°C), accompanied by a slightly higher total weight loss of the sample. EGA analysis of P1 revealed compounds characteristic of acrylamide polymers, mainly: ammonia, unsaturated hydrocarbons, CO_2, amide and imide species. As the content of TMVS in polymers increases, the proportion of ammonia derivatives decreases and aromatic compounds e.g. aliphatic styrene derivatives predominate. In case of the impregnated polymers, at the first stage of decomposition SO_2 is released. At the beginning of the second stage mainly aniline is evolved, but as the process progresses, other hydrocarbon components, originating from DVB mers, also appear in the decomposition products. At this stage also increasing amounts of CO_2 are recorded. Interestingly, that above 600°C beside CO_2 also methane was found in gaseous decomposition products. This observation suggests, that at this stage the polymer is already carbonized and further structural changes result from the internal transformation of this newly formed charred matter. XPS studies of the obtained carbon materials did not show the presence of sulfur, and the presence of nitrogen was negligible. The conducted experiments showed that the activator was completely decomposed, and the products of its decomposition contributed to the formation of both the porous structure and the chemical heterogeneity of the surface of carbon products.

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Porous polymer by solvent treatment and controlled crystallization for high solar-reflectivity and passive radiative cooling

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Keywords: porous structure, solar reflectance, passive cooling material, polypropylene, nucleating agent

Reducing energy consumption and carbon dioxide emissions, as well as reducing the environmental footprint, has become a key concept recently, as climatic change is undoubtedly related to human industrial activity. Increasing demands and improving living standards in developed and developing countries with the need of regulated temperature buildings highly contributes to the increased energy consumption. Energy consumption could be reduced considerably if the incoming solar radiation (200-2500 nm) could be reflected from the walls. Thus, the temperature rise of the buildings can be minimized and the heat can be radiated through the mid-infrared window without energy expenditure. As a part of this endeavour, technologists seek the possibility of increasing the solar reflectance and radiative cooling of plastic surfaces. One common method to increase the Total Solar Reflectance (TSR) and thermal emissivity of polymers is the addition of mineral fillers with high refractive index (such as TiO_2). In recent years, researchers have shown great interest in the porous polymer matrix due to its peculiar structure, which helps to increase the heat-reflective property of materials. In a porous polymer matrix, the high TSR and high thermal emissivity are the result of the refractive index difference between polymer matrix and air voids, meaning that the light scattering air voids fulfil the role of the purpose of the mineral fillers [1].

In our previous study, we presented a novel solvent-based method capable of producing polypropylene (PP) sheets with controllable porous structures [2]. Since the formed porous structure has a light-reflecting ability, we investigated its effect on TSR and thermal emissivity values. Thermal and morphology studies were conducted to understand the role of nucleating agents in this system and their contribution to solar reflectivity. The purpose of adding nucleating agents into the PP matrix is to generate material inhomogeneities, interfaces where the light scattering occurs, on the other hand, supporting the formation of a porous structure.

Scanning electron microscopy (SEM) results show that the surface and cross-sectional morphology of solvent-treated materials are important and contributes to heat reflectivity. The crystallization behavior, crystal structure and crystal form was characterized by differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) analysis. The results show that the structure can be effectively manipulated by nucleating agents and has clear effect on solar reflectance. By diffuse and total reflection measurements, we proved that the combination of the porous structure with random pore size and controlled crystallization has a synergistic effect and gives better results (TSR ~ 95%) than separately. The thermal emissivity of porous PP samples in the mid-infrared window was calculated from the reflectance and transmittance spectrum measured by Fourier-transform infrared (FTIR) spectroscopy. The thermal insulation ability of the new materials was tested and quantified with a sun test (by artificial sunlight irradiating the plastic boxes made by the developed materials).

Acknowledgments

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Evaluation by DSC of the Joule curing process of carbon epoxy composites

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Keywords: carbon composites, Joule curing, DSC

The current technology for curing high-performance composites, as those used in industries such as aeronautics and the automotive industry, are based on the use of autoclaves, where the material is cured by external heating, in large ovens. [1–3] This type of curing requires enormous amounts of energy, of which only a small part is invested in the actual curing of the material, and the rest is mainly used for heating and maintaining the temperature of the autoclave. An alternative method that entails a lower energy cost compared to the traditional methodology is curing through the Joule effect, in which an electric current is passed through the material, so that it acquires temperature from the inside due to the passage of current through the carbon fibres, triggering and accelerating the curing process of the composite. While Joule curing may provide a much more efficient and faster curing, a control technology is needed to ensure that temperatures all throughout the composite match the temperature program. [4]

The evaluation of the Joule curing process using different conditions, will be made by comparing the properties of the thus cured material with those of oven cured samples.

Acknowledgments

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Thermal Properties of PHB/PCL investigated by using DSC and TGA

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Keywords: polycaprolactone, polyhydroxybutyrate, thermogravimetry analysis, differential scanning calorimetry

At present, 3D printing is experiencing a great boom which also brings about a demand for new materials suitable for 3D printing. New materials should possess improved physical and mechanical properties [1] so that durable 3D printed parts can be made to tight tolerances in relatively short times. Therefore, the study of thermal properties is one of the most important characterizations of these materials. It is generally recognized that polyhydroxybutyrate (PHB) is a completely biodegradable, highly hydrophobic thermoplastic material containing almost 80 % of crystalline fraction with moderate tensile strength and Young's modulus, resembling polypropylene [2]. Polycaprolactone (PCL) is a biodegradable semi-crystalline linear aliphatic polyester that has been extensively investigated for use as implantable biomaterials [3].

In this study we focused on combination of PCL mixed with PHB at various proportions. The combination of these two materials can be very interesting in terms of combining their thermal and mechanical properties. Using thermogravimetry (TG) and differential scanning calorimetry (DSC) we mainly focused on the thermal behaviour of combination of these materials. Interestingly, the addition of only 5 wt.% of PHB into the PCL shifted the main degradation step to the lower temperatures. The main finding by DSC was that with the higher addition of PHB to PCL, the melting peak for PHB splits into two peaks during the second heating with the additional peak appearing at about 160 °C. This effect can probably be caused by random splitting of long chains of the original polymer.

Acknowledgments

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Aging and degradation processes in polymer coatings of optical fiber cables

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Keywords: flame retardant non-corrosive compounds, thermal decomposition, thermal stability, cable extrusion

Fibre optic cables are commonly used in long-distance and high-performance data networks, including telecommunication, military, and medical purposes. Fibre optic cables could be divided into two groups according to their application area: indoor and outdoor [1]. Indoor cables must meet rigorous fire-safety requirements in the European Union, which guide the selection of Flame Retardant, Non-Corrosive (FRNC)/Low Smoke Zero Halogen (LSZH) for their sheath materials. These are highly filled polymer composites with reduced flammability and smoke generation, ensuring a higher level of human safety during fires in buildings [2]. Constantly increasing telecommunication market demand requires development of cable manufacturing technology to provide higher production capacity and cost optimization as well. Speed of cable production lines are often limited by extrusion performance of FRNC materials. A further increase in extrusion speed could cause unpredictable changes in the cable FRNC sheaths, which could negatively affect the quality of the cable to the customer.

Objective of this work was to characterize an influence of temperature and thermomechanical degradation in extrusion process on properties of commercial FRNC cable compounds. The research hypothesis assumes that the conditions of the large-scale extrusion process strongly impact aging and degradation processes in the fibre optic cable sheaths. Their optimisation may significantly improve the durability and performance of the products. Incorrect selection of process parameters may have a negative impact on the quality of the product causing unpredictable degradation processes resulting in premature aging.

Studies on thermal degradation and evaluation of thermal stability of cable materials have been performed with use of Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Fourier-Transform Infrared Spectroscopy (FTIR) and Parallel-Plate Rheometry. The materials used in the analysis were commercial FRNC granulates dedicated to production fibre optic cables, based on linear low-density polyethylene (LLDPE)/ethylene-vinyl acetate (EVA) composites with high filler loading of aluminium trihydroxide (ATH) and magnesium dihydroxide (MDH). The findings from laboratory-scale tests on raw materials were used to design the experiments on full-scale production line. Two materials were used to produce series of optical fiber cables under different processing conditions. As the result, extrusion line output constrains were determined, material behaviours were characterized in real production environment and mechanical parameters of fiber optic cable coatings were verified. The influence of process parameters on materials degradation, mechanical performance and aging resistance of the cables was comprehensively characterized.

Acknowledgments

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Pyrolysis

Laboratory scale production and thermal characterization of charcoals from variously tanned leathers

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Keywords: carbon, leather, TG/MS

Every year, millions of tons of solid leather waste are generated mainly in the automotive and light industry [1]. The recycling of this by-product is not an easy task due to the presence of potentially toxic chromium. One way to convert leather waste to value-added products is produce high nitrogen containing carbon. These materials can be used different ways like filters or catalyst support. The relatively cheap functionalized nitrogen-containing carbon catalysts may substitute the expensive platinum catalyst in the fuel cells.

In this work the thermal properties of charcoals produced from leathers were studied. Three different samples: vegetable (quebracho), metal salt (chromium) and mixed (aluminum and myrobalan) tanned leathers were used during the experiments. The charcoals were produced in a horizontally oriented laboratory scale tube furnace at 400, 500 and 700 °C under nitrogen atmosphere. The yields of the carbons decrease while the final temperature increase. The amount of the carbonaceous residue of the chromium tanned leather sample was the lowest compared to the vegetable and mixed tanned ones. The thermal behavior and the composition of the native and the produced carbonaceous samples were studied by thermogravimetry/mass spectrometry (TG/MS). Among the decomposition products hydrogen cyanide and pyrrole were released in larger quantity from the chromium containing charcoal. The composition of the volatile decomposition product mixture released from the leathers and charcoals applying high heating rate was studied by pyrolysis-gas chromatography/mass spectrometry. The nitrogen content of the leathers and charcoals was determined using Dumas method. The highest nitrogen content was found in the sample originated from chromium tanned leather. During the preparation of the charcoals the metals (aluminum and chromium) enrich which could be beneficial in case of usage as catalyst.

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Thermogravimetric analysis and Kinetic modeling of the pyrolysis of different biomass types by means of model-fitting, model-free and phenomenological modeling approaches

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Keywords: biomass, thermogravimetric analysis, kinetic modeling, model-fitting, model-free methods, phenomenological model

Given the ever-growing concerns related to increasing energy demand, the depletion of fossil fuel resources and the need to reduce greenhouse gas (GHG) emissions, interest in the use of renewable and carbon-neutral energy resources, such as biomass, continues to grow. In this context, pyrolysis has proven to be a promising route to convert raw biomass into a wide variety of biochemicals and high-value biofuels. More specifically, the biopolymers composing biomass typically decompose into products formed in three states when being heated under an inert atmosphere. These consist of a carbon-rich solid residue called biochar, a bio-oil made up of a complex mixture of water and organic species, and a non-condensable gaseous phase composed of CO, CO_2, H_2, CH_4, etc., also referred to as syngas. While biochar can be of interest for soil amendment and GHG capture, syngas and bio-oil are more particularly devoted for use as substitute fuels for boiler and engine applications. In expanding the application of pyrolysis to produce biofuels having a higher energy density as compared to raw biomass, a key challenge is to develop the computational codes required to design and/or optimize the functioning of pyrolizers. Doing so implies gaining a fundamental knowledge of the mechanisms underlying the conversion of solid fuels. Nevertheless, and due to the wide variety of biomass in existence and to the significant heterogeneity that can be observed within a given feedstock type, current modeling tools (including phenomenological ones) are still unable to fully capture the complexity of biomass decomposition, which is influenced by numerous operating factors, including the temperature and the heating rate (HR). Continuous effort is therefore ongoing to assess kinetic triplets allowing simulating the decomposition process of a wide variety of biomass types. Doing so, however, requires parametrizing kinetic modeling tools against trusted data, thus prompting the need for additional experimental investigations. With this in mind, the present work aims at comparing the predictive capability of 7 different modeling approaches in order to simulate the pyrolysis of 5 kinds of biomass, namely, spruce wood, wheat straw, switchgrass, miscanthus and swine manure. These feedstocks were thermally treated under an inert atmosphere using a thermogravimetric analyzer (TGA). Measurements were carried out with 4 HR of 5, 10, 15 and 30 K/min. The results obtained were then processed by means of 3 classical isoconversional models (namely, Kissinger–Akahira–Sunose (KAS), Flynn-Wall-Ozawa (FWO), and Friedman), together with one-step and three-step Kissinger modeling approaches, in addition to an advanced fitting method recently proposed by [**1**]. Based on the obtained rate constant parameters, the variation of the fuel conversion degree (α) as a function of the temperature was simulated while considering different reaction models commonly employed in the literature. The suitability of each method was then assessed by computing the root-mean-square deviation between simulated and measured conversion degree profiles. To conclude, a phenomenological model (the bio-Chemical Percolation Devolatilization model or bio-CPD [**2**]) was also used to assess its predictive capability as compared to the results obtained from the implementation of the above listed model-free and model-fitting approaches. As highlights, the results derived from the implementation of the 3 isoconversional approaches were found to accurately reproduce TGA results. The agreement between simulated and measured data was found to be higher in the case of the Friedman model, followed by the KAS and FWO, the three-step, and the one-step Kissinger modeling approaches. Alternatively, the bio-CPD model failed to satisfactorily predict measured data, while the fitting method from [**1**] led to the worst agreement and was thus found to be unsuitable to properly simulate the pyrolysis of the tested feedstocks.

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Pyrolysis of hydrothermally pretreated carrot pomace – investigation using Py-GC-MS, Py-FT-IR, and tga techniques

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Keywords: carrot pomace, biomass, hydrothermal treatment, thermochemical conversion, pyrolysis, biofuels

Carrots are one of the most popular vegetables in Poland. The production of carrots has varied in the last decade between 638 thousand tonnes and 887 thousand tonnes, which placed Poland among the top producers in the European Union. A noticeable part of these fresh products is used by the food processing industries towards the production of juices, concentrates, or pastes. As a consequence, it generates abundant quantities of residual matter, mainly carrot pomace, which is characterized by a high moisture content and low biochemical stability. Thus, new approaches allowing for efficient conversion of this type of feedstock towards value-added products are sought. The present study focused on investigating the thermal decomposition of carrot pomace and its residual matter after subjecting the raw material to various pretreatment methods. Tested pre-treatment methods, i.e. (i) hot water extraction (ii) hydrothermal hydrolysis, and (iii) hydrothermal acid hydrolysis, aimed at the isolation of sugars. Subsequently, raw carrot pomace as well as hydrolysis and extraction residues were pyrolyzed to generate precursors of value-added chemicals. Pyrolytic studies were carried out using coupled microscale techniques i.e. thermogravimetric analysis (TGA), pyrolysis – gas chromatography/mass spectrometry (Py-GC-MS) and pyrolysis – Fourier Transform Infrared Spectroscopy (Py-FT-IR). Thermogravimetric analyses indicated that the application of two-stage processing allowed for an increase in the thermal stability of all hydrolysis residues compared to raw material and a reduction in the number of stages in which thermal degradation occurs. The activation energies calculated for hydrolysis residues were higher than that noted for raw material, proving their higher structural stability. The pyrolytic volatiles that evolved during the decomposition of carrot pomace constituted a highly complex mixture dominated by oxygen-containing compounds (e.g. ketones, organic acids, and phenols). Initial isolation of sugars noticeably affected the reduction of the relative share of some sugar derivatives such as 2,5-dimethyl furan. The performed studies proved that the application of prior hydrothermal hydrolysis of carrot pomace could beneficially affect the composition of pyrolytic volatiles, resulting in a reduction of its complexity that ultimately could serve for the obtaining precursors of value-added chemicals.

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Pyrolysis kinetics and volatile release of hydrothermally aged asphalt

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Keywords: pyrolysis kinetics, volatile release, hydrothermally aged asphalt, tunnels

Asphalt combustion releases large amounts of heat and hazardous gases in a tunnel fire, which poses severe threats to life security and has important research significance. When the asphalt material is exposed to fire, it is prone to start pyrolysis with a great deal of toxic gaseous products released[1], thus many studies focused on the pyrolysis characteristics of base asphalt[2]. However, asphalt suffers hydrothermal ageing owing to the warm and humid environment in underwater tunnels, which could affect the substance composition and rheological properties of asphalt[3], while the effect of hydrothermal ageing on the pyrolysis characteristics of asphalt has gained little attention. In the current study, a laboratory preparation method was proposed, a rolling thin-film oven (RTFO), a pressure ageing vessel (PAV), and a circulating water bath tank were used to simulate the short-term thermal oxidation ageing, the long-term thermal oxidation ageing, and the immersion ageing of asphalt in underwater tunnels. The hydrothermally aged asphalt (HA) samples were prepared and comparatively studied with base asphalt (BA) and thermal-oxidatively aged asphalt (TA) as references. The thermal stability and volatile release of asphalt before and after hydrothermal ageing were investigated through Fourier transform infrared spectrometry (FTIR) and thermogravimetry and mass spectrometry (TG-MS), and the kinetic parameters were calculated by different dynamic analysis methods based on thermogravimetric experiments. Results indicated that the C=O and S=O bonds increase significantly after ageing, and the S=O bond of HA is lower than that of TA. The volatile products including alkanes, H_2S, and SO_2 decrease dramatically after ageing, and the H_2O, H_2S, and SO_2 generation during the pyrolysis of HA increase prominently compared to TA. The distributed activation energy model (DAEM) and the Ozawa-Flynn-Wall integral method (OFW) could well describe the kinetic process of the pyrolysis of BA, TA, and HA. The conversion ratio (α) shows obvious effects on the calculated activation energy (E) and pre-exponential factor (A), and the calculated E and A of HA are lower than those of TA but slightly higher than those of BA in the initial pyrolysis stage. Ageing causes the unsaturated bond fractured and the generation of saturated bonds, which enhances the energy barrier of asphalt pyrolysis, while hydrothermal ageing inhibits this process. This work reveals the thermal decomposition mechanism of asphalt after hydrothermal ageing, which could advance the understanding of pyrolysis characteristics of the asphalt and provide scientific guidelines for the fire-safe design of asphalt pavement in underwater tunnels.

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Pyrolysis of alkali modified rice husks: combustion, kinetics and thermodynamic parameters using thermogravimetric analysis

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Keywords: alkali, bioplastic, combustion, kinetics, pyrolysis, rice husks, TGA

Pyrolysis of raw and NaOH alkali modified rice husks using thermogravimetric analysis (TGA) was carried out to determine combustion and kinetic parameters at three different heating rates of 20, 40 and 50 °C/min for application in bioplastics. Combustion performance was analyzed from results of ignition temperature, burn-out temperature, combustion rates, flammability index and combustion characteristic index. The increase in heating rate from 20 to 40 and further to 50°C/min increased the onset of degradation, burnout and peak temperatures as observed by curve shifts to the right. This was likely due to shorter reaction time when higher heating rate was utilized, hence increasing the temperature required for degradation. Flammability and combustion characteristic index ranged between $0.6\times10^{-5}-1.1\times10^{-5}$%/min.°$C^2$ and $0.1\times10^{-8}-0.4\times10^{-8}$%/min/°C respectively, and their values decreased with increasing heating rates since it takes longer to transfer heat from the external environment to the interior of the rice husks, thereby creating a hysteresis effect. The average pre-exponential factors (KAS and OFW) for raw rice husks are 2.9E+02 and 1.9E+11 respectively while those for modified rice husk are 1.1E+00 and 7.2E+09. The average activation energies using Kissinger-Akahira-Sunose (KAS) method ranged 95.9−118.3kJ/mol and 101.2−122.6kJ/mol using the Ozawa-Flynn-Wall (OFW) method. Enthalpy, Gibbs free energy and Entropy changes were in ranges 95.6−117.0kJ/mol, 160.8−167.5kJ/mol and 0.07−0.11kJ/mol respectively. The low energy barrier (≤7.0kJ/mol) between activation energy and enthalpy changes indicated that initiation occurs easily.

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From plastics to carbon materials and methane by pyrolysis under autogenic atmosphere

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Keywords: waste plastics, pyrolysis under autogenic atmosphere, char, methane

Pyrolysis of plastics is a promising technique towards high-value utilization and solvent-free treatment of plastic waste. However, low product selectivity and broad product distribution may restrict the application of plastic pyrolysis. In this study, polyolefins, polystyrene (PS) were converted into methane and carbon spheres through pyrolysis under autogenic atmosphere (AAP)[1,2]. At 450 ºC, polyolefins were converted into 89.3–96.91 wt% pyrolysis oil; PS was converted into 88.4 wt% of pyrolysis oil, 2.3 wt% of gas and 9.3 wt% of char. As the increase of temperature, the yields of methane and pyrolysis char increased significantly. At 700 ºC, the yields of pyrolysis chars were as high as ~45 wt% and 74.1 wt% for polyolefins and PS, respectively, and the rest products was mainly pyrolysis gas with less than 1 wt% of pyrolysis oil. Pyrolysis chars were well carbonized spheres with diameters of 2–8 µm. Pyrolysis gas contained 93.83–95.74 vol% of methane, and possessed higher heating values of 35.8–36.2 MJ m^{-3}. The pyrolysis products with high purity and narrow distribution can be attributed to the enhancement of AAP on the secondary reactions of primary decomposition products, such as cracking, hydrogenation, aromatization and condensation.

Polyethylene terephthalate (PET) and real-world high-density polyethylene (HDPE) waste with additives of $CaCO_3$ and carbon black were upcycled into methane and hierarchical porous carbon materials (HPCs) for energy storage through AAP and post-activation[3,4]. The pyrolysis gas from PET contained 34.58 ± 0.23 vol% CH_4. After CO_2 removal, the high caloric value of the pyrolysis gas could reach 29.2 MJ m^{-3}, which could be used as a substitute natural gas. Pyrolytic carbon from PET was further activated by KOH and $ZnCl_2$. KOH-activated carbon (AC-K) obtained a hierarchical porous structure, a high specific surface area of 2683 m^2 g^{-1} and abundant surface functional groups. Working as supercapacitor electrodes, AC-K exhibited an outstanding specific capacitance of 325 F g^{-1} at a current density of 0.5 A g^{-1}. After 5000 charge-discharge cycles, AC-K still retained 91.86% of the initial specific capacitance. The HDPE waste were converted into high-purity methane (>93 %) and s) and HPCs with high specific surface area (2785–2913 m^2 g^{-1}) through AAP-KOH activation. Applied in supercapacitors, HPCs exhibited outstanding specific capacitance (301 F g^{-1} at 1 A g^{-1}), rate performance (89.1 % at 20 A g^{-1}), and cyclic stability (82 % after cycling for 5000 times). The additives showed little influence on the product distribution and methane content, but changed the morphology and properties of HPCs. With additives, the meso- and macro-pore proportion and surface functional groups increased, but the graphitization degree decreased, which further altered the capacitive performances of HPCs. HPCs from plastic wastes with additives exhibited higher specific capacitance, and better rate performance, but lower cyclic stability. This study provides a sustainable way to control plastic-derived pollution and alleviate the energy crisis.

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Theory and instrumentation

McGill Chemistry Characterization (MC^2) facility

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Keywords: facility, instruments, thermal analysis

The McGill Chemistry Characterization (MC^2) facility regroups expert personnel and state-of-the-art instrumentation for the study of materials in a wide range of disciplines. The MC^2 staff are scientists with expertise in these areas and serve both the experienced and novice researchers by providing training, measurements and/or data interpretation. Here we describe one of our platforms: the Thermal Analysis and Spectroscopy Lab (TAS Lab) with the new Perkin Elmer hyphenation system. What we do and who uses our lab. Beyond research training, we provide support to external industrial users, but also to undergraduate teaching laboratories. Some examples will be presented.

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Thermal conductivity

Determination of 3-d geometry of buried defects using angled flash thermography

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Keywords: flash thermography, non-destructive evaluation, 3D reconstruction, thermal tomography, additive manufacturing

Flash thermography is a non-destructive evaluation technique that involves inducing a thermal gradient throughout the depth of a sample's surface by applying a heat source. This process involves recording the surface temperature of the sample over time to measure the propagation of heat through the material, which is influenced by the thermal properties of the materials. The excitation of the surface creates a deviation from the thermal equilibrium of the system, which can help to detect defects, through the identification of variations in thermal propagation. This is due to the presence of material interfaces, such as voids, cracks, or contaminants, within a sample, result in deviations from uniform conduction paths of heat. Analysing the geometry or material characteristics of such non-homogeneity at or below the surface of the stimulated sample allows for the identification and characterization of the non-homogeneity.

Heat diffusing from the bulk of an object manifests at the surface of an object. Due to variations in structure and materials, which can give rise to thermal property variations, it is possible to detect: their size, shape, and location within an object. As such, Infrared Thermography (IRT) finds its applications in aerospace industry, additive manufacturing, welding and carbon fibre composites and medical diagnostics, by remotely measuring the surface temperature of an object, internal features can be measured. The approach outlined here intends to determine the z-direction geometry of a defect from a set of 2D surface images, varied over angle of excitation, enabling the 3D reconstruction of buried defects. Previous work in time domains and pulsed regimes have also been explored in 3D thermography [1-3]. These methods though have shortcomings in edge resolving, resolution and material of use. In this paper, we demonstrate a relatively simple approach for enhancing z-contrast, with tilting the heat source.

When a light source is placed directly above a defect, it produces a uniform heating of the surface, which leads to a clear contrast of the defect on the surface. However, this method has limitations in providing comprehensive information about the full three-dimensional (3D) shape of the defect. To further develop the technique for measuring the full shape of the defects features, the heat source can be tilted, capturing sections of the penetrating heat through the sample. This technique is similar to thermal tomography, but is achieved by tilting the heat source, rather than the cameras measuring angle (from the surface of the sample). This approach allows for the visualization of defect features that would be impossible to observe with symmetric heating.

This paper investigates the interaction between optical and thermal pathing and internal boundaries with respect to both geometry and material properties. Our approach utilizes a Multiphysics finite element model, which we validate with experimental data. To achieve this, we compare thermographic images a PLA block with an adjustable defect, in terms of material, depth and length. Our work demonstrates the feasibility of real-time 3D active infrared thermography (IRT) for detecting buried defects, with the aim of enhancing quality control and process optimization in additive manufacturing.

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Energy analysis of u-type deep borehole ground source heat pump system

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Keywords: borehole, model, TRT, thermal conductivity

In the design of geothermal systems, an important aspect is determining the thermal parameters of the soil. In the case of residential systems, these values are usually estimated, but for larger systems, it is necessary to measure these parameters for proper sizing, for which the TRT (Thermal Response Test) equipment is a useful tool. In our work, we focused on accurately determining the thermal conductivity of the soil. At the beginning of the measurement, the surface temperature was To=13,53 °C. The obtained results were between λ_{eff}= 1,71 W/mK – 2,029 W/mK.

Thermal hazards, lifetime prediction

Study of thermal stability of ionic liquids [pyr14][dca] in different atmospheres

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Keywords: Ionic liquids, TGA/DSC, TGA-FTIR

Ionic liquids (ILs) are ionic compounds composed of organic cations and organic or inorganic anions. Due to their relatively low vapor pressure and high thermal stability, they are considered as green alternatives to traditional organic solvents. Ionic liquids have been regarded as non-flammable substances in the literature due to their extremely low vapor pressure. However, many studies in recent years have shown that ionic liquids are combustible. The difference from traditional organic solvents is that the flammability of ionic liquids is due to the combustion of the decomposition products, rather than the combustion of the substance's own vapor [1]. In addition, literature research has also shown that ionic liquids may have different reaction mechanisms under nitrogen and air atmospheres [2-3]. The ionic liquid 1-Butyl-1-methylpyrrolidinium dicyanamide [PYR14][DCA] has been widely used in various engineering fields, such as extraction, desulfurization technology, electrolytes, etc. However, there is a lack of research on its flammability characteristics and thermal stability. Therefore, in this study, the flammability and thermal stability of 1-Butyl-1-methylpyrrolidinium dicyanamide were systematically evaluated using the thermogravimetric/differential scanning calorimetry (TGA/DSC) analysis technique.

The experimental conditions were as follows: the sample mass was 2 ± 0.1 mg, using a 70 μl alumina crucible, the heating rate was 20 K/min, and the temperature range was from 298 K to 1073 K, with nitrogen and air as the reaction gases. The results indicate that under a nitrogen atmosphere, the DTG curve of [PYR14][DCA] has two peaks at 591K and 713K. Combined with the TGA curve, it is known to be a two-stage reaction. The residual weight of the TGA test is about 9%. The DSC curve shows a very small exothermic phenomenon (-60 J/g) at 570K and an endothermic phenomenon (792.8J/g) at 748K; Under an air atmosphere, there are also two peaks in the DTG curve of [PYR14][DCA] at 589K and 993K. Combined with the TGA curve, it also shows a two-stage reaction, but the temperature of the second stage is about 280 K higher than that under the nitrogen atmosphere. The residual weight of the TGA test is about 0%, which is significantly different from the residual weight under the nitrogen environment. The DSC curve shows the occurrence of an exothermic phenomenon at 578 K (-578.36 J/g) and a second exothermic phenomenon at 987 K (-301.79 J/g). The temperature at which the first exothermic event occurred is similar to the temperature of the first exothermic event under a nitrogen atmosphere, but the total heat released is significantly different in these two atmospheres, suggesting that the products of the decomposition reaction may have self-ignited due to high temperature in an atmosphere. The second exothermic peak in an air atmosphere is markedly different from the endothermic peak in the nitrogen atmosphere. By comparing the TGA curves of the two atmospheres, it is possible that different decomposition reactions occurred at this stage for each atmosphere. To verify the reaction mechanism under different atmospheres, TGA-FTIR experiments are planned for future work.

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Thermooxidative stability of lignin- and lignosulfonate-filled rubber compounds based on NBR and SBR

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Keywords: thermooxidative stability, induction period, protection factor, NBR, SBR

This work is focused on the study of the thermooxidative stability of lignin- and lignosulfonate-filled rubber compounds based on nitrile-butadiene rubber (NBR) and styrene-butadiene rubber (SBR) using DSC. The effect of three different concentrations of lignin and lignosulfonate in both matrices is also investigated. Thermooxidative stability of the materials was estimated by non-isothermal DSC measurements in oxygene atmosphere. For the treatment of the experimental results, a method for the evaluation of the kinetic parameters describing the temperature dependence of the induction periods of thermal oxidation based on non-Arrhenian temperature function, was employed[1]. From the obtained kinetic parameters the values of induction periods for several temperatures were calculated. Subsequently, protection factors[2] and antioxidative effectiveness[2] of lignin and lignosulfonate on the stability of both rubber matrices were evaluated. The results achieved document that stabilizing effect of lignin and lignosulfonate depends on the rubber matrix. Both additives exhibit only weak stabilizing effect in NBR and SBR; better effects have been obtained for NBR.

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Experimental investigation on the temperature distribution of corrugated steel web box girder with and without encased concrete

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Keywords: corrugated steel web box girder, encased concrete, field test, maximum temperature gradient, temperature inertia

To investigate the temperature field of the corrugated steel web box girders with and without encased concrete, field tests were conducted on a 188 m main span continuous rigid structure bridge with corrugated steel web girders. Temperature monitoring was carried out for 268 days on both sections with and without encased concrete. The environmental parameters included air temperature, humidity, wind speed, and solar radiation. Different from the conventional temperature gradient prediction methods, which were based on daily maximum environmental temperature difference, daily total solar radiation, and daily average wind speed. This study proposed moment-based normalized environmental parameters temperature prediction equations considering temperature inertia and environmental humidity, which had higher accuracy compared with the measured results and ensured positive correlations between solar radiation and the box girder temperature. The analysis results showed that: The vertical temperature on the sunny side was larger than that on the shady side; for the encased concrete box girder, the vertical temperature gradient of the corrugated steel web on the sunny side was larger than that of the encased concrete, with the maximum temperature difference of 16.7 °C; for the corrugated steel web without encased concrete on the sunny side, the vertical gradient in winter was significantly larger than that in summer, with the maximum temperature gradient difference of 21 °C. The lateral temperature distribution of the top plate showed that the lateral temperature gradient was distributed in a "U" shape along the width of the girder. Because of the "L"-shaped outsourcing connection between the corrugated steel web and the bottom plate, the lateral temperature gradient on the sunny side of the bottom plate produced a larger temperature gradient in the corrugated steel web, with a maximum value of 15.1 °C.

Thermochemistry

Removal of metallic radionuclides from irradiated graphite by chlorination roasting

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Keywords: irradiated graphite waste, decontamination, chlorination roasting, metallic radionuclides

Metallic radionuclides account for a considerable proportion of the total radioactive activity in irradiated graphite from nuclear reactors[1]. Due to metallic radionuclides combining with carbon atoms to form metal-carbon compounds[2], there is no promising treatment to remove them from irradiated graphite for now. Based on that, we have proposed an innovative method for removing metallic radionuclides by means of chlorination roasting[3], which has been confirmed by thermodynamic analysis and quantum mechanics. In the current work, the reaction mechanism and the kinetics of the chlorination process of metallic radionuclides were investigated. In order to simulate metallic radionuclides, ^{56}Fe ions were implanted in IG-110 graphite instead of metallic radionuclide ^{55}Fe at the energy of 35 keV and a fluence of 3E17 ions/cm^2. XPS showed that ^{56}Fe mainly distributed on the surface of graphite with a depth of 30-40 nm, which reacted with carbon atoms to form Fe-C compound. After the graphite being ground into powders, the samples were fully mixed with chlorinating agent NH_4Cl. The mixed powders were heated in an inert atmosphere. The maximum decontamination efficiency of ^{56}Fe was 33%, 82%, 94%, and 96% at 900, 1000, 1100, and 1200 °C respectively. XRD showed that the chlorinated product was $(H_3O)_2FeCl_5(H_2O)$, indicating that the chlorinated ^{56}Fe volatilized from graphite in the complex compounds. Chlorination process could be dived into three steps. (1) Induction period with low reaction rate, where the new phase formed on surface of the old phase. (2) Acceleration period. The reaction rate increased rapidly at higher temperature. The reaction interface expanded with the growth of new nuclei to accelerate the chlorination process. (3) Reduction of reaction interface period. Continuing to increase treatment time, the reaction rate of chlorination decreased rapidly. The reaction interfaces reached the maximum in step (2), and then they began to overlap each other to make the reaction interfaces shrink to hinder the reaction. Chlorination of ^{56}Fe followed the shrinking unreacted core model. The apparent activation energy was about 125 kJ/mol. This study can provide basic data for the decontamination of metallic radionuclides in irradiated graphite.

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Poster Presentations

Bio sciences, including food, soil, textile, wood

Evaluation of the growth-promoting effects of two different types of *Pleurotus* spp. mushroom polysaccharides on probiotics using microcalorimetry

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Keywords: polysaccharide, Radiation, *Pleurotus eryngii, Pleurotus citrinopileatus*, *Lactobacillus plantarum*, *Kluyeromyces marxianus*, microcalorimetry

This study aims to cultivate two probiotics, *Lactobacillus plantarum* (*L. plantarum*) and *Kluyveromyces marxianus* (*K. marxianus*), with the addition of polysaccharides from two types of mushroom, *Pleurotus citrinopileatus* (*P. citrinopileatus*) and *Pleurotus eryngii* (*P. eryngii*). Polysaccharides have been shown to have various health-promoting benefits, such as regulating immune function, reducing inflammation, fatigue, and blood sugar, as well as scavenging free radicals and having anti-tumor effects. By adding polysaccharides to the probiotics, this study aims to investigate whether the polysaccharides have a synergistic or inhibitory effect on the growth of the two probiotics, in order to develop functional products for human health. Additionally, this study attempts to modify the structure of the polysaccharides by varying the doses of gamma rays and pulsed light irradiation to investigate the potential benefits of polysaccharides with different structures that would promote the growth of the two probiotics. The physical and chemical properties of different polysaccharides were determined through differential scanning calorimetry (DSC) to control suitable processing conditions for subsequent food processing. The study also employed isothermal microcalorimetry using the isothermal microcalorimeter (TAM Air) to investigate the optimal mixing ratio of glucose and polysaccharides from *P. citrinopileatus* and *P. eryngii* in the culture medium to promote the growth of the probiotics. The results indicate that *K. marxianus* is more sensitive to carbon source selection, and the concentration of glucose in the medium directly affects its growth. Using microcalorimetry technology, polysaccharides from *P. citrinopileatus* and *P. eryngii* were found to have significant growth-promoting effects on *L. plantarum*. The suitable mixing ratio of polysaccharides from both mushrooms was also determined, and it can even completely replace the carbon source in the culture medium to promote the growth of probiotics and enhance the functional effects of polysaccharides.

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Assesment of fibre release susceptibility by pilling experiments and thermal analysis techniques

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Keywords: textiles, fibre release, thermogravimetric analysis, thermal analysis, polyester, cotton, elastane, acrylic, wool

The concern regarding microplastic pollution has increased in recent years, including microfibres which come from textiles. It is well known that wear and tear of clothes produce fibre loosing, resulting in a loss of their aesthetic and physical requirements and contributing to environmental pollution. It has been reported that some properties of fibres are relevant to understand fibre loosing from clothes [1,2]. The aim of this work is to evaluate the effect of physical, thermal and mechanical properties of the textiles on the susceptibility to fibre release. To this aim, thermal and mechanical characterization is performed by thermogravimetry (TG), differential scanning calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). Fibre release is evaluated in a pilling machine [3]. Both sets of results are analysed by principal component analysis (PCA).

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Antioxidant, Oxidation Stability via thermal analysis, and Anti-inflammatory Properties of Antrodia Camphorata and Sanghuangporus Sanghuang Complex Extracts

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Keywords: *Antrodia camphorate*, *Sanghuangporus sanghuan*g, antioxidant, anti-inflammatory, isothermal calorimetry, oxidation stability

Antrodia camphorata and *Sanghuangporus sanghuang* are highly sought-after edible and medicinal fungi with unique physiological functions, making them the subject of intense research and consumer interest. The purpose of this study is to investigate the antioxidant activity, oxidation stability, and anti-inflammatory properties of three different ratio extracts of *A. camphorata* (AC) and *S. sanghuang* (SS), with the aim of maximizing their biological activity. We extracted various ratios of AC and SS using 70% ethanol, and evaluated the resulting compound extracts for their antioxidant activity, oxidation stability using test tube and microcalorimetry models, and anti-inflammatory properties using cell tests. Three ratios were examined: AC1:1SS, AC2:1SS, and AC1:2SS. The antioxidant capacity of the complex extracts was analyzed using three oils: camellia oleifera, linseed oil, and perilla oil by isothermal calorimeter (TAM Air). The extraction rate of AC1:2SS was found to be 14.90±0.45%, which was significantly higher than the 12.07±0.06% obtained when AC and SS were extracted separately. Preliminary analysis of the antioxidant capacity of the compound extract showed that the total phenolic content of SS was the highest at 0.23±0.01 mg g^{-1}. Next, differential scanning calorimetry (DSC) was used to determine the thermal stability of the oil after adding antioxidants, and the peroxide value was used to measure the degree of oxidation of the oil. The results showed that the three ratios of AC and SS had different antioxidant levels when using different oils for experiments. The ethanol complexes of the composite extracts enhanced the oxidative stability of camellia oleifera oil, linseed oil, and perilla oil, with potent antioxidant potential. The complex extract of AC1:2SS was more effective than the other ratios in inhibiting the production of nitric oxide, with a concentration-dose effect. Additionally, the compound extract of AC2:SS1 exhibited the strongest inhibitory effect on the generation of reactive oxygen species induced by lipopolysaccharide. These results suggest that the AC1:2SS and AC2:SS1 complex extracts have promising potential for use as natural anti-inflammatory and antioxidant agents. Overall, our study found that the compound extract of *A. camphorata* and *S. sanghuang* had a proportionate effect on both antioxidant and anti-inflammatory capacities. Specifically, the AC1:2SS and AC2:SS1 complex extracts exhibited the highest levels of antioxidant and anti-inflammatory activity, respectively. These results suggest that these complex extracts could have promising potential as natural anti-inflammatory and antioxidant agents for use in the development of health foods and supplements.

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Calorimetry

The thermodynamic and kinetic study of protein denaturation and renaturation using isothermal titration calorimetry

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Keywords: isothermal titration calorimetry, protein folding, burst-phase intermediate, folding/unfolding kinetics

The phenomenon of protein folding has been extensively studied ever since its discovery. The solutions to some of the great challenges including Levinthal's paradox have been found already, but there are still a lot of unanswered questions in the field [1]. A series of circular dichroism (CD) spectroscopy, hydrogen/deuterium exchange nuclear magnetic resonance (NMR) and mass spectrometry experiments have shown that small globular proteins reach their native conformation via a quickly formed intermediate state [2,3]. It is formed within the "dead" time of the stopped-flow instruments, and therefore is often referred to as the "burst-phase intermediate" in the literature. The physical properties of this state resemble molten globule: it has high content of secondary structure but remains quite flexible. Despite extensive studies of this intermediate, there is no experimental evidence showing how hydrated the protein side chains in this burst-phase state are. Two opposite cases are usually considered: either water can penetrate the pores of this compact state as single molecules, or the side chains are exposed to water as a bulk solvent. In other words, whether the burst-phase intermediate is a "dry" or a "wet" molten globule remains unknown.

Calorimetry is the only physical method which allows direct measurement of the thermodynamic potential changes, in particular enthalpy change. The enthalpy change during the protein folding/unfolding process can then be interpreted in terms of the side chain groups hydration [4]. Therefore, calorimetry studies of protein folding can be used to determine the degree of hydration of the burst-phase intermediate state. Unfortunately, modern calorimeters are not suitable to study fast processes in multi-stage reactions because of their large characteristic times. In our study we have tried to develop a method to obtain kinetic information for fast processes like the burst-phase formation based on the total enthalpy of the process combined with the kinetic studies of the slow stage. All the parameters needed for this analysis can be obtained in a single isothermal titration calorimetry experiment. Firstly, the dynamics characteristics of NanoITC (TA Instruments, USA) were studied to correct the signal distortion caused by the instrument response time. Secondly, the mathematical algorithm for the study of fast kinetics using ITC was developed and verified by model experiments. Lastly, the kinetics and thermodynamics of the fast stage of the folding process for small globular protein have been studied using lysozyme as model protein. Overall, the developed approach allows to determine the enthalpy of burst-phase formation, which can elucidate the degree of protein hydration at this stage.

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Investigating Thermal curing behaviour of phenol formaldehyde resin using Differential scanning calorimetry and dielectric analysis

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Keywords: cure monitoring, cure kinetics, dielectric analysis, phenol formaldehyde, paper sensor

Phenol formaldehyde (PF) resin is a versatile material used in a variety of applications, such as adhesives, impregnation resins, tire tackifiers, and binder resins for manufacturing composite panels. In this study, we analyzed the curing behavior of PF resin-impregnated paper, which is a B-stage resin system. Typically, curing behavior is analyzed using Differential scanning calorimetry (DSC), and the kinetics of curing can be predicted using several model fitting and model-free kinetic methods. However, DSC is limited to lab-scale testing and cannot replicate the real-time conditions in which composites are made on an industrial scale. To overcome this limitation, we used dielectric analysis (DEA) to predict curing behavior in real-time. DEA measures the thermoset or composite cure by analyzing the change in dielectric conductivity at defined frequencies. In this study, we employed paper-based printed sensors, which are advantageous over commercially available polyimide-based sensors due to their ultra-thin, biodegradable, low-cost, flexible, and thoroughly impregnated nature. We studied the cure kinetics of PF curing using a model-free kinetic method and predicted the degree of cure at different isothermal temperatures using the Vyazovkin method [1]. We cured PF-impregnated papers in a hot press at three isothermal temperatures (140°C, 160°C, 180°C) and compared the conversion curve obtained from DSC and DEA (**Figure 1**). Both techniques are temperature-dependent and deliver a good agreement with the degree of cure, confirming the possible use for real-time cure monitoring for cure kinetics. Our results demonstrate that DEA can be an effective method for predicting curing behavior that is also viable for industrial use. Further research on pressure influence and other parameters could be conducted in the future to improve the accuracy of the technique.

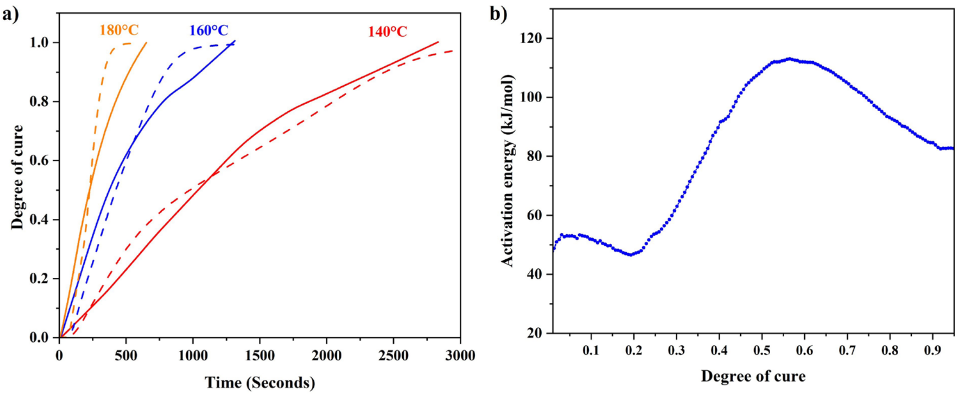

Figure 1: a) Correlation of DEA and DSC data at different temperatures, Solid lines represent DEA data (Experimental), and dotted lines represent DSC data (predicted), b) Change in activation energy with respect to the degree of cure.

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Enthalpy of immersion of activated carbon in aliphatic and aromatic organic solvents: benzene, toluene, cyclohexane, hexane and in binary mixtures of these compounds

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The enthalpies of immersion of activated carbons with different surface characteristics in benzene, toluene, cyclohexane, hexane are determined. Activated carbons obtained from a granular activated carbon prepared from coconut shell (CAG), which was subjected to oxidation processes with a nitric acid solution and heat treatment at different temperatures (723 K, 1023 K and 1173 K), are studied. The values for the immersion enthalpies are exothermic in nature and range between 16.36 and 145.1 Jg^{-1}.

The five samples were also immersed in binary mixtures of: benzene-cyclohexane (B/CH: benzene solute, cyclohexane solvent), benzene-hexane (B/H: benzene solute, hexane solvent), toluene-cyclohexane (T/CH: toluene solute, cyclohexane solvent), toluene-hexane (T/H: toluene solute, hexane solvent) and cyclohexane-hexane (CH/H: cyclohexane solute, hexane solvent) at different mole fraction concentrations between 0. 2 and 0.8, in order to show the effect of the solute-solvent-solid interaction as the solute concentration increases. The results obtained show values for the enthalpy of immersion between 145.2 and 25.65 Jg^{-1}

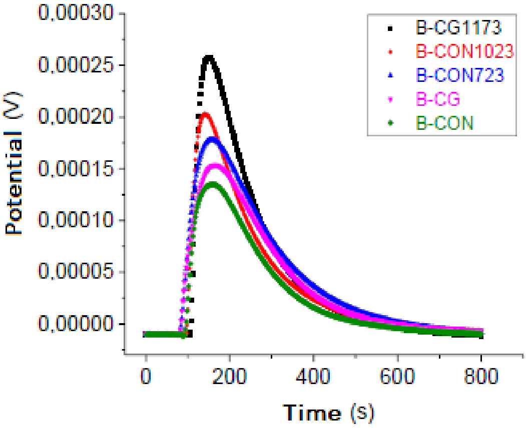

Figure 1. Curvas de potencial en función del tiempo para la inmersión de carbones activados en benceno

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Adsorption Calorimetry: Comparative study between experimental determinations and theoretical models using Gas-MOF´s

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Keywords: adsorption calorimetry, metal-organic-framework, storage CO_2, ammonium gas adsorption, Clausius-Clapoeyron.

The heats of adsorption determined by a direct method (adsorption calorimetry, Ad-Cal) and an indirect method, in which adsorption isotherms are measured at different pressure and temperature levels using thermodynamic arguments by means of the Clausius-Clapeyron (CC) equation, are presented to determine the isosteric heats. The results are interpreted using CO_2 and NH_3 as adsorption probe molecules on five organometallic frameworks (MOF) synthesized in this research: zeolitic imidazolate framework (ZIF)-9, MOF-199, MOF-101, MOF-177 and MOF-74, with the intention of establishing the similarities and/or differences between these methods. The experimental results of the heats of adsorption were fitted to the Dubinin-Astakhov (DA), Toth, and Unilan models modified to determine the range of each of the methods used in this analysis. The aim of this work established that there is reasonable agreement between the adsorption heats measured by adsorption calorimetry and the DA model over the entire loading range of the probe molecules used. The adsorption capacity of these molecules was also analyzed.

Figure 1. Adsorption calorimeter, "home-made"

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The authors acknowledge the framework agreement between Universidad Nacional de Colombia and Universidad de los Andes (Bogotá, Colombia) under which this work was carried out. Prof. Dr. Juan Carlos Moreno-Piraján also acknowledges the Facultad de Ciencias of Universidad de los Andes for the grant (No. INV-2021-128-2257).

Hybrid liposomes of DPPC/cholesterol/octyl-βeta-D-glucopyranoside with and without Ibuprofen: calorimetric and morphological study

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Keywords: calorimetry, liposomes, drug delivery systems, phase transition, membrane fluidity.

Investigation of new materials for biomedical applications has represented a relevant subject in the latest decade, enhancing versatile properties of lipids. It has been documented that the capabilities of lipid-based systems improve when they combine with polymers, proteins, and sugars. In this field, understanding the driving forces behind such hybrid systems is mandatory for biomedical applications. From this perspective, it is crucial to investigate the biophysical properties of this kind of material. Here, we investigate the biophysical properties of hybrid membranes composed of 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC), cholesterol, and octyl-β-D-glucopyranoside (OGP). Lipid/sugar materials could have potential properties to use as nanovesicles for drug delivery. We encapsulate ibuprofen in lipid/sugar vesicles and evaluate their thermodynamics, hydrodynamics, and morphological properties by differential scanning calorimetry, dynamic light scattering, and scanning electron microscopy. We found that OGP combined with cholesterol modifies thermodynamic parameters of membranes such as phase transition temperature, enthalpy change, and cooperativity. Lipid vesicles containing OGP at 6.0 mM loaded with ibuprofen demonstrated good stability after three months of storage. Furthermore, electronic microscopy revealed the presence of well-defined liposomes. We conclude that cholesterol and OGP can act synergistically in polar-nonpolar spaces of the DPPC bilayer, where the hydrophobic nature of ibuprofen leads to incorporation into this hybrid core, which implies changes in the fluidity and compactness of the membrane occurring at temperatures of biological relevance. This investigation provides crucial knowledge regarding the biophysical properties of thermo-responsive biohybrid vesicles potentially to use in nanomedicine, which could be of practical reference for designing innovative drug-delivery systems.

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Biophysical study of copolymer-bioconjugates decorated liposomes with and without amantadine

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Keywords: calorimetry, antiviral, viral tropism, bioconjugated copolymers, lipid domains, drug-delivery.

Over the last decade, liposome-based technologies for biomedical applications have represented a relevant subject in nanomedicine. Liposome properties, such as high biocompatibility, low toxicity, and capacity to encapsulate hydrophilic and hydrophobic molecules, lead to use in a wide range of therapeutic advances. Hybrid liposome systems resulting from the combination of lipids and polymers, for example, PEGylated systems, have been recognized by their applications in human therapies. However, it has been recently documented immune reactions to PEGylated nano-biopharmaceuticals. For this reason, new biohybrid materials are necessary for improving the efficacy of drug delivery. Here, we present a biophysical investigation of copolymer-bioconjugates decorated liposomes free and payload with an antiviral compound, amantadine. For this end, we first synthesized bioconjugated copolymers of poly(N, N-dimethyl acrylamide)-block-poly(N-isopropyl acrylamide) (PDMA-*b*-PNIPAM) enhanced with short peptides that resemble the sequence of the loop 220 and loop 130 of the receptor binding of HA of influenza A virus. After that, large unilamellar vesicles composed of three biologically relevant lipids: 1,2 dimyristoyl-*sn*-glycero-3-phosphocholine, sphingomyelin, and cholesterol (MSC), were decorated with the bioconjugated copolymers. And finally, the calorimetric and hydrodynamic properties of copolymer-bioconjugates liposomes with and without amantadine were investigated by differential scanning calorimetry (DSC) and dynamic light scattering (DLS). The investigated hybrid systems present long-term stability, thermo-responsive, hydrophilic-hydrophobic properties, fluorescence-labelled, targeting properties integrated with the amino acid sequences, and probably resembling viral tropism. All in all, the capabilities of these nanosystems make them a promising technology to implement in drug delivery systems.

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Cements, building materials

Study of supplementary cementitous materials influence on the hydration course of fiber reinforced heavy-weight self-compacting mortars by Thermal analysis and mercury intrusion porosimetry

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Keywords: heavy-weight concrete, self-compacting concrete, supplementary cementitious materials, fibres, thermal analysis

The hydration of the clinker minerals present in the cement leads to the release of hydration heat. The amount of hydration heat depends on cement composition, admixtures used, additives, water-binder ratio, and initial curing hydration temperature. Supplementary cementitious materials (SCMs) are commonly used in cementitious binders to partially replace clinker in cement or concrete, respectively. The partial replacement of clinker by SCMs leads to temperature reduction during the cement hydration course, which influences the initial strength characteristics and durability of concrete [1-2].

The present work aims at understanding the influence of SCMs and plasticizing agent addition on the development of hydration heat in multi-component binder systems. Binder systems were composed of Ordinary Portland cement CEM I 42.5 R, Ground Granulated Blast-Furnace Slag (BFS), finely Ground Limestone (GL), and metakaolin (MK). The replacement levels within the study were used as follows: 85, 80, and 65 mass%. For the design of heavy-weight Self-Compacting Mortars (FRHWSCMs), magnetite and barite were used as the aggregates, which were supported by dispersed reinforcement in the form of steel microfibers, carbon nanotubes, and polypropylene fibres. The slump flow test and the V-funnel test were used to determine of optimal concentration of plasticizing admixtures in each system in full accordance with the requirements of The European Federation of Specialist Construction Chemicals and Concrete Systems (EFNARC).

Thermal analysis techniques were used to study proposal binder compositions on 2-, 7- and 28-day samples. In addition, the pore structure development of proposal compositions was investigated by Mercury Intrusion Porosimetry. On the other hand, the physicomechanical characteristics (i.e., flexural strength, compressive strength, and longitudinal deformations) of the prepared composites were determined. Even more, in the study of the evolution of the hydration phases in all types of proposal systems, the binder mixtures with the lowest and highest concentrations of plasticizing admixtures were investigated.

Acknowledgments

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Lightweight cement pastes submitted to accelerated carbonation

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Keywords: lightweight cement pastes, accelerated carbonation, silica fume, metakaolin

Lightweight cementitious mixtures are used in geothermal wells in order to decrease the hydrostatic pressure, which can be responsible for the formation of fracture zones in a weak unconsolidated rock foundation as well as for the lost circulation [1]. However, mixtures with lower bulk densities and open porosity have higher tendency to carbonation and carbonic corrosion, which can have a detrimental effect on the stability of wells.

In the present study, cement pastes with compositions demonstrated as resistant to carbonation [2] were prepared in a lightweight form. The so-called pre-foaming method was used to introduce pores into the structure of pastes consisting of high sulphate resistant Portland cement Class G, metakaolin L05 (MK), and silica fume (SF) in different ratios and total cement substitution levels. The lightweight cement pastes with two different amounts of protein foaming agent were prepared and submitted to accelerated carbonation (CO_2 concentration 20.0 ± 1 vol%, a temperature of 50 ± 1 °C, relative humidity of 90 ± 2 %) up to 90 days. The influence of this parameter as well as the effect of the composition on the stability of the samples under carbonation were evaluated by TGA, SEM, bulk density, and compressive strength measurements.

Mechanical properties of lightweight cement pastes depended on the following factors relating to each other: pore structure and bulk density, amount of hydration and carbonation products, and type of reaction products participating in carbonation reactions. As a result of porosity, carbonation progressed into the inner parts of samples immediately. A higher amount of portlandite present in the referential cement pastes enabled faster carbonation than in blended ones. Consequently, higher amounts of carbonates were formed in corresponding samples regardless of the foaming agent amount and carbonation duration. As expected, the rate of carbonation was promoted by higher porosity of the samples prepared with a larger amount of foaming agent. In addition to portlandite, also other hydration products started to react with CO_2 from the beginning. This was evidenced by the differences between inner and surface parts, the decomposition of sulphoaluminate phases leading to the formation of gypsum, and the formation of higher amounts of amorphous and metastable calcium carbonates. Contrary to unblended cement pastes, the presence of supplementary cementitious materials resulted in the fast consumption of portlandite and loss of buffering capacity. Despite lower amounts of carbonates and in some cases also larger quantities of pozzolanic and hydration products, carbonation of these phases led to the rise of porosity, lower bulk density, and consequently to the decrease of compressive strength.

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Combined chemical corrosion of cementitious binders at hydrothermal conditions

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Keywords: hydrothermal conditions, combined chemical corrosion, geothermal water, supplementary cementitious materials

While the effects of temperature and pressure on the phase composition and properties of cementitious materials are widely studied (1, 2), information about the influence of geothermal water is almost missing. Present study was therefore focused on the investigation of simultaneous acting of these parameters. Applied conditions simulated those in real geothermal wells in Slovakia: 150 °C, 18 MPa, geothermal solution of sodium-chloride type. In addition to temperature-induced changes, combined chemical corrosion mainly involving the action of chlorides, sulphates, and carbonates could be expected considering the composition of geothermal water.

Samples prepared from high sulphate resistant Portland cement Class G, metakaolin L05 (MK), silica fume (SF), and ground granulated blast-furnace slag (BFS) were submitted to hydrothermal curing for 7 days. Single effect of geothermal water was evaluated based on the comparison with experiments performed without its action. The impact of degradation processes on the cementitious binders was assessed by means of TGA, XRD, FTIR, and compressive strength measurements.

The most significant changes, not only because of hydrothermal conditions but also as a result of geothermal solution action, were detected for referential unblended cement paste. Although the same crystalline phases were developed regardless of the used liquid media, the portion of individual phases changed. In accordance with the results of the middle hydration stage study (3), hydration was promoted in the presence of geothermal solution. However, thermal stability of the formed primary products seemed to be lower than those in water and more α-C_2SH was evidenced. Besides, the presence of shorter C-A-(S)-H chains can be considered based on the results of FTIR. Higher amounts of katoite demonstrated in the solution can relate to higher pH value.

Blended cement pastes proved to be resistant to both high temperature as well as geothermal solution for the duration of the experiment. More polymerized structures and promotion of hydration and pozzolanic reactions by geothermal solution resulted in higher values of compressive strength of corresponding samples.

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Influence of selected grain size fractions of coal fly ash on properties of clay-cement mortars used for the flood levees construction

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Keywords: coal fly ash, particle size distribution, ash mineralogy and properties, clay-cement suspensions, flood levees

The properties of coal fly ash changes depending on various factors, including the type of coal, combustion method, and methods of reducing flue gas emissions. Within a given type of ash, there is variability in qualitative and quantitative composition of grains properties depending on their size fractions. These and other variabilities cause limitations in the direct usage of ashes as a raw material in industrial applications. In this article, different fly ashes size fractions received by means of dry aerodynamic separation were used to modification of properties of clay-cement mortars dedicated for the construction of flood levees.

The influence of size fractions on the chemical and mineralogical composition variability, loss on ignition (LOI) and grain microstructure of two types of fly ashes (high-calcium and silica) were determined. An increased amount of calcium and sulphur compounds was observed in the finest fractions (<20 μm). The finest and coarsest (>100 μm) fractions were found to contain a significant amount of unreacted mineral grains that did not pass through the combustion core, while the intermediate fraction (20…100 μm) mainly contained amorphous silica of varying degrees of modification. A trend towards a decrease in the Si/Al ratio and an increase in the amount of oxide modifying agents in the amorphous phase were presented as the grain size decreased.

The effects of ash adding to the clay-cement suspensions used for flood levees construction were investigated, and it was demonstrated that the fractionated fly ashes significantly influenced the rheological properties of fresh mortars and mechanical properties of hardened samples. Rheological measurements indicate high reactivity of the ashes, which excludes some of the finest fractions from their applications in levees clay-cement suspensions due to rapid increasing of viscosity immediately after mixing caused by the presence of reactive calcium components. By adding fine fractions to clay-cement suspensions, the compressive strength measured at 90 day increased from 2 to 6 MPa compared to the samples with raw fly ash additives.

The use of dry fractionation methods enables to extract from fly ash a different groups of products with varying parameters and properties. Their selective application in specific industrial areas can provide significant benefits in terms of economic, engineering and ecological means.

Diagnostics of concrete materials´ deterioration – a case study

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Keywords: cement composite, degradation, carbonation, corrosion of concrete

Concrete a representative of cement composites is considered a durable material with a long service life. However, it is subject to deterioration due to various corrosion processes due to environmental influences. Corrosion processes are induced by the action of physical, chemical and biological factors due to the exposure of cement composites to liquid and gaseous aggressive environments. Various forms of degradation, such as sulphate and chloride corrosion or carbonation, may also occur during the lifetime of a building as a result of atmospheric influences. The presence of chlorides is particularly dangerous for reinforced concrete as it induces electrochemical corrosion of the steel reinforcement. The corrosive processes result in a progressive loss of functionality of the cementitious materials.

This work deals with the diagnosis of the condition of cement composite materials of a selected masonry residential house. Deterioration parameters such as moisture content, sulphate and chloride content in concrete were monitored to determine the degree of corrosion attack; alkaline reaction of masonry and presence of hydration phases, portlandite and carbonates were detected to estimate the extent of carbonation. Several analytical methods such as X-ray fluorescence analysis (XRF), X-ray diffraction analysis (XRD), thermal analysis – differential scanning calorimetry and thermogravimetric analysis (DSC/TG) and Fourier-transform infrared spectroscopy (FTIR) were used to determine the deterioration parameters of concrete.

The degree of damage to the material was found to vary depending on the orientation of the building on which the material was located, as well as the depth of sampling. The moisture content of the concrete materials ranged from 2 to 9 % on average for the individual samples analysed, with some exceeding the value at which masonry remediation measures are already required. The pH values measured in some samples clearly indicated an ongoing carbonation process. The degree of carbonation of the aerated concrete materials, as determined from the results of the thermal analysis, ranged from 12.5 to 44,8 %. Thermal analysis has proven to be an effective tool for determining the degree of deterioration of cementitious materials and predicting necessary remedial actions.

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Mechanism of Thermal activation of low-grade mixed clays

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Keywords: supplementary cementing material; calcined clay; dehydroxylation

The reduction of CO_2 emissions related to concrete, and specifically to Portland cement production, is nowadays the biggest challenge for the construction industry. There is a number of approaches how to reduce the negative environmental effects of Portland cement calcination; it can be replaced by cements fired at lower-temperature (e.g. belitic or calcium-sulfoaluminate), by alkali-activated materials or supersulfated cement [1]. Another approach lies in the utilization of Supplementary Cementing Materials (SCM) which are substituting a significant portion of clinker in cement [2]. Probably the most promising – both technically and environmentally – today's approach is called LC^3 cement, i.e. "limestone calcined clay cement" [3]. In this cement, the content of clinker is reduced to 50% while the rest of the material is limestone (15%), gypsum (5%) and calcined clay (30%). So far the highest attention has been paid to calcined kaolinitic clay as the LC^3 component since calcined kaolinite is providing the highest pozzolanic reactivity among the clay minerals [4]. On the other hand, pure kaolinites are relatively valuable raw materials while low-grade clays, often containing more clay minerals, are easily available all around the world.

The present paper deals with the thermal activation of four different clays which are intended to be used as a component of cementitious binder. Two of these clays are kaolinite-illite with different content of quartz; the other one is kaolinitic-illitic loess with higher content of calcite. Finally, a well know kaolin is used as a benchmark. The thermal activation was studied by means of TG/DSC thermal analysis and by XRD collected at significant points of interest. The evolution of the pozzolanic activity of intermediates was monitored by the lime-saturation test.

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Characterization of asbestos-containing wastes by thermal analysis

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Keywords: cement-asbestos, asbestos-containing wastes, thermal decomposition, thermal analysis

Asbestos is a general name used to describe a group of several naturally occurring minerals that have unique chemical and physical properties. Chemically, these minerals belong to the group of hydrated silicates containing various metal ions, mainly magnesium, iron and calcium. From the mineralogical point of view, asbestos minerals are divided into two groups: the serpentine group and the amphibole group. A characteristic feature of all asbestos minerals is their fibrous structure.

Asbestos gained the greatest importance at the turn of the 19th and 20th centuries. It was used in the manufacture of more than 3,000 different products, depending on their end use, mainly in the construction industry. One of the most popular assortment based on asbestos were cement-asbestos products. It was estimated that more than 80% of the world mined asbestos was used for the production of this type of building products.

Nowadays we've known that asbestos is dangerous and asbestos fibres possess carcinogenic properties. Due this fact, asbestos-containing materials are considered as dangerous wastes and they are stored in special landfills designated for dangerous wastes. This is not a final solution for the asbestos problem, because fibrous structure of asbestos in this wastes is still maintained and there is no guarantee of no secondary contamination. It is necessary to find more adequate methods in which the dangerous fibrous structure of asbestos could be destroyed. One of proposed methods should be thermal decomposition. During heating of asbestos chemical water from asbestos minerals is released what leads to changes in crystal structure and formation new mineral phases. A similar mechanism should be expected in the case of cement-asbestos products, but in this case there are also cementitious matrix in the system which could influence on the whole process.

In the present study asbestos-containing wastes in the form of cement-asbestos materials coming from different places were examined. These asbestos-containing materials were characterized by chemical analysis (XRF) connected with mineralogical phase analysis by powder X-ray diffraction (XRD) as well as scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS). Thermal decomposition of samples was studied by differential thermal analysis (DTA), thermogravimetric measurements with evolved gas analysis (TG-EGA) as well as high-temperature microscopy. Change of microstructure was also determined based on infrared spectroscopy (IR) and mercury porosimetry. Obtained results show that during thermal treatment significant changes occurs in the material allow for further re-use of thermally treated asbestos wastes.

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Studies on the reactivity of aluminosilicate addition in the hydrated calcium aluminate cement system

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Keywords: calcium aluminate cement, aluminosilicate addition, hydration

The usage of mineral additions as a substitution part of cement is a well-known method of economical and ecological benefits. It is advisable to the minerals to be not only a microfiller but also react in the hydrating cement matrix. Calcium aluminate cement (CAC) hydration process is very sensitive to conditions, especially temperature. At low and ambient temperatures metastable calcium aluminate hydrates form firstly which then transform to stable products within time or/and with the temperature rising, while at elevated temperature the stable products already arise. Therefore the effect of any additional materials incorporated in such complicated system needs to be study precisely.

The aim of this work was to evaluate the activity of aluminosilicate addition in hydrating calcium aluminate cement system depending on time of the hydration process at different curing temperature. The hydrates formed were recognized by thermal analysis and X-ray diffraction and the microstructure were observed by SEM/BSE method. Moreover the TG analysis, presented in work [1], was used to estimate the effect of the studied addition on conversion degree of CAC. On the basis of obtained results it was found, that the potential reactivity of studied minerals strictly depends on the temperature conditions [2].

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Mix proportion and experimental study of heavyweight self-compacting concrete based on magnetite and barite

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Keywords: heavyweight concrete, self-compacting concrete, heavy aggregates, material composition, hydration heat, particle size distribution, mechanical and physical properties

Heavyweight Self-Compacting Concrete (HWSCC) can be considered as Heavyweight Concrete with the rheological requirements of Self-Compacting concrete at fresh state or Self-Compacting Concrete with bulk density higher than 2,600 kg.m^{-3}. Self-compacting concrete is an advanced concrete with wide applications because of its high filling ability, passing ability, segregation resistance and excellent workability [1,2]. One major benefit of SCC is that it can be used in the specific infrastructure with complicated design architecture where it is hard to use vibrators for concrete consolidation [2]. A specific class of concrete using high density aggregates, the so-called heavyweight concrete was developed and used mainly as biological shielding in operating nuclear power plants (NPPs), medical units, particle accelerator facilities or repositories for radioactive nuclear wastes where the concrete is exposed to neutron or gamma-ray radiation [3].

The present study aims at determining the mix proportion of binder, heavyweight aggregates, water-to-binder ratio, and additives to develop self-compacting concrete with bulk density higher than 2 600 km^{-3}. The hydration heat of the binder was determined by TAM AIR 8-Channel isothermal calorimeter for the purpose of massive structures. Indeed, massive constructions are under strict control of durability due to the temperature gradient that can cause the crack or surface shrinkage and fissure during the lifetime of concrete. Exothermic hydration reaction of cement generates fast temperature rise in core of concrete structure originating thus temperature difference with concrete surface. As consequence of non-uniform heat distribution and thermal conductivity, the temperature gradient will cause tensile stress [4]. The work also aims at evaluating the engineering properties, pore structure, and microstructure of established heavyweight self-compacting concrete. Barite (BA), magnetite (MAG) or their mix (MIX) were used as fillers, while binder was composed of Portland cement, blast furnace slag, metakaolin, and limestone at a ratio of 65:15:5:15. Basing on text results of V-funnel, S-Cone diameter and S-Cone time, the proportion mix and binder: filler: binder to cement ration was optimized as follows1) BA 1: 3.5: 0.42, 2) MAG 1: 4: 0.42, 3) MIX 1: 3.75: 0.42 with maximal aggregate size not exceeding 2 mm. Not only was bulk density influenced by aggregate density, but also the mechanical properties, shrinkage, dynamic modulus of elasticity pore structure and microstructure were found dependent on fillers.

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Analyzing the thermal properties of geopolymers: a case study on energy conservation for the construction sector

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Keywords: geopolymers, thermal conductivity, thermal diffusivity, energy conservation, sustainability, iron waste.

In recent years there is a greater awareness and need to adopt more sustainable attitudes. One example is the research into new building materials to replace normal Portland cement (OPC). To contextualize, manufacturing OPC contributes about 6-7% of CO_2 release into the atmosphere, which contributes to climate changes [1]. Additionally, there is a need for greater awareness regarding energy conservation when designing the buildings, which requires using strategies to improve energy efficiency. To address this, recently, there has been increased interest in geopolymers production, due to their excellent mechanical and thermal properties [2]. These new construction materials consist of geomaterials, mainly metakaolin (MK) that are activated by alkaline solutions. To make them even more sustainable, by-products from other industries are used as additives in geopolymer´s formulations. This work is focused on preparation of metakaolin-based geopolymers containing iron ore residues in order to better conserve thermal energy in the interior of the buildings.

To achieve this goal, we analysed the thermal properties: conductivity (λ), diffusivity (α) and specific heat (Cp) of geopolymer samples composed of 100% MK (100MK), 50% MK plus 50% hematite ore from Moncorvo Mine, Portugal (50MK50HEM) and 50% MK plus 50% pyrite and chalcopyrite waste from Tinoca Mine, Portugal (50MK50MT). Alkaline activators used for geopolymers formulation were sodium hydroxide and sodium silicate. Geopolymer pastes were inserted into a cylindrical specimen of 39 mm diameter and 100 mm height. Curing was performed at a room temperature for 28 days. OPC sample prepared with ratio of 1:3 (cement: sand) was used as a reference. Two techniques were applied, one using a thermal needle (Thermtest) and the other using lateral heating (non-stationary method) and the software Matlab with the objective of solving the diffusivity in the differential heat equation, from temperatures acquired at three different points along the specimen with the software LabView and a DAQ (Data Acquisition).

Obtained λ results show that the highest values has 50MK50HEM with results between 0.663-0.699 W/m.K and the lowest value shows 50MK50MT with 0.280-0.360 W/m.K. The 100MK has a lower λ value compared to the OPC, between 0.391-0.455 W/m.K and 0.545-0.576 W/m.K, respectively. As for the α results, the formulation 50MK50HEM has the highest value with $1.14x10^{-6}$ m^2.s and 50MK50MT the lowest value with $2.01x10^{-7}$ m^2.s. 100MK shows a lower value of α than the OPC with $2.76x10^{-7}$ m^2.s and $3.16x10^{-7}$ m^2.s, respectively. Concerning Cp values, it was found that both 100MK and OPC reach similar values, 1100 J/Kg.K and 1082 J/Kg.K, respectively. Regarding the formulations with iron residues it was found that the formulation 50MK50HEM has a lower value with 346 J/Kg.K and 50MK-50MT has the highest value with 1208 J/Kg.K.

When comparing the results, it is highlighted that the thermal properties of geopolymers are better than the OPC, reinforcing the idea that it is possible to substitute and choose a more environmentally friendly construction improving energy efficiency. In addition, when checking the values between the geopolymers with the addition of iron waste, it is possible to conclude that the formulation 50MK50MT has a lower value of λ and α, which improves heat storage and temperature conservation in interior of the buildings.

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Phase development of lime-based plasters blended with waste calcined shale studied by means of thermal analysis

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Keywords: lime-based plasters, waste calcined shale, thermal analysis, phase development

Restoration of historical buildings requires an application of suitable and convenient materials which are compatible with historical legacy. On the other hand, the used materials have to show adequate durability and fulfil current tendencies of environmental-friendliness policy. When focused on historical buildings, most of them have their facades made of lime-based, more precisely blended-lime-based plasters. On that account, the issue of blended-lime plasters has re-become of great importance as the attention to historical restoration has increased [1, 2].

Contrary to pure air-lime plasters, blended-lime show hydraulic properties (according to particular additive and its dosage), and therefore promises better mechanical properties and improved durability. Apart from Portland cement which is not really suitable from a historical point of view, metakaolin belongs to one of the most common representatives of pozzolanic admixtures used for lime-based plasters [3,4]. Metakaolin is an artificial product, which arises by the calcination of kaolinitic clay or claystone at temperatures of about 550-900°C. Similarly to every other production process, a remarkable amount of waste rises also in the case of metakaolin. This study is aimed at the utilization of this waste; specifically, the waste calcined shale (WCS). It is composed of not properly burned particles with varying compositions. Contrary to metakaolin, it contains a lower amount of amorphous phase and a higher amount of kaolinite and mullite minerals.

Lime-based plasters with a dosage of up to 50% WCS are investigated and their phase development in time is described. During the hardening of these plasters, the carbonation process takes place in combination with the pozzolanic reactions. It gives rise to a higher amount of amorphous structures; about 15% in the case of pure lime contrary to up to 45% in the highest dosage of WCS. These are not possible to be characterised using X-ray diffraction which is suitable for phase analysation. However, a combination with thermal analysis seems to be a promising way how to estimate the composition of an amorphous part and thus complement the phase development of designed blended plasters. Obtained phase analyses are supported by the determination of mechanical properties and SEM analysis, also measured depending on time.

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Ceramics, glasses

Microstructure and mechanical properties of ceramic material in system Al_2O_3-Y_2O_3 prepared by horizontal directed crystallization method

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Keywords: eutectic microstructure, high-temperature applications, thermal analysis, mechanical properties

Ceramic materials in the system Al_2O_3-Y_2O_3 with eutectic composition were successfully grown by the Horizontal Directed Crystallization Method in the boat shape molybdenum container, forming a bulk with the dimensions of 210 x 180 x 25 mm. The thoroughly mixed powders of the composition 81.5 mol.% aluminium oxide and 18.5 mol.% yttrium oxide were pressed, then annealed at the temperature of 1400°C for 10 hours, and subsequently used as a starting material. The pulling rates of crystallization container for eutectic growth were 10 mm.h^{-1} and 20 mm.h^{-1}, and the temperature ranged from 1800°C to 2000°C depending on the distance of individual parts of the container from the heating element. The five cylindrical samples (height ~ 5 mm, diameter ~ 12 mm) were cut from different parts of finished bulk material and subjected to X-ray diffraction analysis, which confirmed only the presence of YAG and α-Al_2O_3 phases with a preferred crystal growth orientation in all samples. The densities of studied samples, measured using a He-pycnometer, were around 4.32 g.cm^{-3}.

The microstructure and mechanical properties of polished samples were investigated in both planes – on the surface and in cross-section of the samples. The SEM analysis showed a very fine and highly homogeneous microstructure with the Al_2O_3-rich grains regularly distributed in the YAG matrix. The Vickers hardness $H_V \sim 16 \pm 0.4$ GPa and fracture toughness $K_{IC} \sim 3.8 \pm 0.5$MPa m$^{1/2}$ were measured, and the best results were obtained in case of the sample prepared at the pulling rate of 20 mm.h^{-1}.

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Thermal properties and thermodynamic model of lithium doped 45S5 bioglass

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Keywords: 45S5 Bioglass, Li_2O, thermodynamic model, TMA,

Shakhmatkin and Vedishcheva thermodynamic model (SV TDM) [1] of 45S5 bioglass [2] doped with three different amounts of Li_2O (0.0, 4.1, 9.9, and 12.3 mol. %) was evaluated at T = 800 K. 55 components of TDM were considered, among them 12 lithium containing compounds. Only 9 components were present in significant equilibrium molar amount for each studied glass composition. In all glass compositions containing nonzero amount of Li_2O, the three Lithium compounds with not negligible equilibrium amount were identified, i.e. $Li_2O.SiO_2$, $3Li_2O.P_2O_5$, $Li_2O.2CaO.2SiO_2$. In the 45S5 glass composition four phosphate compounds with negligible abundance were identified: $9Na_2O.6SiO_2.2P_2O_5$, $Na_2O.2CaO.P_2O_5$, $5Na_2O.4SiO_2.P_2O_5$, and $Na_2O.CaO.P_2O_5$. In all other glasses the $3Li_2O.P_2O_5$ was found with not negligible abundance. Moreover, in the glass with 4.1 mol.% Li_2O the $Na_2O.2CaO.P_2O_5$ compound was found with not negligible abundance. For each studied glass the glass transition temperature (T_g), coefficient of thermal expansion of glass (α_g) and metastable melt (α_m) were measured by thermodilatometry. The low temperature viscosity was measured by thermomechanical analysis. The viscous flow activation energy was evaluated from the viscosity temperature dependence [3]. The compositional dependence of measured thermal properties was evaluated by correlation analysis with the Q-distribution of silicate and phosphate units [4].

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Heat induced reactions in ceramics described in terms of dc electrical conductivity

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Keywords: DC conductivity, ceramics, clay, thermal analyses

To produce ceramic material from raw clays, the firing of the prepared body is required. During the transformation from clay to ceramic, several reactions occur in the sample – dehydration, burning of organics, dehydroxylation, etc. These reactions can be well monitored using conventional thermal analyses – differential thermal analysis, differential scanning calorimetry, thermogravimetry, and dilatometry. Nevertheless, changes in the material often are linked to a movement of ions, the charge carrying species in dielectrics. In the initial stages of firing, where the physically bound water is removed, H^+ and OH^- ions are the dominant charge carriers. Once this reaction is finished, the conductivity decreases as only a few ions are involved in the conduction mechanism. However, as the temperature increases, the ions receive more energy in the form of heat and they eventually overcome the potential barrier of the well. In turn, the electrical conductivity increases. Starting at ~450°C, the structurally bound water is removed from the illite and/or kaolinite lattice. The concentration of the free charge carriers increases which leads to an increase in the electrical conductivity. After the dehydroxylation process is complete, the thermal energy of the ions becomes high enough to enable their participation in the conduction mechanism. At high temperatures crystallization of new mineral phases takes place. The crystallization results in the collective arrangement of ions, which affects the electrical conductivity. Moreover, the appearance of a glassy phase at high temperatures allows the formation of continuous conduction paths, which in turn steeply increases the electrical conductivity.

Stemming from the above-described response of electrical conductivity to the reactions running in the materials, it is clear that the use of electrical conductivity measurements during heating provides valuable information about these reactions. Moreover, measurement of the temperature dependence of electrical conductivity allows the calculation of activation energy (of conduction), which provides information about the nature of the charge carrying species. Therefore, the temperature dependence of electrical conductivity of an illitic clay with oil shale ash is presented and analysed. Conventional thermal analyses – differential thermal analysis, differential scanning calorimetry, thermogravimetry, and dilatometry – were employed to support the results of the conductivity measurements.

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Thermogravimetric analysis of oxidation reaction of graphites for refractory materials

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Keywords: graphite, oxidation, refractory materials, kinetics, isoconversional methods

Graphite is compound of refractory materials because of low thermal expansion and hight thermal conductivity what causes good thermal shock resistance and high liquid medium corrosion resistance due to low wettability. Despite the fact that graphite-containing refractories work in places where there is a relatively small amount of oxygen for example metallurgical industry, the oxidation of graphite with oxygen from the gaseous phase is one of the most important factors affecting the destruction of graphite refractory materials. [1] In order to improve the oxidation resistance of graphite materials, attempts are made to apply protective layers to the finished refractory product or to the graphite raw material used for the production of the refractory material. [2–4]

In this work, thermogravimetric tests were carried out to assume the effectiveness of the protective layer applied to the graphites. Two grades of graphite used in the production of graphite contain refractory materials were tested. The tested graphites differed in grain size and carbon content. The tests were performed on graphites without additional preparation and after applying a protective layer of SiO_2, and CaB_6 as antioxidant. Thermogravimetric tests were carried out in non-isothermal conditions with four different heating rates of 2, 5, 8 and 10 K/min. For the recorded measurement data, a kinetic analysis was carried out in the temperature range of 873 K to 1373 K. The use of the isoconversional methods for kinetic analysis made it possible to calculate the apparent activation energy of the oxidation reaction of four tested graphite samples in function of conversion (α). It was shown that the apparent activation energy of the graphite oxidation reaction changes with the change of the degree of conversion (α). The apparent activation energies of the oxidation reaction of graphite samples with protective coatings are higher than the apparent activation energies of the oxidation reaction of the same graphites without coatings.

The selection of the kinetic equation describing the oxidation reaction mechanism of the examined graphites revealed that all four graphite samples react according to the mechanism in which the rate of the process is controlled by the diffusion of gaseous substrates and products.

The performed thermogravimetric tests and kinetic analysis confirmed the protective effect of the coatings applied to the graphites.

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Thermodynamic model of 45S5 bioglass

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Keywords: thermodynamic model, Bioglass, 45S5, Q-distributions, MAS NMR

Shakhmatkin and Vedishcheva thermodynamic model (SV TDM) [1] of 45S5 bioglass was evaluated at T = 800 K. From 42 considered system components only 7 components ($Na_2O.SiO_2$, $Na_2O.3CaO.6SiO_2$, $3CaO.2SiO_2$, $CaO.SiO_2$, $9Na_2O.6SiO_2.2P_2O_5$, $2CaO.SiO_2$, and $Na_2O.2CaO.P_2O_5$) were present in significant equilibrium molar amount. The calculated Q-distribution of silicate units (22.6 % of Q^3, 63.1 % of Q^2, 10.1 % of Q^1, and 4.2 % of Q^0) was compared with the Q-distribution for so called crystalline reference state (CRS) evaluated by Conradt [2] (6.3 % of Q^3, 93.7 % of Q^2). Further both Q-distributions were compared with the MAS NMR experimental data obtained by different authors (e.g. 33.3 % of Q^3, 54.5 % of Q^2, and 12.2 % of Q^1 obtained by Pedone, or 17.8 % of Q^3, 76.7 % of Q^2, and 5.5 % of Q^1 published by Bhaskar) [3, 4]. It was concluded that there is no principal difference between SV TDM and MAS NMR distributions of silicate units. Further the Q-distribution of phosphate units was analyzed. The CRS resulted in 100% presence of Q^0 units (i.e. PO_4^{3-}). The SV TDM resulted in significantly broader distribution, i.e. 4.5 % of Q^2, 10.4 % of Q^1, and 85.1 % of Q^0. This distribution is comparable with those obtained by MAS NMR (e.g. Pedone reported 26.7 % of Q^1, and 73.3 % of Q^0).

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Preparation of monophasic yag raw material by multi-stage process

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Keywords: yttrium-aluminium garnet, solid-state reaction, micrometer-sized powders, simple model, multi-stage synthesis process.

The paper is aimed at developing a technique acceptable for a large-scale production of $Y_3Al_5O_{12}$ (YAG) monophasic raw material by the solid-state reaction method (SSR) from commercial powders of micrometer-sized Y_2O_3 and Al_2O_3 using a simple and affordable equipment. The SSR proceeds according to the phase formation mechanism: $Y_2O_3 + Al_2O_3 \rightarrow Y_4Al_2O_9 + Al_2O_3 \rightarrow YAlO_3 + Al_2O_3 \rightarrow Y_3Al_5O_{12}$ and is limited by Al^{3+} diffusion through the intermediate product layers [1]. The hypothesis assuming destruction of the diffusion layers between the contacting powder grains and subsequent reaction rate acceleration by grinding a partially reacted mixture was proposed.

On this basis, a study of multi-stage synthesis (MSS) scheme including the pre-milling in ethanol (24 h, 48 h and 72h), annealing at 1150 °C (24 h) and 1250 °C (10 h) followed by grinding after each step and final stage consisting of cold uniaxial pressing and firing at 1450 °C (10 h) was carried out. The morphology characterization of the powders was carried out by SEM and SEM EDX. The phase composition of the mixture of Y_2O_3 (99.99%) and Al_2O_3 (99.99%) with the garnet molar ratio subjected to various thermal and mechanical treatments were quantified by XRD and Rietveld refinement.

Sufficient time of pre-milling yielding the maximum content of YAG after the firing at 1150 °C was 48 h. At the second stage, the effect of intermediate mixing on the phase formation of YAG was shown: for the powder that was not ground before firing (at 1250 °C) YAG increment was not observed, while in the case of the ground powder, the phase increment was about 13%, which confirmed the hypothesis defined above.

In the individual MSS processes three-stage and two-stage (1150 °C+1450 °C) process a different increment in garnet content from 79 % to 93 % and from 63 % to 100 %, was observed respectively, which indicates a significant slowdown of the reaction kinetics in the first case.

A simple model determining the concept of an intermediate critical product concentration was proposed. In case a critical concentration of the product at the intermediate stage of the process is exceeded, grinding negatively affects the SSR.

The two-stage scheme of YAG synthesis was found to exhibit higher efficiency in comparison with the conventional one-stage method.

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Thermal, structural and optical aspects for germanate ceramics

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Keywords: ceramics, lanthanide ions, structure, properties

Germanate ceramics are perspective materials for numerous practical applications. They are suitable low-phonon matrices for transition metal and lanthanide doped laser materials and the efficient phosphors emitting visible light or infrared radiation. Among others, Li_2MgGeO_4 belongs to wide family of germanate compounds with olivine structure [1] and shows superior dielectric and optical properties. Germanate ceramics $Li_2MgGeO_4:Mn^{2+}$ were proposed as green-emitting phosphors adopted for persistent luminescence applications [2]. However, germanate olivines containing lanthanide ions have not been often studied, to the best of our knowledge. Here, we present some thermal, structural and optical aspects for un-doped and lanthanide doped germanate ceramics. Preliminary results are presented and discussed by us in the previous work published recently [3]. Thermal properties have been examined based on DSC measurements. For Li_2MgGeO_4 compounds, two reversible phase transitions were verified during heating and cooling process. Structural aspects were evidenced by X-ray diffraction, scanning electron microscopy, Raman and IR-ATR spectroscopy. The X-ray diffraction analysis confirmed that Li_2MgGeO_4 ceramics crystallize in monoclinic crystal lattice. Optical studies revealed that broad blue/green emission attributed with the presence of magnesium in ceramic matrix and assigned to F-type centers is well overlapped with narrow emission lines characteristic for lanthanide ions. Optical data are well correlated with thermal and structural results obtained for olivine-type germanate ceramics.

Acknowledgments
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Influence of Titanium dioxide concentration on thermal properties of germanate based glasses

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Keywords: glasses, thermal properties, thermal stability parameters, structure-property relationship

Previous results published for inorganic glasses proved that the presence of modifier oxides [1] or rare earths [2] playing the role as the optical activators has an important influence on their thermal properties. Among metal oxides that are components of photonic glasses emitting visible light or infrared radiation, titanium(IV) oxide (TiO_2) deserves particular attention. The introduction of titanium dioxide to the glass increases the refractive indices and the radiative transition rates. Thermal investigations demonstrate that glasses with low TiO_2 content exhibit high stability against crystallization. Moreover, small quantities of TiO_2 enhance the glass-forming ability and chemical durability of the glass systems [3]. Our studies indicated that multicomponent germanate based glasses with relatively high TiO_2 concentration are preferred for near-infrared luminescence of Er^{3+} ions at 1500 nm in the third telecommunication window [4]. Therefore, it is necessary to synthesize thermally stable and fully amorphous precursor systems with high TiO_2 concentrations, which can be applied to optical fiber drawing. In this work, the influence of TiO_2 concentration on thermal behavior of germanate based glass has been studied using differential scanning calorimetry (DSC). From DSC curves characteristic temperatures such as the glass transition temperature T_g, the crystallization onset T_x, the maximum of crystallization peak T_p and the melting temperature T_m were evaluated. Based on characteristic temperatures obtained for the studied glass samples, the thermal stability parameter ΔT referred as T_x-T_g was also calculated. The larger values of ΔT give a larger working range during operations for fiber drawing. If ΔT is higher than 100°C, glass can be considered as a glass with relatively good thermal ability. In our case, the glass transition temperature T_g increases whereas the thermal stability parameter ΔT is reduced with increasing TiO_2 concentration in glass composition. However, the values of ΔT are still higher than 100°C suggesting that titanate-germanate glass samples exhibit good thermal stability against devitrification, giving quite large working range during operations for fiber drawing. The Hruby parameter the Saad-Poulain criterion [5, 6] were also applied to further evaluate the thermal glass stability. These aspects are presented and discussed in details.

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Implications of sulfate addition on glass forming properties of the SiO_2-P_2O_5-K_2O-MgO-CaO system

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Keywords: silicate-phosphate glasses, sulfates, thermal properties, glass transition, crystallization

A commonly accepted theory suggests that if the rate of cooling of any solid substance's melt is sufficiently high, the subsequent crystallization phenomenon may be avoided and the substance undergoes vitrification instead, incorporating an amorphous form. Although this supposition may hold true for the broad range of substances, there are certain systems, transformation of which into the glassy state constitutes quite an endeavor. Such formulations are composed of elements which chemical properties as well as the character of their bonds with network anions are markedly different, excluding at the same time the possibility of creating shared bonds between their polyhedra. Among such systems one can find silicate-based sulfate-bearing glasses known of very low capability to incorporate SO_4^{2-} anions to their vitreous, spatially polymerized framework. Intricacies governing this unusual system have prompted numerous scientists to investigate the factors determining the glass forming range of such materials. Given the above, the primary purpose of the present study constituted an incorporation of sulfate species into the silicate-phosphate glass system enriched with two alkaline earth glass modifiers, MgO and CaO (in accordance with the theory stating that network modifiers facilitate glass formation in incompatible systems), and analysis of their subsequent glass forming properties. Furthermore, the study has been driven by the goal of formulating a glass composition of optimal sulfate-bearing properties, which, in turn, would enable the development of environmentally-friendly vitreous fertilizers, supplying plants not only with bioavailable sulfur, but also – phosphorus, potassium, and magnesium to name a few. Therefore, materials from the SiO_2-P_2O_5-K_2O-MgO-CaO-SO_3 system have been acquired via conventional high-temperature melting of glass batches and quenching the as-obtained melts by pouring them into the water-filled container (fritting). The investigation of the implications of sulfate addition on glass forming properties of glass samples have been proceeded by combining: preliminary study of acquired materials (XRF, XRD methods), in-depth analysis of their thermal behavior (DSC technique combined with an estimation of glass-stability parameters), detailed characteristics of their crystallization course as well as an identification of the as-formed crystalline phases (XRD, Raman Imaging technique). Performed investigations revealed that sulfur addition exerts a marked effect on the thermal properties of tested glasses, limiting their glass-forming range, increasing their propensity towards crystallization and lowering thermal stability as well as altering the domain structure of such materials. Due to the lack of sufficient data regarding the effect of sulfur on the thermal behavior of silicate-phosphate melts, the obtained results will provide a substantially contribution to the knowledge of SO_4^{2-}-containing glasses family and may serve as guiding suggestions for optimizing not only their composition but also - the production process.

Acknowledgments

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Kinetic analysis of the formation of high-temperature phases in illitic clay and limestone mixtures

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Keywords: illite; anorthite; gehlenite; DSC, activation energy

The production of traditional ceramics consists of many steps, such as clay mining, mixing with other additives, drying, or firing [1]. Among these processes, the firing is the most important step. During firing, the final properties of the ceramic product are obtained, such as mechanical strength, hardness, or microstructural durability. The most significant changes in ceramics occur when they are thermally treated. During this thermal treatment new phases are formed. The addition of materials with a high content of CaO, such as fly ash or waste limestone, into clays is connected with a formation of anorthite [2–4]. For this purpose a non-isothermal kinetic analysis of the anorthite and gehlenite crystallizations in an illitic clay and limestone mixtures are studied. In this study, the illitic clay with over 80 wt.% of illite content and limestone are used as basic materials. The measurements are performed using a differential scanning calorimetry with heating rates from 1 to 15 °C/min in a dynamic Ar atmosphere. The Kissinger method is used for the parameterization of the processes.

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Cultural heritage

Multiple technique analysis of pottery and clay samples from the eneolithic settlement Şoimuş – Avicola Site/ Şoimuş – Teleghi (Șoimuș, Hunedoara County, Romania)

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Keywords: pottery, eneolitic period, thermal analysis, FTIR, TG/DTA, DSC, Raman,

The purpose of this study is to present results from analyzing pottery samples from ceramics found within the archaeological site Neo-Aeneolithic settlement Şoimuş - Avicola / Şoimuş - Teleghi site (Șoimuș, Hunedoara County, Romania), a settlement inhabited during the Neolithic, Aeneolithic, Bronze Age, first Iron Age (Hallstatt) periods, as well as during the Roman era and Medieval times [1–3].

The analyzed samples come from 10 pottery sherds, belonging to the Neolithic period of the settlement's existence and attibuted to Vinča culture (phase A3 to phase B1). The samples cover the main types (fine, semifine, coarse). The analysis was aimed at determining the composition of the wares and firing temperatures. The pottery's relation to local clay sources was also investigated through analysis of 3 clay samples from the site.

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

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Energetic materials

Manipulation with mineral chalcopyrite $CuFeS_2$ via mechanochemistry: thermoanalytical and thermoelectric performance

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Keywords: chalcopyrite, mechanical activation, thermal analysis, thermoelectrics

The properties of natural mineral chalcopyrite $CuFeS_2$ after mechanical activation in a planetary mill have been studied. The intensity of mechanical activation was controlled by changing revolutions of the mill in the range 0-600 min^{-1}. Set of characterization techniques such as XRD, SEM, TEM, BET, TA (DTA, TG, DTG), particle size analysis and UV-Vis spectroscopy was applied. Reactivity studies were also performed. Thermoelectric performance was evaluated by measuring the transport properties (Seebeck coefficient, electrical and thermal conductivity). Several new effects were revealed for mechanically activated chalcopyrite, e.g. polymodal distribution of grains in micrometer scale, agglomeration effects at higher milling time, possibility to modify shape of particles, X-ray amorphization and the shift from the non-cubic (tetragonal) structure to pseudo-cubic (or cubic-like) chalcopyrite structure. Thermoanalytical parameters like peak temperature T_m and loss of weight Δ_m for $\alpha \rightarrow \beta$ transformation was influenced by intervention of mechanical activation. The possibility of band-gap manipulation by milling and correlation between thermal conductivity and energy supply were also identified.

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Promising optoelectric and thermoelectric properties of mechanochemically synthesized skinnerite Cu_3SbS_3 and wittichenite Cu_3BiS_3

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Keywords: skinnerite Cu_3SbS_3**,** wittichenite Cu_3BiS_3, semiconductor; mechanochemistry; nanocrystals, optoelectric properties, thermoelectric properties

In recent years, ternary copper-antimony-sulphide (Cu-Sb-S) and copper-bismuth-sulphide (Cu-Bi-S) materials have received significant attention as potential absorber materials for photovoltaics as well as promising materials for thermoelectric applications due to their low-toxicity, low cost and earth-abundant elements. Optoelectric and thermoelectric properties of mechanochemically synthesized skinnerite Cu_3SbS_3 for 30 minutes and wittichenite Cu_3BiS_3 only for 5 minutes in planetary ball mill from elemental precursors in stoichiometric ratio were investigated. The synthesized nanoparticles are present in the form of microcrystalline agglomerates. The crystallite size 10 nm of monoclinic Cu_3SbS_3 and 38 nm of orthorhombic Cu_3BiS_3 was confirmed by Rietveld refinement. The nanocrystalline character of samples was also proven by transmission electron microscopy. Photoresponse was confirmed by I-V measurements under dark and light illumination. Cu_3SbS_3 nanocrystals showed ~45% enhancement of the photoresponsive current at a forward voltage of 0.6 V and Cu_3BiS_3 nanocrystals ~26% enhancement of the photoresponsive current at a voltage of 1 V compared to the current in the dark. The achieved results confirm that synthesized skinnerite Cu_3SbS_3 and wittichenite Cu_3BiS_3 are promising absorber materials for solar cell applications. Moreover, thermoelectric performance was evaluated by measuring the transport properties (Seebeck coefficient, electrical and thermal conductivity). The mechanosynthesis followed by spark plasma sintering enables to prepare such nanostructured materials with a favourable thermoelectric response.

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Predicting detonator failure using DSC data

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Keywords: PETN, detonator, thermal damage, operability, DSC

Exploding bridgewire detonators (EBWs) containing pentaerythritol tetranitrate (PETN) exposed to high temperatures may not function following discharge of the design electrical firing signal from a charged capacitor [1-3]. Knowing functionality of these arbitrarily facing EBWs is crucial when making safety assessments of detonators in accidental fires. Orientation effects are only significant when the PETN is partially melted which can be measured with differential scanning calorimetry (DSC). Non-melting EBWs will be fully functional provided the detonator never exceeds 406 K (133 °C or 271 °F) for more than 60 min. Conversely, EBWs will not functional once the average input pellet temperature exceeds 414 K (141 °C or 286 °F) for 45 seconds ensuring that the PETN completely melts. Functionality of EBW at temperatures between 406-414 K will depend on orientation and can be predicted using a stratification model for downward facing detonators but is more complex for arbitrary orientations. A conservative rule of thumb would be to assume that the EBW is fully functional until the input pellet completely melts.

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Reactivity studies of mixed metal iron-manganese based oxygen carriers

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Keywords: CLC, TGA analysis, oxygen carriers

Chemical Looping Combustion (CLC) is a novel technology that allows to burn wide range of fuels (gaseous, liquid or solid) without atmospheric air. It is possible due to application of two reactor system with substance called Oxygen Carrier (OC) circulating in-between them. OC is usually a material composed with one or more metal oxides capable to release and bonding oxygen due to direct reaction with a fuel or spontaneously, due to changes in temperature or partial pressure of the oxygen. One of most popular materials used as oxygen carriers are oxides of iron and manganese. Iron oxides are relatively cheap while manganese oxides are capable for spontaneous releasing oxygen (so called CLOU properties, Chemical Looping with Oxygen Uncoupling). Addition of inert materials, like ZrO_2 or TiO_2 to active phases as iron oxide may be beneficial. For example addition of inert is used to reinforce physical properties of oxygen carrier like mechanical durability.

In this work, reactivity study results of selected mixed iron-manganese oxides, oxygen carriers are shown. Tests were performed to determine OCs CLOU properties and reactivity toward selected solid fuel.

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Energy conversion and storage

The effect of calcium amount and non-stoichiometry in the A-sublattice on the properties of doped strontium calcium titanate

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Keywords: calcium-strontium titanate, perovskite structure, redox properties

Calcium titanate ($CaTiO_3$) and strontium titanate ($SrTiO_3$) are representative examples of perovskite-type compounds (ABO_3) with a wide and constantly growing spectrum of applications, e.g. in modern technologies in the field of energy storage and conversion. Appropriate doping of these materials (mainly with *d*-block elements) can modify their properties, especially electrical, catalytic and thermal. The aim of the research was to investigate the effect of calcium content and assumed non-stoichiometry in the A-sublattice on the structural, redox and electrical properties of the materials.

A series of samples based on a mixed system of $SrTiO_3$ – $CaTiO_3$ doped with cobalt, differing in the presence of non-stoichiometry and calcium content, was synthesized using the modified sol-gel method. It is expected that the introduced cobalt can be incorporated into the perovskite structure and/or can form oxides on the surface of the perovskite. In addition, previous studies have shown that the introduction of non-stoichiometry in the strontium sublattice should result in an increase in the amount of dopant incorporated into the titanium sublattice.

Systems with the following nominal compositions: $Sr_{0.8}Ca_{0.2}Ti_{0.95}Co_{0.05}O_3$, $(Sr_{0.8}Ca_{0.2})_{0.95}Ti_{0.95}Co_{0.05}O_3$, $Sr_{0.2}Ca_{0.8}Ti_{0.95}Co_{0.05}O_3$ and $(Sr_{0.2}Ca_{0.8})_{0.95}Ti_{0.95}Co_{0.05}O_3$ were obtained as powders (after calcination at 900°C) and porous and dense sinters (obtained by sintering at various temperatures: 1200 and 1400°C). The resulting materials were examined in terms of their structure (XRD analysis and Rietveld refinement), microstructure (SEM observations) as well as redox (TPR/TPOx) and electrical properties (DC measurements). In order to observe the distribution of cobalt and calcium in the samples after sintering, the energy-dispersive X-ray spectroscopy (EDS) analysis in the mapping mode was performed.

Based on the Rietveld refinement it can be stated that all materials, except of $Sr_{0.8}Ca_{0.2}Ti_{0.95}Co_{0.05}O_3$ in the form of powder, were single-phase since strontium titanate or calcium titanate was the only observed phase. For $Sr_{0.8}Ca_{0.2}Ti_{0.95}Co_{0.05}O_3$ material in the form of powder small amount of strontium carbonate was also detected. The shape of the TPR profiles and temperature range of reduction effects (Figure 1) indicate the existence of cobalt in the form of oxides on the surface (REGION I) and/or cobalt incorporated into the perovskite structure (REGION II) for all samples. However, intensification of reduction effects for materials sintered at 1200°C is observed. Additionally, TPR results indicate that the higher amount of Ca in the perovskite structure privilege the incorporation of cobalt into strontium titanate.

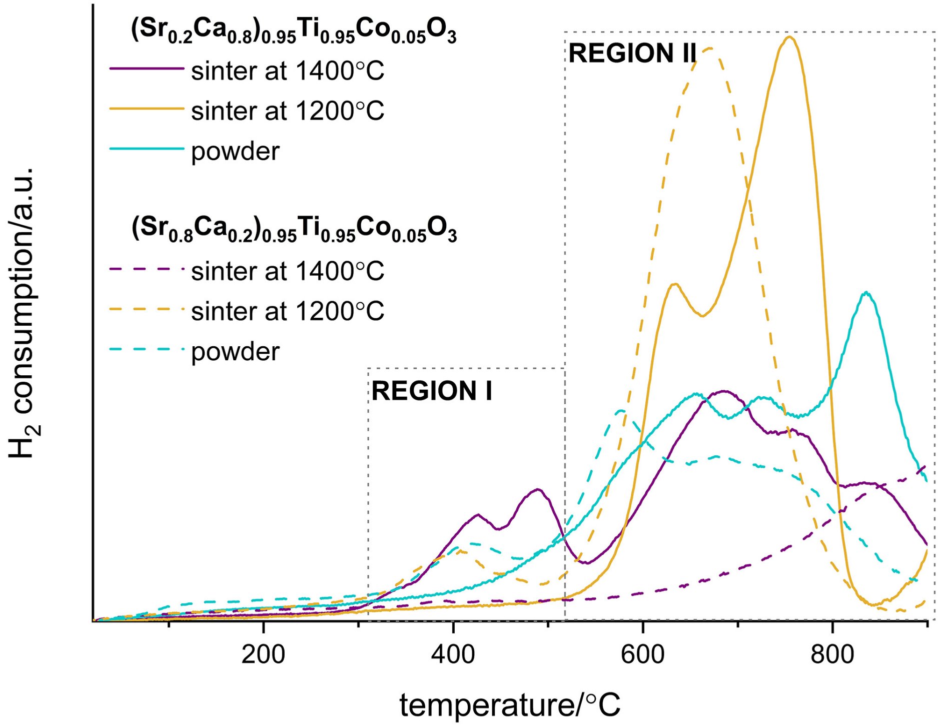

Figure 1. TPR-H_2 profiles for $(Sr_{0.2}Ca_{0.8})_{0.95}Ti_{0.95}Co_{0.05}O_3$ and $(Sr_{0.8}Ca_{0.2})_{0.95}Ti_{0.95}Co_{0.05}O_3$ samples.

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Electrochemical properties of sulfates of transition metals and sodium as electrode materials in hybrid metal-ion batteries

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Keywords: electrode materials, $Na_{2+2\delta}(Me_{1-x}Mn_x)_{2-\delta}(SO_4)_3$, electrolyte based on ionic liquid, hybrid metal-ion batteries

The modern requirements for lithium-ion batteries are that they are more efficient, safer, and more environmentally friendly than those created till now. The main groups of chemical compounds that are studied in this area are oxides and polyanionic compounds. Among the polyanionic compounds, sodium transition metal sulfates are one of the promising materials due to their low cost as electrode materials and high operating voltage for alkali ion intercalation. Most of these compounds have an aluaudite-type structure, which is an excellent intercalation matrix, providing the possibility of high alkali ion mobility [1]. By combining the high-performance, high-energy-density electrode materials of LiIBs with the safety and low cost of NaIBs, a new type of hybrid Li/Na batteries have been introduced. In these hybrid metal-ion batteries (HMIBs), energy storage is performed due to co-intercalation reactions of Li^+/Na^+ ion pairs [2].

With the present study, we provide expanded data on the redox properties of sodium transition metals sulfates $Na_{2+2\delta}(Me_{1-x}Mn_x)_{2-\delta}(SO_4)_3$ ($0 < x > 1$; Me = Co, Cu) as positive electrodes in hybrid metal-ion batteries. Cycling voltammetry experiments are done to monitor the redox properties using the Swagelok-type model three-electrode cells vs. Li metal as a negative and reference electrode. The electrochemical experiments were carried out in different electrolytes, including conventional carbonate-based electrolyte and ionic liquid: 1M $LiPF_6$ in EC:DMC (1:1 vol.%), 1M $LiPF_6$ in EC-DMC-DEC (1:1:1 vol.%), 1M LiFSI in EC:DMC (1:1 vol.%), LiTFSI-$Pyr_{1,3}$FSI (1:9 ratio) and etc. The best electrochemical performance is observed when the electrolyte is LiTFSI dissolved in an ionic liquid N-Propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide. The sulfate materials display a hybrid behavior, where the Me-to-Mn ratio affects the Faradaic and non-Faradaic reactions in a different way. Further, the electrochemical performance is improved at elevated temperatures of 40 and 60 °C. Based on these data, the sulfates are used as positive electrodes in hybrid metal-ion cells vs. $Li_4Ti_5O_{12}$ negative electrode.

The results from our research could contribute to synthesizing sulfate polyanionic electrode materials for hybrid metal-ion batteries that are thought to be of future interest.

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A hybrid prediction method for study the effect of the shell-side flow microparticle fouling process on the thermal efficiency of shell and tube heat exchangers

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In the present study, a combination of deep-forward neural network-boundary conditions (DFNN-BC) and computational methods are employed to develop a long-term approach to the fouling process in the shell-side flow of a shell-and-tube heat exchanger. A 3D shell-and-tube heat exchanger with hot oil flow (800<Reynolds number<3000, T_{inlet} = 370 K) in the tube side and pure water flow and caring microparticles (dp = 1 micron) on the shell side is developed for this goal, and it operates for one month. To determine the effect of fouling on thermal efficiency, a computational method simulates the deposition of microparticles on the inner surface of the shell and the outer surface of the tube for 10,000 s. After careful verification, the results of the computational method are used to generate the DFNN-BC training data set. This supervised machine learning uses temperature variation, surface and average component velocity, deposition rate, and average thermal conductivity of tube wall as input parameters, with thermal efficiency, heat transfer rate, and fouling pattern as outputs. On the basis of the adaptive training ratio, the ADAM optimization method, and the tensor-based data transfer between computational results and DFNN-BC, distinct prediction layers with a specific number of layers and trainable neurons are developed to predict the output parameter for two months. After careful validation of the DFNN-BC results, a neural-network model-based regression method predicts the behaviour of DFNN-BC outputs for one month. The results indicated that a hybrid approach could provide a long-term solution to a complicated process such as fouling with minimal calculation costs.

Thermochromic phase change materials for thermal energy storage

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Keywords: phase change materials, thermochromic system, energy storage, leuco dyes

Latent heat storage by phase change materials (PCMs) is one of the most preferred forms of excess energy accumulation. PCMs use the latent heat of phase change to control temperatures within a particular range. Materials with different types of phase transition (solid-liquid, solid-solid, solid-gas, liquid-gas) can be used for thermal energy storage. However, due to the lowest volume changes during the phase transition, PCMs with solid-liquid and solid-solid phase transitions are the most popular [1,2]. An increase in temperature above a definite point causes a breakdown of chemical bonds in the material and heat absorption in an endothermic process during changing from solid to liquid. Also when the temperature drops material releases energy and returns to a solid state. The incorporation of the additional 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 [3,4].

In this study, TPCMs were obtained for potential energy storage applications. Three-component thermochromic systems were prepared using bromocresol purple (BCP) as leuco dye, stearic acid (SA) as a color developer, and behenyl alcohol (BA) as an organic solvent. Various mass ratios of ingredients were applied and then studied. Thermochromic, thermal, and structural properties of the obtained TPCMs were examined. Materials are characterized by high enthalpies, good thermal stability, and reversible thermochromic performance. The obtained TPCMs have the potential to be used not only as energy storage phase change materials but also as color indicators.

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Hydrolic balance effect of heating systems considering exergetic sustainability

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Keywords: large settlements, mechanical installations, hydraulic balance, energy analysis,efficiency

Energy has been evaluated quantitatively until the 21st century, and this approach has always been taken as a basis for determining efficiency strategies as well as efficiency calculations. Recent studies; The rational management of energy and the consideration of its quality instead of its quantity has shown that it is a valid parameter in the evaluation of energy efficiency. In studies aiming to keep the sustainable environment and carbon emissions constant, considering the quality of energy has been accepted as a more realistic approach. The concept of exergy, which expresses the quality of energy, is defined as the maximum work that can be obtained in the process at reference environmental conditions, and exergy is a measure of the quality of the mass-dependent energy flow. Exergy analysis is an effective concept for industrial processes and is used as an advanced tool in modern thermodynamic methods. Exergy analyzes guide the comparison of the importance of different thermodynamic factors, a good understanding of the effects of thermodynamic conditions on process effects, and the identification of the most effective ways to improve the process under consideration. An accurate understanding of exergy and information that can be provided with efficiency is necessary for scientists and engineers working in the field of environmental impact and sustainable energy systems. For this reason, links between sustainable development and energy, environment and exergy, and exergy and energy have been created in the formation of energy strategies.

In this study, energy-efficient solutions of the mechanical system that feeds a certain portion of the university campus were discussed, For this structure, mechanical system performance by hydraulic balance developed with together system choice 90/ 70 C which is preferred instead of the steam system are investigated. First, energy saving and cost-effectiveness provided with an energy-efficient system approach of mechanical system balanced hydraulics are evaluated. Besides, In this study, energy and exergy analyses have been made, and the saving potential in providing a comparative analysis is calculated considering the CO2 emission equivalent. In this study, preferences of heating water (90/70 °C) developed with hydraulic balance, improvement potentials in energetic and energetic performances are found as 51.47% and 48.55%. Besides, the saving potential of CO2 emission is provided at approximately 61.57%. In the end of the study, hydraulic balance in mechanical systems and applications, and some recommendations about the importance of exergy analysis are made.

Fire dynamics (or others for fire safety)

A mathematical model to predict the flash point behavior of solvent + ionic liquids mixtures

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Keywords: ionic liquids, thermal decomposition, flash point, activation energy, thermogravimetric analyzer (TGA).

Ionic liquids are referred to as green solvents that are an effective alternative to volatile organic solvents due to their unique property of having an extremely low vapor pressure [1,2]. Ionic liquids' low vapor pressure had led one to underestimate their fire and explosion potential [1]. It has been demonstrated that ILs' flammability hazard increases when exposed to high temperatures [3]. In this case, the ILs emit volatile organic compounds and change from their original structure. This behavior was attributed to the thermal decomposition of ILs into small ignitable molecules at high temperatures, rather than the evaporation of the original molecules of ILs [4]. As a result, high temperatures can form a high concentration of ignitable gases, reduce the liquid's flash point (FP), and so increase the flammability hazard. In potential applications in chemical processes, the ILs will be used by mixing with solvents. In the present study, a novel mathematical model was developed to predict the FP of binary mixtures of ILs + solvents. 1-Hexyl-3-methylimidazolium chloride ([C_6mim][Cl]) and 1-Ethyl-3-methylimidazolium ethylsulfate ([Emim][$EtSO_4$]) were the two investigated ILs. The two solvents used in the current study are methanol and ethanol. Totally, four binary mixtures composed of an IL and a solvent were investigated (i.e., [C_6mim][Cl] + methanol; [C_6mim][Cl] + ethanol; [Emim][$EtSO_4$] + methanol; [Emim][$EtSO_4$] + ethanol). Since the models are developed related to the decomposition theory of ILs, the decomposition products and the activation energy of the decomposition reaction of ILs are necessary. The activation energy will be estimated based on the measured data of the thermogravimetric analyzer (TGA), and the decomposition products will be analyzed by the TGA-FTIR and Py-GC/MS. The simulations showed considerably close prediction when compared to the experimental FP data. This approach can be utilized to predict the FP of ILs + solvents. The findings would greatly benefit the related industries by providing them with a better understanding of the FP behavior of ILs mixtures.

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Analysis of thermal and smoke generating properties of selected leathers

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Keywords: flammability of leather, smoke properties, thermal decomposition

Leather is widely popular due to its valuable properties. In prehistoric times, this raw material was used for outer clothing enabling the survival of ancient tribes. Currently, leather is used not only for the production of clothes and haberdashery (clothing and haberdashery industry), but has also found wide application as furniture upholstery (furniture industry), as car upholstery (automotive industry), and even in interior finishing, e.g. walls in facilities such as hotels (construction industry). The increase in the production of products and the wide range of leather applications makes it necessary to conduct experimental research and use new technologies, not only improving the performance properties, but also increasing fire safety. Products of thermal decomposition and combustion released from leather may contain easily flammable harmful organic substances, such as among others compounds left after fat liquefaction, dyeing and finishing processes of those materials [1]. Study [2] presents the impact of individual leathers processing operations (e.g. tanning, oiling) and of additives used in them, such as tannins and oiling, retanning agents and those that reduce flammability, on the quality of produced materials. Subsequent studies – [3,4] – comprise analyses pertaining to the impact exerted by tanning, including the application of diverse tannins (chromic tannin, tannin based on glutaric aldehyde and vegetal tanning agents) on the flammability of leather. The aim of this work was to analyze the thermal and smoke-generating properties of four selected leathers: grain bovine leather, lacquered bovine leather, artificial leather (leatherette), velour bovine leather. All materials were of natural origin, tanned from cow hides and tanned using different technologies. For needs of executing the objective of the study, testing has been conducted with the use of a TA INSTRUMENTS Q500 thermogravimeter and smoke tests according to EN ISO 5659-2, Second edition 2006-12-01, Plastics – Smoke generation – Part 2: Determination of optical density by a single – chamber test. The highest value of the specific optical density was achieved by the burnt artificial leather (leatherette) (362) sample in the exposure with the heat flux intensity of 25 kW/m^2 without the presence of the pilot burner flame. The grain bovine leather and velour bovine leather achieved comparable values, respectively 312 and 297, while lacquered bovine leather has the lowest value of the tested parameter and is 220. Not all tested leather samples meet the requirements of the second part of the international code of fire test procedures [5]. Grain bovine leather and lacquered bovine leather meet the requirements for smoke generation at sea, because the average maximum value of the specific optical density $D_{s,max}$ for the analyzed conditions of combustion and thermal decomposition does not exceed the value of 200. These leathers can be successfully used for interior finishing of ships. The thermogravimetric analysis has shown that the commencement of thermal decomposition for all types of samples with the exception of leatherette has proven to be quite similar and remained within the range of 272-282°C. Leatherette has been found to have the smallest value of commencement of thermal decomposition, and namely 247°C. The highest percentile of remnants after thermal decomposition has been obtained for bovine leather and amounted to 9%. This implies that this type of leather generated the least gaseous phase during its thermal decomposition in testing conditions. The lowest percentile of the remnants has been recorded for leatherette – 1.7%. The difference between the remaining samples as insignificant and was contained within the range of 6.5 to 7.32%. The quickest mass loss has been recorded for bovine leather, which amounted to 174%/min.

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Comparative analysis of the explosion parameters of selected gluten-free flour dusts

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Keywords: dust explosion, fire protection, gluten-free flour

Fires and explosions in the food industry not only pollute the air but also disrupt the food supply chain. The knowledge of the flammability and explosive parameters of gluten-free flour dusts makes it possible to determine the appropriate active and passive protection against fire and explosion. Flour dust explosions are chemical explosions characterized by a violent reaction of decomposition and oxidation, accompanied by a sudden increase in pressure and temperature. The phenomenon of flour dust explosion, despite the fact that the particles of these dusts are fragmented solids, is considered to be similar to the explosion of gas mixtures with air (Eckhoff 2009). Flour explosions in the food industry have been the subject of many studies (Freschi et al. 2017, Kuracina et al. 2019), but there are definitely fewer publications on the dangers of gluten-free flours. Five dusts were used for thermal, ignitability and explosiveness analysis: dust of green pea flour, dust of soybean flour, dust of millet flour, dust of lentil flour, dust of cornmeal flour. In the study, the determination of the minimum ignition temperature of the layer (MITL) and the cloud of test dust (MITD) of the precipitate was carried out and at a constant temperature heated surface setting according to EN ISO/IEC 80079-20-2. The following explosion parameters were determined: maximum explosion pressure (p_{max}) and maximum rate of explosion pressure rise $(dp/dt)_{max}$, the lower explosion level of dust cloud, according to EN 14034 standards. Thermogravimetric analyzes were done by means of a dynamic method in accordance with EN ISO 11358. Determination of heat of combustion of the tested dusts was performed with the use of a calorimetric bomb, according to the EN ISO 1716. The lowest values of parameters p_{max} have been recorded for millet flour dust, but the lowest $(dp/dt)_{max}$ have been obtained for cornmeal dust. On the other hand the LEL for soybean flour dust was found to be the highest 250 g/m^3. All studied dusts are classified to class 1 explosion hazard based on the K_{St} constant. The determined values of combustion heat of the studied samples proved to be similar and are contained within a range typical for this type of samples (between 15 and 22 kJ/kg). The analysis of the obtained results shows that the composition, structure and nutrient content of green pea flour ignited from the heated surface at temperatures as low as 310°C, and with thicker layers at oven surface temperatures lower than 300°C. The lowest temperature of the beginning of thermal decomposition equal to 199°C was recorded for soybean flour dust, but the lowest temperature of maximum mass loss (291°C) was recorded for green pea flour. It seems, that the reason results from other material indices, as the soybean flour was found to have the highest derivative of explosion pressure overtime, the highest heat of combustion and lowest (MITL) among tested materials. Based on the above mentioned results, there is a need of applying appropriate explosion protection means in those plants, where production, processing, storage and hauling of the tested dusts takes place.

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Fuels, biofuels

Organic, thermal and model free kinetic of *Çeltek* region oil shale deposits

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Keywords: Oil shale, Geochemical Analysis, Organic Analysis, Mass spectrometry, Thermogravimetry, Thermal Analysis, Model-free kinetics.

This research investigates the geochemical, organic, and non-isothermal thermogravimetry-mass spectrometry analysis and model-free kinetics of Çeltek deposits oil shale samples from Türkiye. In the first part of the research, elemental Analysis, x-ray diffraction (XRD), organic petrography, gas chromatography (GC), isotope analysis, gas chromatography-mass spectrometry (GC-MS), and rock-eval Analysis was verified. In the second part, simultaneous thermogravimetry-mass spectrometry (TG-DTG-MS) analysis was performed at three heating rates in an air atmosphere. TG-DTG curves indicated that the decomposition of the oil shale sample followed two successive reaction stages in different temperature intervals, known as the breakdown of organic matter and mineral decomposition. In these two reaction stages, reaction intervals, peak temperature, mass loss, and gaseous constituent (MS analysis) of oil shale samples were all determined. Also, for each reaction region, activation energy values were calculated using two different model-free methods known as Kissinger - Akahira – Sunose (KAS) and Ozawa - Flynn – Wall (OFW), and the results are discussed.

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Effects on the characteristic of coal-dust explosion from different pre-oxidation coal samples

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Keywords: methane, oxidized coal, pretreatment temperature, cloud concentration, particle size

A large amount of dust is generated during coal mining, including coal-dust and rock-dust. Under certain conditions, explosion accidents occur due to the accumulation of single dust, or the accumulation of dust and methane, and other combustible gases. When coal is oxidized to varying degrees, its internal structure will be affected, the explosive characteristics of the coal-dust produced from oxidized coal will be differential. In this work, coal samples were processed to the primary oxidation, secondary oxidation under air atmosphere, and secondary oxidation under methane atmosphere. Meanwhile, the pretreatment temperatures of coal samples were set to 25, 55, 75, and 115 °C in the temperature programmed experiment. Furthermore, for different parameters (cloud concentration, particle size median diameter, and particle size dispersion), the variation of explosion characteristics for coal-dust with different oxidation degrees was conducted in the explosion test device. The results indicated that the number of active groups in the molecule are changed after different degrees of oxidation pretreatment. The coal-dust between secondary oxidation under air atmosphere and secondary oxidation under methane atmosphere was the remarkably difference. Moreover, the coal-dust explosion characteristics and coal-dust cloud concentration showed a quadratic polynomial law under different pre-oxidation degrees. The optimal coal-dust cloud concentration varied with the pre-oxidation conditions. When the concentration of coal-dust cloud is remained a constant, the explosion pressure with different degrees of pre-oxidation is affected by the median diameter and dispersion degree of particle size.

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Geosciences and minerals

Recycling volcanic fly ash through geopolymers: synthesis and thermal characterization

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Keywords: geopolymer, volcanic ash, hybrid materials

Volcanoes are geological structures widely distributed in different parts of the world. These are responsible for the formation of enormous quantities of fly ash (FA) which often, being considered waste, need to be disposed of in landfills. Currently, among the most innovative technologies for their reuse, there is their inclusion in geopolymers.

In this study geopolymers with 20 wt% of FA as filler are synthesized and analysed (Fig.1). The precursors used are metakaolin (MK), sodium hydroxide solution (NaOH 8 M), sodium silicate solution (Na_2SiO_3), and FA. The samples were cured at room temperature and 40°C for 24 h. The analyses performed evaluated their chemical, thermal, and antibacterial properties. The results of the integrity test, weight loss and TGA study revealed how increasing the curing temperature results in better stabilisation. The shift of the DOSPM (Density of State Peak Maximum) to lower wavenumbers in the FT-IR spectra confirmed the occurrence of the geopolymerization process in all the specimens. Finally, the antibacterial analysis showed how geopolymers, independently from the curing temperature, can inhibit both gram-positive and negative bacteria.

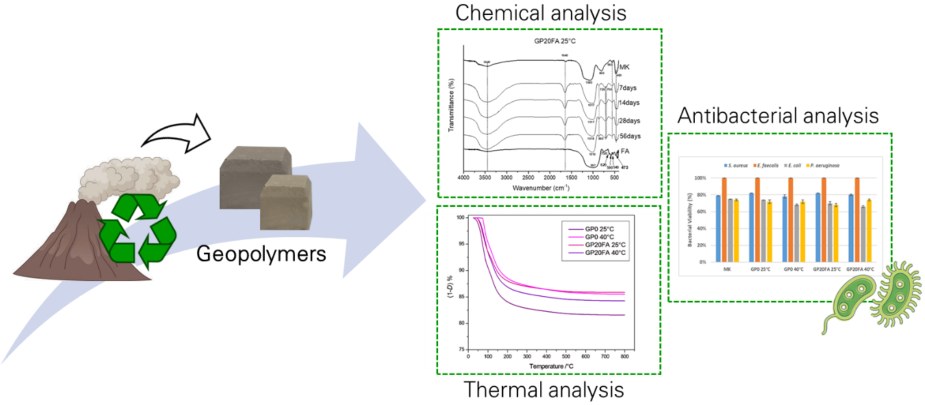

Figure 1: graphical representation of the study performed

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Reactivity and overburning of quicklime: the case of limestones belonging to Tuscan Nappe Sequence (NW Tuscany, Italy)

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Keywords: microstructure, XRF, XRPD, TG-DSC, SEM-EDS, lime reactivity, lime overburning

Calcium carbonate is the main component of limestone. The burning of limestone produces quicklime/calcium oxide (CaO) and carbon dioxide (CO_2) that escapes in the environment [1]. Quicklime is an highly reactive material and in contact with water it changes into slaked lime/calcium hydroxide ($Ca(OH)_2$). The quality of limestone and the calcination process has a great impact on the quality of the products. Therefore, it is interesting to study the chemical, mineralogical and petrographic characteristics of limestone and the influencing factors in the calcination process of limestone for improving the quality of products. This study analyses the effects of both chemical, mineralogical and petrographic characteristics of limestone, and calcination temperature on the reactivity and overburning aspects of the produced quicklime. Five limestones coming from Monti d'Oltre Serchio (NW Tuscany, Italy) [2] have been selected and calcined at four selected temperatures (900°C, 1000°C, 1100°C, 1200°C), and the obtained quicklime was slaked. Chemical and minero-petrographic analyses (OM, XRF, XRPD, TG-DSC, SEM-EDS) have been performed on limestone with the purpose to study the quicklime reactivity during the slaking of samples. Excluding to consider the quality of limestone, the most reliable factors for evaluating quicklime reactivity are the specific surface area of the quicklime and the rate of temperature increasing during the slaking process. The degree of reactivity of lime was measured by the rate of the lime hydration (slaking) reaction. It was evaluated by a slaking test, which measures the heat of hydration produced by a known weight of lime in a known volume of water [3]. The collected data clearly indicates that the lower the limestone calcination temperature is, the more reactive the produced quicklime can be obtained. The CaO grains grow with the increase of temperature and time, which leads to the decrease of reactivity. Notably, the effects of temperature on CaO grain size and reactivity are more remarkable than that of time. The best calcination temperature was found to be 900°C, which was the temperature performed in ancient limekilns. The reactivity of quicklime is related to its microstructure, which also strictly depends on chemistry, mineralogy and microstructural features of the limestones.

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Thermochemical processing as an alternative to acid leaching for improved extraction of aluminium from coal fly ash

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Keywords: coal fly ash, aluminium, thermochemical treatment, acid leaching, TGA

Coal fly ash is the inorganic residue generated during the combustion of pulverized coal in thermoelectric power stations. Al is the second most abundant element in fly ash after Si, which means that fly ash has the potential to be used as a substitute for bauxite in alumina production. The potential for selectively extracting Al from South African fly ash was previously demonstrated by our research group [1-3].

In this study, insight gained from the previous work was applied to compare the efficacies of aluminium extraction through H_2SO_4 leaching versus thermochemical processing with $(NH_4)_2SO_4$ as extracting agent. Three South African coal fly ash samples, with varying chemical and physical properties were used in the comparison. The samples were selected based on varying particle size and mullite content, as these properties were previously determined to influence the extraction efficiency of Al from the fly ash matrix. Changes in the morphology and composition of the fly ash samples during the respective extraction processes were monitored using a combination of XRD, XRF and FESEM analyses, while the extraction of Al was followed by means of ICP-OES. The study also considered the influence of predesilication via NaOH leaching prior to Al recovery. The extraction of Al during H_2SO_4 leaching was found to be less than 20 wt.% but could be improved to approximately 30 wt.% after predesilication. Thermochemical processing with $(NH_4)_2SO_4$ was found to be the most effective extraction method. It resulted in the extraction of more than 40 wt.% of Al from the fly ash matrix.

TGA was particularly useful in determining the extent of conversion of Al from the fly ash matrix into water-soluble $Al_2(SO_4)_3$ during thermochemical processing with $(NH_4)_2SO_4$. Quantitative TGA was used to determine experimental parameters such as $(NH_4)_2SO_4$:fly ash mass ratio required to maximise the amount of $Al_2(SO_4)_3$ formed, and the duration of thermochemical treatment needed for the solid-solid reaction to reach completion.

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Heat transfer

Experimental and numerical investigation of nanoparticle assisted PCM based battery thermal management system

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Keywords: battery thermal management, phase change material, nanoparticles.

The Li-ion batteries at a high discharge rate generate a large amount of heat in electric vehicles. If this heat is not dissipated out of the system, it leads to temperature rise and affects the cell's performance and life cycle. If the temperature continues to rise, it leads to serious damage to the cell and may cause thermal runaway. Thermal runaway is a condition where cells emit flames, leading to a chain reaction. This led to serious fire accidents of which several cases are recorded in different parts of the world. A battery thermal management system enriches both the performance and life cycle of a battery and eliminates chances of thermal runaway. Phase change materials in battery thermal management have many advantages such as high thermal storage capacity at a constant temperature, easy availability, and low maintenance. However, Phase change materials have very less thermal conductivity (0.2-0.5 W/m-K) that resists the flow of thermal energy in the direction of the temperature gradient. Hence in the present work, nanoparticles assisted PCM, and active cooling techniques have been introduced. In this present study, both experimental and numerical work has been performed for developing a water-composite Phase change material-based hybrid battery thermal management (combination of two cooling techniques). It is also important to optimally utilize the amount of phase change material in the system as weight impact the overall performance of the electric vehicle. Battery module has been studied under the different thickness of PCM ranging from 40 to 5 mm with a gradient of 5 mm. Copper and aluminum oxide are introduced in phase change material and the thermal characteristic with various mass fractions (concentration) ranging from 0.1-5 % are studied. It is observed increasing both the mass of the phase change material used and the concentration improves thermal heat dissipation. However, as thickness is more than the critical value, it results in heat accumulation. The vicious nature dominates the hydrodynamics in the phase change material which results in restricting the bouncy forces. The results of the present analysis could help in the improved design of BTMS.

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Regeneration behavior of solid desiccants with microwave-assisted hot air drying

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Keywords: solid desiccant, microwave, regeneration, hot air; multi-magnetron, kinetics.

Solid desiccants have been widely used in dehumidification systems as adsorbents due to their lower regeneration temperature and better operation flexibility, easier transfer and handling, lower corrosion [1-3]. Zeolite, alumina, activated carbon and silica gel are commonly used as solid filling materials of the desiccant rotor. The regeneration of desiccants is significant for the economy and environment protection. The common desiccants regeneration approach is to remove the water out by drying technology such as the hot air heating. Compared with the conventional hot air drying, the microwave heating due to its direct and rapid heating from consistent direction for thermal and moisture migration on materials has the potential to be seen as a novel regeneration technology of desiccants. However, the microwave drying alone can face uneven heating and high energy consumption. Especially, the non-uniform heating of the desiccants can decrease their desorption ratio. Hot air assisted microwave drying is one of the effective methods to get more uniform drying. Combination of both heating methods is expected to get higher regeneration rate by microwave irradiation, and the hybrid system also can reduce the energy consumption. Some investigations mainly deal with the drying characteristics of food, fabrics, sludge, lignite and hematite during microwave and convective or integral drying. However, the regeneration kinetics of solid desiccants and microwave heating uniformity during the microwave or integral heating are rarely reported. In the current work, the regeneration performance of several typical solid desiccants was examined in a microwave combined hot air lab-scale setup. The shortest time required for desiccants happened in combined heating. Among eight desiccants, zeolite in the combined took the shortest time to regenerate. Activated alumina was the most difficult to regenerate, and it in the hot air drying had the highest absorption capacity, while 3A (1.6-2.5) zeolite in the microwave and combined heating had the highest absorption capacity. Silica gels in all heating modes had the minimum absorption capacity. At low power levels (100-300W), the regeneration performance of the silica gels was prompted by the multi-magnetron radiation modes with the top one. The temperature distribution uniformity of silica gel was lifted with the assisted hot air drying. The multi-magnetron could ameliorate the microwave heating uniformity. This study can provide basic data for the design and improvement of the desiccant rotors.

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Linear stability of liquid film with heat and mass transfer under acoustic oscillations

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Keywords: acoustic oscillations; Kelvin–Helmholtz instability; liquid film; heat and mass transfer

This work examined the linear instability of a liquid film theoretically in consideration of the acoustic oscillations. The acoustic oscillations are considered to be the velocity oscillations of gas medium, and the ratio of conduction heat flux to evaporation heat flux is used to characterize heat and mass transfer. Because of the acoustic oscillations, several unstable regions, involving Kelvin-Helmholtz (K-H) instability region and parametric instability region, would occur, and the acoustic oscillations have a destabilizing effect on the interfacial instability. Because the resonant frequency increases as the forcing oscillations frequency increases, the viscous dissipation is enhanced with the increase of forcing frequency, and the growth rate in parametric unstable regions would decrease. In addition, when the surface tension decreases, the interfacial instability is also promoted. Increasing the gas-liquid density ratio can destabilize the interface. The gas viscosity can enhance the interfacial instability, while it is neglectable. Furthermore, the growth rate in both the K-H and parametric instability regions increases when the heat and mass transfer is enhanced, while its destabilizing effect on the indentation between unstable regions is greater. It is significant to note that there is the competition between K-H and parametric instabilities, and the location of the maximum growth rate would be in the most unstable region.

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Inorganic materials

Using of thermal analysis for the study of Barium sulphate reduction

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Keywords: $BaSO_4$, thermal reduction, BaS, activated carbon

Precipitation of sulphates from water solution by barium salts to the insoluble product barium sulphate $BaSO_4$ is the most commonly used technology for treating contaminated water. Benefits of precipitation are high sulphate removal efficiency but limitations are toxicity of barium compounds and high economical costs. For this reason the recycling of $BaSO_4$ to barium sulphide BaS (the precipitating reagent) is very important.

This research was focused on the study of thermal reduction of $BaSO_4$ to BaS by powdered activated carbon in two mixtures with a molar ratio of 1:2 and 1:4. The reduction process was analysed by using thermal analysis methods (DSC/TG mode). It was found that the $BaSO_4$ reduction process took place in the temperature range 800-900 °C and was influenced by the amount of carbon. The presence of larger amount of carbon shifts the peak of the endothermic process by about 27 °C to a higher temperature. For identification of reduction efficiency, the decrease in enthalpy for the endothermic peak belonging to the $BaSO_4$ modification change (β-γ) was used. Sulphate reduction was also confirmed using the Fourier transform infrared spectroscopy (FTIR). The presence of BaS after thermal heating of mixture $BaSO_4$ with carbon was confirmed by colorimetric analysis using methylene blue method.

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$MgO–P_2O_5–Cr_2O_3$ System: phase equilibria and properties of chromium magnesium phosphates

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Keywords: $MgO–P_2O_5–Cr_2O_3$ system**,** phase equilibria, chromium magnesium phosphates, thermal stability, colour properties

Studies of phase equilibria in multi-component oxide systems may lead to obtaining new phases with potential application possibilities in various fields of modern technology.

In this context, the ternary $MgO–P_2O_5–Cr_2O_3$ oxide system caught our attention. It is known that phosphates(V) of divalent and trivalent metals can be successfully applied as pigments or dyes [1, 2]. It is very likely that phosphates(V) formed with the involvement of all components of the $MgO–P_2O_5–Cr_2O_3$ system, i.e. containing both Mg^{2+} and Cr^{3+} ions, will be good candidates for use them as new colouring substances. Unfortunately, literature information on the number of compounds formed in this system is divergent. According to the authors who examined phase equilibria in the entire subsolidus area of this system, only one compound is formed in it, i.e. $MgCr_2(P_2O_7)_2$ [3]. Meanwhile, both from the later publication [4] and from the results of our research [5], the second compound existing in this system is known, i.e. $Mg_3Cr_4(PO_4)_6$. Therefore, we decided to re-investigate phase equilibria in the entire subsolidus area of the $MgO–P_2O_5–Cr_2O_3$ system (in order to check if other unknown double phosphates are formed in it) and then to characterize the unknown properties of all the obtained chromium(III) magnesium phosphates(V), in particular their colour properties. Reactions were carried out by a conventional method of multi-stage heating of samples, until equilibrium was reached. As a result of the conducted research, it was found that another previously unknown compound with the formula $Mg_5Cr_2(P_2O_7)_4$ is formed in the $MgO–P_2O_5–Cr_2O_3$ system. This compound was obtained according to the reactions 1, 2.

$$4MgCO_3\cdot Mg(OH)_2\cdot 4H_2O_{(s)} + 8(NH_4)_2HPO_{4(s)} + Cr_2O_{3(s)} = Mg_5Cr_2(P_2O_7)_{4(s)} + 4CO_{2(g)} + 16NH_{3(g)} + 17H_2O_{(g)} \tag{1}$$

$$Cr_4P_6O_{21(s)} + 5\ Mg_2P_2O_{7(s)} = 2\ Mg_5Cr_2(P_2O_7)_{4(s)} \tag{2}$$

The new compound was characterized in terms of its structure, thermal stability and optical properties. The colour properties of all obtained compounds were tested, i.e. the previously known $MgCr_2(P_2O_7)_2$ and $Mg_3Cr_4(PO_4)_6$ as well as the new $Mg_5Cr_2(P_2O_7)_4$. All these compounds are characterized by relatively high thermal stability in air (above 1300°C). Such property is essential when used them for colouring glazes.

In the subsolidus area of the $MgO–P_2O_5–Cr_2O_3$ system, 14 partial systems were distinguished, in which three solid phases coexist in the equilibrium state. Ranges of thermal stability of mixtures of phases being in equilibrium were determined. These data are important from the point of view of the possibility of using the obtained phosphates, because not only pure compounds, but also their mixtures are applying as pigments or dyes.

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The reactivity of CeO_2 towards MoO_3 in air atmosphere

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Keywords: Ce–Mo–O system, cerium molybdate, $Ce_8Mo_{12}O_{49}$, solid state reaction, thermal properties

MoO_3 and CeO_2 oxides are widely used, e.g. as catalysts for various chemical reactions. Such properties can be expected from compounds formed as a result of their reaction. Phase equilibria in the CeO_2–MoO_3 system have been studied and the phase diagram of this system up to 950°C is known [1]. As follows from this diagram, two compounds are formed in this system: $CeMo_2O_8$ and $Ce_2Mo_3O_{13}$. While $CeMo_2O_8$ is well known [1-3], information about the physicochemical properties of $Ce_2Mo_3O_{13}$ is rather scarce. On the other hand, Wu et al. [4] obtained $Ce_8Mo_{12}O_{49}$ and $Ce_2Mo_4O_{15}$ by heating CeO_2, previously impregnated in solution ammonium heptamolybdate, at 500°C. Taking into account the divergent literature data, it seemed interesting to re-investigate what compounds or phases are formed as a result of the reaction of CeO_2 with MoO_3 in a solid state in air atmosphere.

For the investigation, 10 mixtures of CeO_2 and MoO_3 were prepared. MoO_3 content in these mixtures was: 10.00, 20,00, 40,00, 50.00, 60,00, 63.00, 66.67, 70.00, 80.00 and 90.00 mol%. The molar composition of two samples was selected to correspond to cerium(IV) molybdates(VI) known from the literature, i.e. $Ce_2Mo_3O_{13}$ and $CeMo_2O_8$. The reacting substances were weighed in appropriate proportions, homogenized by grinding and heated in several stages up to 650°C in the atmosphere of air. After each heating stage the samples were gradually cooled down in the furnace to room temperature and then, after grinding, they were examined by the XRD method, while some selected samples also by DTA.

The obtained results show that in the air atmosphere the oxides CeO_2 and MoO_3 are not inert towards one another. As follows from XRD analysis of the samples containing in the initial mixtures less than 60.00 mol% MoO_3, they are biphasic and besides the unreacted CeO_2 they contain $Ce_8Mo_{12}O_{49}$. The sample obtained from the initial mixture containing 40.00 mol% CeO_2 and 60.00 mol% MoO_3 was monophasic and contained only $Ce_8Mo_{12}O_{49}$. In the samples containing above 60.00 to 66.67 mol% of molybdenum(VI) oxide in the initial mixtures, the compounds identified were: $Ce_8Mo_{12}O_{49}$ and $Ce_2Mo_4O_{15}$. In the samples representing the remaining range of concentrations, three compounds were identified, i.e.: $Ce_8Mo_{12}O_{49}$, $Ce_2Mo_4O_{15}$ and MoO_3. Mass losses recorded in the samples after successive stages of heating ranged from 0.002 to 0.1 mass%, suggesting that MoO_3 was practically not sublimated under the heating conditions.

Therefore, under the conditions of the syntheses carried out, the formation of the compounds described by Ustinov [1] was not observed. Only one of the molybdates described by Wu [4] was obtained in pure form, according to reaction equation:

$$8\ CeO_{2(s)} + 12\ MoO_{3(s)} = Ce_8Mo_{12}O_{49(s)} + 3/2\ O_{2(g)}$$

In the available literature only information on the preparation of $Ce_8Mo_{12}O_{49}$ and its X-ray characteristics can be found. Due to the fact its basic physicochemical properties were investigated in the presented work. $Ce_8Mo_{12}O_{49}$ is green and crystallizes in the triclinic system. The compound was found to melt incongruently at 960°C with deposition of solid CeO_2.

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Synthesis, structural and thermal characterization of novel fomepizole complexes of Zn(ii) and Ni(ii)

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Keywords: fomepizole, 4-methylpyrazole complexes, pyrazole derivatives, synthesis, thermal decompositions

Pyrazole and its derivatives present an important medical potential with numerous pharmacological activities[1-6]. One such compound is 4-methylpyrazole (also known as fomepizole), which is efficiently used in the standard treatment of poisoning with ethylene glycol or toxic alcohol ingestions. The coordination of 4-methylpyrazole (L) to Zn(II) and Ni(II) ions is studied through the reactions of $Zn(OAc)_2 \cdot 2H_2O$ and $Ni(OAc)_2 \cdot 4H_2O$ with 4-methylpyrazole (in a molar ratio of M:L = 1:2) in ethanol at room temperature. From the reaction mixtures novel complex compounds were crystallized of formulae: $[Zn(OAc)_2L_2]$ and $[Ni(OAc)_2L_4]$. The synthesized complexes have been characterized by X-ray diffraction and spectroscopic techniques. Since for further application of the compounds, their thermal stability is crucial, these compounds are also characterized by thermoanalytical techniques. The thermal decomposition routes of complexes were compared to determine the effect of central metal ions on the decomposition mechanism. During the thermal decomposition, stable intermediates are formed and isolated by sample-controlled TGA. The IR spectra of the isolated intermediates are recorded. To examine the influence of the atmosphere on the thermal stability and decomposition path of $[Zn(OAc)_2L_2]$ and $[Ni(OAc)_2L_4]$, the thermal characteristics of the complexes were studied in an inert atmosphere and air. In the oxidative atmosphere, the final decomposition products are the corresponding oxides, identified by IR spectra. The decomposition mechanism of the complexes is examined based on evolved gas analysis measurements.

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The phase equilibria of Na_3AlF_6–NdF_3 and $(Na_3AlF_6–NdF_3)_{eut}$–Nd_2O_3 systems

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Keywords: rare earth, molten salt, phase equilibria, thermal analysis

Electrowinning (molten salt electrolysis) is the dominating industrial method for rare earth metal extraction from their oxides in the salt extraction process [1]. Molten salts provide a unique working environment. They offer an ionic, nonaqueous habitat wherein various metal oxides may be dissolved. This also applies to neodymium. It is industrially produced by high temperature electrolysis of Nd_2O_3 dissolved in molten LiF–NdF_3 electrolyte with oxide concentration in the molten fluoride electrolyte to be around 2 wt. % (0.96 mol %) and the operational temperature between 1050–1100 °C [2, 3]. The very low solubility of the neodymium oxide in the molten electrolyte is an obvious disadvantage of the current industrial electrolysis. It has a direct impact on the low current efficiency of the process.

Therefore, the phase equilibria of Na_3AlF_6–NdF_3 and $(Na_3AlF_6–NdF_3)_{eut}$–Nd_2O_3 systems have been analyzed by means of thermal analysis and for the first time, to our knowledge, presented. Both investigated mixtures seem to form a simple eutectic system. It can be concluded that the solubility of Nd_2O_3 in the molten eutectic system of Na_3AlF_6–NdF_3 is relatively high compared to the solubility of Nd_2O_3 in the current molten industrial electrolyte (2 wt. %) for the electrowinning of neodymium (LiF–NdF_3).

Acknowledgments

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Determination of Curie points of selected oxygen carriers using TGA method

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Keywords: Curie point, TGA analysis, oxygen carriers, spinel

Oxygen carriers (OCs) are substances used in Chemical Looping Combustion (CLC) process as an oxygen donor. In the CLC process, OCs are constantly circulating between the fuel and air fluidized bed reactor. Since the oxygen used in the combustion process comes directly from OC, fuel does not have contact with atmospheric air, and emission of thermal nitrogen oxides is reduced to zero, significantly simplifying the process of carbon dioxide capture from the fumes. CLC allows combusting gaseous, liquid and solid fuels. Because loss of the OCs generates significant costs for the process, one of the problems related to solid fuel combustion in CLC technology is separation of the OC from the ash. Usually a system of pneumocyclones is used, additionally magnetic separation could be applied for further recovery of OC particles.

Magnetic separation can be applied for oxygen carriers that have ferromagnetic properties such as some spinel-based OCs; furthermore, the temperature of the oxygen carrier intended for recovery should be lower than the Curie point for that certain type of substance.

The Curie point of ferromagnetic materials may be determined by using thermogravimetric analysis. At a temperature equal to the Curie point, the sample is changing its magnetic properties. When the material is heated in the presence of a strong magnetic field, the TGA analyzer registers sudden mass change. In the presented research, Curie point for selected spinel-based oxygen carriers was determined using the TGA method on a SEIKO SII TG/DTA 6300 analyzer in the presence of external magnetic field generated by a ferrite magnet.

Acknowledgments

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Kinetics and catalysis

Thermal curing behavior of bio-based Melamine formaldehyde impregnating resins using sorbitol

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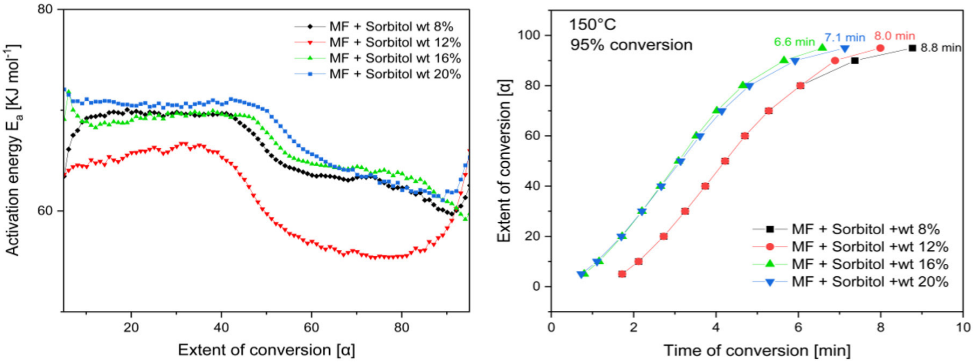
Keywords: thermal analysis, curing kinetics, bio-based polymers, melamine-formaldehyde resins, sorbitol

Bio-based impregnating resins intent to provide a greener alternative to established resin systems for industrially produced particle boards. There are alternatives available serving as substitutes for melamine or formaldehyde, however these substitutes are hindered by challenges which include limitations of surface properties and high costs. Nevertheless, with the starch derivative sorbitol, a natural building block is available, enabling the synthesis of MF resins with enhanced biobased properties. In this investigation, the curing of melamine-formaldehyde impregnating resins with a higher content of biobased materials was studied using differential scanning calorimetry (DSC). The MF resins containing different wt.% (8%, 12%, 16% and 20%) of sorbitol were synthesized and their cure kinetics were determined. Since curing kinetics and pressing conditions play an essential role for the final excellent optical and mechanical properties of the particle boards pressed with impregnated MF resin, they also represent a highly critical aspect in pressing technology. As the MF system is highly complex, with many occurring side reactions, this study attempted to evaluate, how the modification of the established resin system toward more sustainable components, affects the curing process and properties of the cured polymer. DSC was employed to perform thermal analysis of the liquid sorbitol-modified MF resins, using four different heating rates (5, 10, 15 and 20°C/min), followed by an isoconversional kinetic approach for thermo-stimulated polymers, using the method of Vyazovkin.

Results of this study conclude that the activation energy (Ea) is not constant, but the regime changes as the thermal curing reaction proceeds, revealing the complexity of this curing conversion, which was also observed with ATR-FTIR curing experiments (figure not shown). Fig. 1A illustrates, that the degree of conversion (α) slightly decreased after ~40%, showing an overall downward trend. The obtained correlation between Ea and fractional conversion α further revealed that the MF resin containing 12% sorbitol depicted the most drastic decrease after ~40% conversion and lowest overall E_a. Moreover, sorbitol modified MF resins containing 16% and 20% sorbitol, were shown to reach the curing conversion of 95% after 6.6 min and 7.1 min respectively, which is faster as compared to MF resins containing 8% and 12% of sorbitol, reaching a cure conversion of 95% after 8.8 min and 8.0 min. The fastest cure at 150°C toward a 95% cure conversion was observed for the MF resin modified with 16% sorbitol. However, as depicted in Fig. 1B, an increase of curing time was seen with MF resins containing 20% sorbitol, which needs to be further investigated. Furthermore, DSC analysis revealed that the curing Enthalpy for the sorbitol-modified MF resins was 70-80 Jg-1, and thus correspond to resins with a high residual curing capacity (H>70 Jg-1). Moreover, the residual curing capacity was reduced due to paper impregnation, as DSC employed on paper impregnates (heating rate: 10°/min) yielded decreased Enthalpies (H=30-38 Jg-1) as compared to the liquid resins. In conclusion, highest cure conversions were seen with MF resins containing 16% and 20% sorbitol, which showed shortest curing times toward a 95% cure conversion, as compared MF resins with 8% and 12% sorbitol, potentially rendering them suitable for industrial use. As the curing behaviour and pressing temperature was previously revealed to vastly influence the quality and surface properties of laminates, kinetic analysis therefore also allows predictions of the mechanical and optical properties of the sorbitol-modified thermoset MF resins.



A

B

Fig 1: **A:** E_a of the respective MF resins modified with wt. 8%, 12% 16%, 20% sorbitol. **B:** Comparison of curing times (95% conversion) of the sorbitol modified resins.

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Recovering of metals and metal oxides through thermal decomposition process of coal bottom ash: a comprehensive kinetic analysis

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Keywords: bottom ash, TG-DTG, metals recovery, kinetic analysis, catalyst

In this work, the thermal decomposition process of coal bottom ash (collected after lignite combustion in coal-fired power plant "Kostolac B" (TEKO-B), Serbia) was investigated, using simultaneous TG (thermogravimetry) – DTG (derivative thermogravimetry) techniques in an inert (Ar) atmosphere, at various heating rates (10.3, 20.9 and 32.1 K/min). In addition to thermal characterization of the sample, the chemical composition and naturally occurred radionuclides were also determined. Using the model-free (isoconversional) (by Friedman (FR), Kissinger-Akahira-Sunose (KAS), Ozawa-Flynn-Wall (OFW) and Vyazovkin (VY) methods) analysis, the complex kinetic nature of the process was successfully resolved. The conducted numerical optimization of the process (using non-linear least square optimization) had confirmed accuracy and reliability of estimated kinetic parameters. Model-based (model-fitting) kinetic analysis showed the existence of a complex reaction scheme, over two consecutive reactions steps and one single-stage reaction step, *via* mechanism order A*n*, F2, F*n*, R3, C*nm* (through *n*-dimensional nucleation/growth, chemical reactions, and *n*-th order and *m*-power with autocatalysis mechanisms). Through physicochemical interpretation of mechanism scheme, an assessment of recovery of valuable metals and metal oxides was performed, by analysing the concentration of reaction species in a function of temperature of individual steps. Likewise, the influence of certain precursor involved in decomposition process as catalyst (in order to increase the yield of targeted product) was also inspected. Finally, the simulation of actual process using the results obtained from applied methods/models was performed, through application of modulated dynamic (MD) prediction.

Acknowledgments

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Prediction of kinetic triplets for thermal curing of bio-based epoxy resin

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Keyword: epoxidized linseed oil, thermal and mechanical properties, cure kinetics, principal component analysis

Epoxy resin is a thermoset polymer known for its excellent adhesion, thermal stability, chemical resistance, and mechanical properties. To achieve more sustainable growth with environmental concerns, the development of new advanced materials based on biobased feedstock is necessary. The novelty of this work is to predict and compare the kinetic triplet (apparent activation energy for curing-Ea; reaction model-f(α); and the pre-exponential factor-A) by model-free [1,2] and model-fitting methods between bisphenol-A based epoxy (DGEBA) and epoxidized linseed oil (ELSO). The cure kinetics for DGEBA have been reported extensively in the literature, and here DGEBA was taken as the reference epoxy and was cured with an anhydride-based hardener in stoichiometric way along with 2-ethyl imidazole (2-EI) as an accelerator. The ELSO_2 wt % 2-EI showed 33% lower enthalpy of curing, compared with DGEBA_2 wt % 2-EI. The methodology of predicting kinetic triplets, which represents the whole understanding of the reaction, will be applicable for selecting appropriate strategies for the study of curing reaction in epoxy resins. The activation energy, one of the important parameters for characterizing the curing reaction, is calculated by differential (Friedman) and integral (Advanced Vyazovkin) methods. The kinetic study concludes that the resins has the same activation energy for thermal curing of 60-70 kJ mol^{-1} (from the advanced Vyazovkin method-Figure 1), which fits the typical range for epoxy systems. The low Ea values for ELSO in initial stage indicate that the bio epoxy is less reactive and the reactivity nearly similar to reference epoxy at 50 % conversion. Both the DGEBA and ELSO resins follow a first-order reaction model which is predicted by Criado method. The highlight of this work is also to predict the reactivity of the accelerator with epoxy, and the influence of temperature during the epoxide-imidazole adduct formation is studied by Real-time FTIR, Principal Component Analysis (PCA), and by Hydrogen bromide (HBr) titration method. The decrease in epoxy band (820 cm^{-1}) and the increase in secondary alcohol band at 1100 cm^{-1} (C-O-H stretching) of FTIR spectra over the period confirm the formation of the adduct. The PCA results confirm that irrespective of the amount of catalyst, the decrease in the epoxy band lies in the same range at 100 °C. But at 80 °C, 1 wt % of 2-EI is not enough for adduct formation. The addition of 2 wt % in epoxy at 80 °C need additional time for adduct formation. The well-correlated results from conversion plots of Real-time FTIR, PCA, and the HBr method confirm the importance of epoxide-imidazole adduct either via pyrrole-type or pyridine-type nitrogen in imidazole. This multivariate data analysis improved the understanding of relationships between the accelerator concentration and the temperature and the study of these systems with important variations.

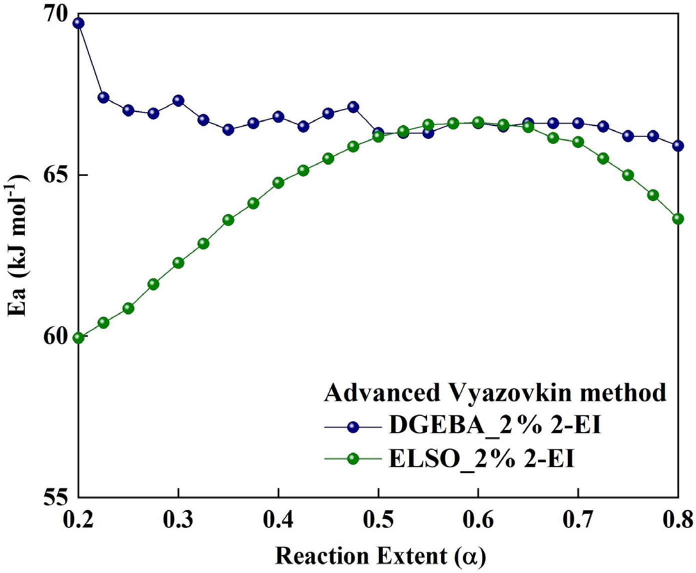

Figure 1: Activation energy of curing for DGEBA and bio epoxy (ELSO)

Acknowledgments

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Life sciences

Thermal analysis of the EB1 protein

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Keywords: DSC, cytoskeleton, EB1, MAPRE1

EB1 (End-binding protein 1, also known as MAPRE1) is involved in various processes such as angiogenesis [1], spermatogenesis [2] and cancer [3]. It belongs to the +TIPS (microtubule plus-end tracking proteins) recruiting other factors to the plus end of the microtubules. The EB1 is built up by an N-terminal calponin homology (CH) domain responsible for microtubule and actin binding, a disordered linker part and a C-terminal region containing an α-helical coiled-coil, a highly conserved EB-homology (EBH) domain and a disordered tail. The EBH domain is essential for the dimerization of the protein.

We investigated the structural changes of the recombinant EB1 protein with DSC (differential scanning calorimetry) between 20 °C and 95 °C. We found a denaturation peak ($T_m \sim 40\text{-}42$ °C; $\Delta H \sim 150$ kJ/mol) in the low-temperature range assuming for the CH domain. Transitions in the higher temperature range (above 60 °C) were also apparent, presumably caused by the denaturation of the α-helical coiled-coil and dedimerization. Analysing the effect of the truncation of either the N-, and C-terminal parts on the denaturation suggests an interplay between the CH and EBH-tail domains of the protein.

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Thermal analysis of biceps tendon of patients underwent reversed shoulder arthroplasty due to comminuted proximal humerus fractures

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Keywords: biceps tendon, differential scanning calorimetry, reversed shoulder arthroplasty, trauma, 4-part fractures, Neer VI

The comminuted 4-part or type Neer VI proximal humerus fractures, mostly in elderly patients, often require total shoulder replacement. Despite the recent advances in imaging technologies, there is still a need for more information about the degree of joint degeneration and changes of the collagen content of tendons to select the proper implant type. It is known that human long head biceps tendon (LHBT) subjected to synovial inflammation and mechanical wear could result in tear and structural damage. Differential scanning calorimetry (DSC) has already been proven to be a reliable tool in the evaluation of collagen in degenerative tendon conditions[1,2]. Therefore, the aim of the study was to evaluate whether changes of thermal parameters detected with DSC correlate with the degenerative alteration of LHBT samples. LHBT tendons were obtained from patients underwent reversed shoulder arthroplasty with trauma indications. The thermal parameters were measured by using DSC. Macroscopical, radiological and histological assessment were also performed. Based on the thermal parameters and denaturation curves, LHBT samples collected of patients underwent reversed shoulder arthroplasty due to comminuted proximal humerus fracture have shown minimal or mild degenerative injuries. These data were supported by preoperative radiological examination and histological analysis. Authors suggest that DSC could be a useful examination tool in the clinical investigation of tendon injuries.

Acknowledgments

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Utilising localised exhaust and air curtain to reduce airborne particle settlement on surgical patients: potential future application in operating rooms?

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Keywords: operating room, airborne diseases, surgical site infections, human health, indoor air pollution

An operating room (OR) is a healthcare facility used to perform surgical operations on a patient. The OR demands high-air cleanliness and sterile conditions to reduce the risk of patients contracting surgical site infections (SSI). This study aims to examine the effectiveness of localised exhaust and air curtains in reducing the number of particles settling on a patient. An OR model was constructed using computer-aided design (CAD), while the airflow and particle simulation was performed using computational fluid dynamics (CFD). The reliability of the present work was verified and validated using established data before the case study. A Re-Normalisation Group (RNG) k-ε model based on the Eulerian approach was used to simulate the airflow, while a discrete phase model (DPM) based on the Lagrangian approach was used to simulate the airborne particle dispersion. Results showed that the activation of the localised exhaust located on the two sides of the operating table could reduce the total particle settlement on the patient by 26% when compared to the baseline ventilation system. The installation of an additional air curtain showed the best performance in terms of reducing the particle settlement, followed by the installation of both an additional air curtain and a localised exhaust outlet. The particle concentration settled on a patient showed a positive relationship with the body surface area which is expressed by equation $y = 0.1088x + 0.2528$ with a coefficient of determination, R^2 value = 0.8764.

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Materials science

The effect of nickel addition on the microstructure of SAC 305 lead-free solders

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Keywords: microstructure formation, lead-free solder, SAC 305, nickel

The Sn-Ag-Cu (SAC) solders as the leading alloys replaced lead-based solders in the electronics industry [1,2]. Alloying elements can be further added to strongly influence the behaviour of the SAC solder balls. It was found that the presence of Ni in the solder ball has a significant effect on the growth rate and the grain size of the intermetallic compounds [3]. The aim of the work is to analyse the microstructure formation of SAC 305 lead-free solders with the addition of Ni. In the experimental investigation, scanning electron microscopy, energy-dispersive X-ray spectroscopy and differential scanning calorimetry were used. The creation of thermodynamic model of microstructure formation was realized by the CALPHAD method using the Thermo-Calc software. A refinement of the lamellar structure was observed at low nickel content. At high nickel content, an undesirable nickel-rich phase was formed. The computational results related to phases, composition of phases and eutectic temperature agree well with the experimental results and enable the more detailed understanding of the processes occurring during the solidification of SAC 305 + Ni solders.

Acknowledgments

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Grain size influence on speciation of selected properties of fractionated coal fly ashes

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Keywords: coal fly ash, granulometry, chemical and mineralogical composition, lost of ignition

Fly ash, a by-product of coal combustion, exhibits varying properties depending on several factors such as coal type, combustion type, method of ash precipitating and removing ashes from the station. Due to this factors and various mineral composition of source coal the direct application of fly ashes in industry as a substitute for natural resources is limited.

In this article the influence of granulometry on the chemical and mineralogical composition variability, loss on ignition (LOI), and grain microstructure of two types of fly ashes (high-calcium and silica) have been studied. Obtained by means of dry aerodynamic separation ashes fractions show changes in their properties as a function of grain size. Finest fractions contained an increased amount of Calcium and Sulphur compounds, while Magnesium, Titanium, Phosphorus and Potassium oxides shows only slight changes in whole granulometric range. Intermediate fraction mainly contained amorphous silica of varying degrees of modification. As the grain size decreased, a trend towards a decrease in the Si/Al ratio and an increase in the amount of oxide modifying agents in the amorphous phase was observed. Thermal roasting tests were performed in the range of up to 1250°C and show a large divergence of the characteristics as a function of grain size. The finest and coarsest fractions were found to contain a significant amount of thermally unreacted mineral grains that did not pass through the temperature core in coal combustion chamber.

The findings of this study suggest that dry granulometric fractionation is an effective method for obtaining fractions of fly ash with similar and stable properties. Those can contribute to a better understanding of the variability in fly ash parameters and assistance in developing methods to obtain qualified products with consistent properties for various industrial applications.

Effect of dopants on the properties of high temperature $SrSnO_3$ perovskite compounds

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Keywords: perovskite pigments, $SrSnO_3$, colour measurements, thermal stability

$SrSnO_3$ is promising material that has been studied extensively in recent years due to its desirable thermal stability, magnetic properties, and catalytic properties. The goal of this research is to explore the use of $SrSnO_3$ as an inorganic pigment. However, strontium stannate only responds to a small portion of the solar spectrum (UV light), making it not attractive as an inorganic pigment. This is because the material has a relatively large band gap (4.1 eV). However, it is possible to change the electronic band structure of $SrSnO_3$ and make it responsive to visible and near-infrared (NIR) light by adding transition metal ions or rare earth element ions [1, 2].

To achieve this goal, perovskite-type compounds of $SrSnO_3$ doped with Mn, Fe, Co, and Ni ions were as synthesized. By partially substituting Sn^{IV} ions with transition metal ions, non-stoichiometric perovskites that exhibit light absorption in the visible region of light and enhanced colour parameters were created. Additionally, this substitution could also affect their NIR reflectivity.

The traditional method for preparing inorganic pigments is solid-state reaction, but in this study, pigments of theoretical composition $SrSn_{0.95}M_{0.05}O_3$, where M = Mn, Fe, Co, Ni, were synthesized by co-precipitation followed by calcination at a temperature determined by TG/DSC measurement. Generally, powders prepared by solid-state reaction tend to sinter and form particles and agglomerates with a wide particle size distribution. However, for effective reflection of near-infrared radiation, the pigment particle size should be less than 1 μm. The synthesis of $SrSnO_3$ doped with Mn ions showed that co-precipitation led to the preparation of materials with a more uniform particle size distribution and higher solar reflectivity compared to solid-state reaction. Therefore, the co-precipitation method was used for synthesis of all compound types of $SrSn_{0.95}M_{0.05}O_3$. Semi-products were obtained from solutions of $Sr(NO_3)_2$, $Na_2SnO_3{\cdot}3H_2O$, and nitrates of Mn^{II}, Fe^{III}, Co^{II}, and Ni^{II}.

Thermal analysis methods, specifically TG/DSC analysis, were used to determine the reactivity of the products of co-precipitation. Based on mass loss and endothermic and exothermic effects, the processes occurring in the precipitates were studied and the optimum synthesis temperatures was determined. The DSC curves showed two endothermic effects at 270 °C and 900-940 °C and one exothermic effect with a maximum between 688-704 °C, which related to the formation of the perovskite structure. Chemical reactions taking place at temperatures of 300 °C, 800 °C, and 950 °C were also identified with the help of X-ray powder diffraction analysis of the reaction products.

The thermal stability of the compounds was studied by using a heating microscope up to a temperature of 1450 °C. The particle size distribution using laser diffraction technique based on Mie theory of light scattering was evaluated. To evaluate the reflectivity of the final powders in the visible region of light, the compounds were applied into an organic matrix (dispersive acrylic paint Luxol, AkzoNobel) and coloured films were prepared by depositing slurries containing 1 g of the pigment and 1 g of the organic matrix on white non-absorbing paper. The colour parameters of the films were objectively evaluated and expressed in the CIE L*a*b* colour space (also referred to as CIELAB).

The obtained results showed that the compounds can be used as the inorganic pigments of brown colour.

Acknowledgments

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Morphology-related thermal properties of nanocomposite membranes used in the renal replacement therapies (RRT)

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Keywords: nanocomposite membrane, NIPS, water thermoporosimetry (TPM), permability

Polymeric materials obtained by wet phase inversion (membranes) are characterized by porosity that allows selective permeation of compounds of different molecular weights [1]. The textural properties of membranes (i.e., developed surface area, surface porosity and volume porosity) play an important role in the dialysis process. Continuous renal replacement therapy (CRRT) is a way to treat acute kidney injury (AKI). A new approach to increase the functionality of dialysis membranes is the preparation of nanocomposite membranes. The nanometer filler strongly influences the morphology of the membrane and thus its functional properties (permeability). The pore size range in polymeric membranes is between 10-50nm while the pore size range in nanocomposite membranes is 1-50 nm. In such cases, standard testing methods dedicated to texture testing do not always work. A good complement is DSC-based thermal testing, which bears the name of water thermoporosimetry (TPM). It is based on the fact that a fluid confined in the pores of a solid material experiences an important shift of its liquid-to-solid transition temperature (ΔT) and this shift is related to the size of the pores, in which the liquid is trapped [2].

The aim of work was to prepare a series of nanocomposite membranes based on polysulfone (PSU, Sigma-Aldrich) with various carbon nanofillers: in the form of carbon nanotubes (CNT, NanoAmor US), oxidized graphite (oGR, SGL Company) and graphene oxide (GR, NanoAmor US). The nanofillers were pre-wetted with solvent (DMF) and then ultrasonically homogenized and cast using the NIPS technique. Pore morphologies were observed on membrane sections by scanning electron microscopy (Nova NanoSEM). Membrane surface development was examined using the BET technique and mercury porosimetry technique (Quantochrome) and full thermal characterization of the membranes was performed in the dry state and in the wet state (Mettler Toledo). The thermal capacity of water removed during heating was equal to the pore volume of the membrane. The obtained results of porosity determined traditionally and thermally show that these methods can be complementary for materials with porosity at the boundary between mesopores and micropores. Additional elements improving and modeling the microstructural and thermal properties are carbon nano-additives present in the polymer matrix.

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Influence of gallium addition on the microstructure and properties of SAC 305 lead-free solders

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Keywords: microstructure formation, lead-free solder, SAC 305, gallium

Many lead-free solders, mainly consisting of Sn and small additions of alloying elements (Ag, Cu, Bi, Zn, Sb), have been proposed as the candidate materials to replace Sn-Pb solders. The most promising are the SnAgCu (SAC) solders [1,2]. In order to decrease their melting point and improve their properties, additional alloying elements can be introduced [1,3-5]. The aim of the work is to study the SAC 305 lead-free solders with the addition of Ga and its effect on the microstructure and hardness. In the experimental investigation, scanning electron microscopy, energy-dispersive X-ray spectroscopy, differential scanning calorimetry and hardness testing were used. It was found that the microstructure of SAC 305 solder contains three types of phases. If gallium is added to the SAC 305 solder, the copper-rich phase enriches with Ga. A change in the stoichiometry of this phase can also be observed. Experimental results were then compared to calculations obtained using the Thermo-Calc software.

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Nanobainite formation in high-Al medium-Mn steels: Thermodynamic approach

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Keywords: medium-Mn steel, thermodynamic calculations, nanobainite, heat treatment

Currently, advanced high-strength medium manganese multiphase steels belong to the group of modern iron alloys of high research interest. The studies address the development of an optimal heat treatment or a thermomechanical treatment allowing to obtain a good combination of high strength and plastic properties [1]. On the one hand, thermomechanical rolling is used ensuring high strength with limited elongation; on the other hand, intercritical annealing can be used, which provides good plasticity but it is at the expense of strength reduction. This difference is due to the microstructure of the steel. The more hard phases are, the higher strength but the lower plasticity can be achieved [2]. At the same time, the retained austenite present in the multiphase steel microstructure plays an important role. During plastic deformation, it undergoes martensitic transformation, which locally increases the strength and allows for further deformation of the material. This effect lasts as long as retained austenite is present in the microstructure of the steel.

In the present work, it was aimed to introduce nanobainite into the microstructure of 0.17C-(3.1-3.6)Mn-1.6Al-0.2Si-0.2Mo-0.04Nb type steels, which is characterized by high strength and better plasticity than martensite. However, due to the relatively high M_s temperature, a two-stage heat treatment was proposed to reduce this temperature and produce the nanobainite. The reduction of the M_s temperature is important as nanobainite is formed at relatively low temperatures (200-300 °C) [3]. The presence of nanobainite together with retained austenite and some fraction of ferrite could allow for a good combination of mechanical properties. Nanobainite ensures high strength and moderate elongation, whereas retained austenite allows for greater elongation. The ferrite occurrence is required to reduce the M_s temperature and to increase elongation, unfortunately at the expense of strength. Therefore, it is important to develop parameters that allow the M_s temperature to be reduced with the lowest possible ferrite amount.

The study presents the thermodynamic analysis and calculations concerning the possibility of obtaining nanobainite in medium manganese steels with high-Al and different manganese contents. The performed calculations were used to determine intercritical annealing temperatures providing higher thermal stability of austenite (which M_s will be between 200-300 °C). Then, the estimation of the nanbainite and retained austenite size was performed based on the chemical composition from the intercritically annealed austenite to determine the isothermal holding temperatures. The isothermal holding temperatures need to be selected in such a way that the size of bainite is around 100 nm, which ensures its high strength. At the same time, some fraction of retained austenite should stay in the final microstructure to enhance the properties of the steel during deformation.

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Thermal and structural characterization of fipronil

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Keywords: fipronil, sublimation, evaporation, vapour pressure, polymorph, TGA, DSC, XRD

Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD) and single crystal X-ray diffraction (SCXRD) were applied to study the vaporisation and polymorphic behaviour of fipronil. Sublimation and evaporation rates were determined using isothermal TGA. From these results, vapor pressures were deduced on the assumption that the released vapours behaved like ideal gases and that mass loss was controlled by diffusion through the gas present in the partially filled crucible. For the latter process, the diffusion coefficient was estimated using the Fuller correlation [1]. Results obtained using benzoic acid, as the calibration standard, suggested that it should be possible to estimate vapour pressures to within 12 % with this TGA method [2]. The enthalpies of sublimation and of evaporation were determined as 120 ± 4 kJ·mol^{-1} and 72 ± 5 kJ·mol^{-1}, respectively.

DSC proved particularly useful for differentiating between two different crystal forms present in the as-received neat fipronil. Pure samples of these two polymorphs were obtained via sublimation. The metastable, lower melting polymorph, and the thermodynamically stable, higher melting polymorph melted at approximately 196 °C and 205 °C, respectively. Careful analysis of the DSC results, obtained at different temperature scan rates, showed that the lower melting polymorph converted to the higher melting form via a solid-solid phase transition.

Five different crystal forms of fipronil were obtained by recrystallization from different solvents. Their polymorphic behaviour was systematically studied by comparing the thermal and structural properties of the obtained different crystal forms, including those reported in the literature. TGA curves revealed that all forms, except for the acetone-derived sample, were solvates. All of these pseudo-polymorphs exhibited solvent loss between 60 °C and 100 °C. The acetone-derived sample was found to be a hemihydrate exhibiting mass loss at 120°C. SCXRD studies revealed that three of the five forms had similar structural characteristics, while the other two forms differed notably from each other and the rest of the structures. Despite these differences, all five forms exhibited near-identical intra- and intermolecular hydrogen bonding networks.

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Thermal analysis of sulfonated polysulfone

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Keywords: sulfonated polysulfone, ioniomer, thermal analyses, glass transition, ionic conductivity

Commercial polysulfone with average molar mass M_n=22 000 was sulfonated with trimethylsilyl chlorosulfonate [1]. Two sulfonated polysulfone with different sulfonation degree were obtained. The materials were analysed by Fourier Transform Infrared Spectroscopy (FTIR) (Fig. 1), Scanning Electron Microscopy (SEM), Thermal Gravimetry coupled with Differential Scanning Calorimetry (TGA-DSC) and Electrochemical Impedance Spectroscopy (EIS).

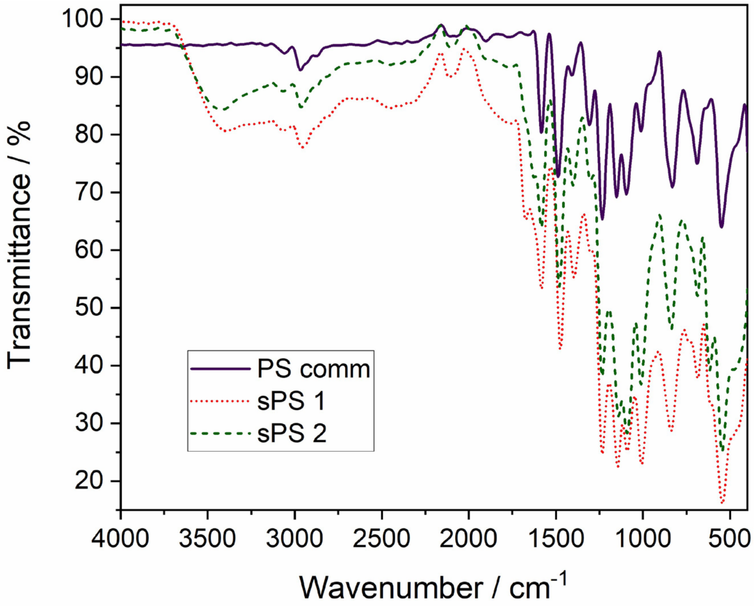

Fig. 1 Overlapped FTIR spectra of non-sulfonated and the two sulfonated polysulfone

The broad absorption between 3600-3200 cm^{-1}, due to hydrogen bond, from the FTIR spectra is proof of the successful sulfonation. The high values of ion conductivity between 0.03 – 0.1 S/cm were obtained by EIS. The materials were prepared and tested as proton exchange membranes (PEM) for fuel cells.

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Structural and thermal investigation of the ternary Mg-Zn-Ca system

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Keywords: Mg-based alloys, mechanical alloying, DSC, XRD

Due to their good mechanical properties, biocompatibility and biodegradability, magnesium alloys have become suitable candidates for potential biomedical materials. Among different Mg alloys, Mg-Zn-Ca system are the most popular degradable implant materials. The preparation methods of Mg-Zn-Ca are predominantly based on forming by liquid alloys under cooling. Other alternative method is mechanical alloying, which ensure more advantages. This method allow to form solid state from two metals without the need for a high-temperature excursion. Whereas if the two metals are insoluble in the liquid or solid state, an extremely fine dispersion of one of the metals in the other can be accomplished. In this paper, attention was paid to produce a controlled, extremely fine microstructure of the $Mg_{66}Zn_{30}Ca_4$ alloys by a high-energy ball milling process for 5, 8, 13 and 20 hours. The influence of ball-milling duration on structure, mechanical properties, thermal and phase evolution of Mg-based alloys were investigated. Structural changes were investigated by X-Ray diffraction (XRD) method. The morphology of the obtained powders and the chemical composition were examined using a scanning electron microscope (SEM) with the energy dispersive spectrometer (EDS). The distribution of powder size of the four samples was determined using the laser particle size analyzer. The thermal characteristic of the powders has been investigated up to 450°C by differential scanning calorimetry (DSC). The mechanical properties were determined using a Vickers microhardness tester.The XRD diffraction patterns of powders show the presence of the magnesium-based solid solution and the MgZn ($Mg_{51}Zn_{20}$) phase. The characteristic Bragg lines of unreacted Zn and Ca can be observed in addition.The DSC analyses have revealed the presence of MgZn phase. SEM analysis showed a lamellar structure, which is the results of deformation process within milling. The results of the microhardness ($HV_{0.05}$) measuring showed that increasing the milling time improved the microhardness of $Mg_{66}Zn_{30}Ca_4$ alloy.

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Thermal behaviour of Mg-Zn-Ca-Pr alloy synthesized by mechanical alloying

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Keywords: Mg-based alloys, mechanical synthesis, phase analysis, DSC

Magnesium based materials an interesting solution in terms of medical applications. Alloys normally hard to obtain may be manufactured via mechanical alloying which allows to produce materials with complex chemical composition and non-equilibrium structures. This work aims to investigate Mg-Zn-Ca-Pr alloy obtained with MA in terms of their phase composition and changes during heating. The paper presents the results of tests conducted for alloys after 5, 8, 13 and 20 hours of milling.The DSC analysis revealed the T_x temperature at 259.9°C which corresponds to the $MgZn_2$ phase formation. It is supported by the results of thermal XRD analysis performed in the range of 25–360°C, which revealed $MgZn_2$, $Ca_2Mg_5Zn_{13}$ phases and Mg solid solution. The melting points of the resulting phases are respectively 380.3°C and 341.5°C.

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Thermal characteristics of polyurethanes for joints applications of wooden structures

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Keywords: polyurethanes, FPUR, RPUR, thermal conductivity, thermal expansion, DMA, thermal analysis

Central Europe has seen a steady increase in using natural materials for wood construction in recent years. On the one hand, the type of wood is essential, which guarantees the appropriate mechanical properties. On the other hand, unlike standard metal components, adhesive bonding can achieve the required structural dimensions, eliminating the problem of thermal bridging in the structure and energy dissipation from stresses that generally occur during the vibration of a wooden structure. The research carried out within the framework of the present work focuses on learning about and determining selected thermophysical properties of flexible polyurethanes (FPU) and rigid polyurethanes (RPU). The FPU and DPU will be used to join beech wood components. As part of the research, a series of analyses were carried out using modern research techniques, including differential scanning calorimetry (DSC) with thermogravimetry (TGA), dilatometric measurement of thermal expansion (DIL), diffusivity and thermal conductivity tests of the polyurethanes under study using LFA and Isomet analysers. Dynamic mechanical testing (DMA) was also carried out at different load frequencies and over a wide temperature range. The thermal stability of analysed polyurethanes was also controlled in cyclic measurements.

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Preparation of alkaline earth metal stannate perovskites by thermal decomposition of $ASn(OH)_6$ (A = Ca and Sr)

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Keywords: stannate perovskites, double hydroxides, decomposition

Oxide perovskites are highly versatile materials whose functionality can be altered by modifying chemical composition and/or the synthesis process [1]. Among oxide perovskites, the ternary oxide type ABO_3 is particularly interesting due to its unique combination of A and B cations with varying oxidation states. These includes $A^{1+}B^{5+}O_3$, $A^{2+}B^{4+}O_3$ and $A^{3+}B^{3+}O_3$ types, as well as oxygen- and cation-deficient species and various aliovalent solid solutions. In view of the broad range of technological applications of oxide perovskites, the development of cost-effective synthesis approaches for basic ABO_3 perovskites with variable characteristics is of great interest. This work focuses on the preparation of well-known calcium and strontium stannate perovskites of $ASnO_3$ via the thermal decomposition of $ASn(OH)_6$ (A = Ca and Sr) and evaluation of the impact of the synthesis parameters on the properties of the final product.

The double hydroxides ($ASn(OH)_6$) were obtained by co-precipitation under varying conditions. It is shown that the phase composition of the precipitate and its thermal behavior did not depend on the precipitation conditions or the type of atmosphere (inert or oxidizing), but its decomposition path varied according to the nature of A element. DSC-TGA analysis of $CaSn(OH)_6$ showed that the compound decomposes in one step between 300 and 400 °C associated with a very strong endothermic effect and a substantial weight loss of more than 20%. The analysis of $SrSn(OH)_6$ showed three-step decomposition: (1) dehydration above 100 °C associated with 3% weight loss and a week endothermic effect; (2) the main decomposition step that occurred between 200 and 300 °C associated with 10% weight loss and a strong exothermic effect; (3) an exothermic process associated with 3% weight loss between 700 and 750 °C. Thus, also the chemical properties of Ca^{2+} and Sr^{2+} are very similar, the decomposition of the double hydroxides is shown to follow a different path. In both cases, the thermal decomposition of $ASn(OH)_6$ resulted in the formation of a pure $ASnO_3$ perovskite phase: a low-crystalline $ASnO_3$ was detected by XRD already after calcination at 400 °C, while the formation of a well-crystalline product required treatment at 600 °C or higher. The crystallinity of the product did not change with the calcination temperature increase to 800 °C. Too high calcination temperatures (1000 °C or higher) led to the degradation of $CaSnO_3$, resulting in the formation of an additional phase of Ca_2SnO_4, whereas the $SrSnO_3$ phase remained stable up to 1200 °C.

Further, impact of the different synthesis parameters on the properties of the formed perovskites was studied. It is shown that the nature of the initial reagents and their concentration, the presence of additives (PEG and triethanolamine), the initial pH and the aging time did not influence the properties of $ASnO_3$. However, the processing temperature and the sequence of the mixing of the ingredients influenced the surface area and porosity of the formed perovskites. Moreover, the trend in the change of the surface area and porosity highly depended on the composition and was very different for Ca and Sr, which also agrees with the observation of their different thermal behavior.

In conclusion, this work demonstrated a cost-effective universal method for the synthesis of $ASnO_3$ perovskites (A = Ca and Sr) with variable surface properties. The method is based on the thermal decomposition of $ASn(OH)_6$ and allows the control of the surface properties of the product by adjustment of the co-precipitation conditions of $ASn(OH)_6$ or by controlling the calcination temperature. This research provides a foundation for further development of stannate perovskites for a wide range of applications.

Acknowledgements

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Assessment of thermal stability of two N-ethoxyethyl-N-methylpiperidinium oxalatoborate ionic liquids by thermal analysis and Knudsen effusion techniques

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Keywords: piperidinium ionic liquids, evaporation, thermal decomposition, Knudsen effusion

Due to their desirable properties, such as high ionic conductivity, negligible flammability and tunability, ionic liquids (ILs) have been recognized as promising electrolyte materials in lithium-ion batteries with improved safety. To suppress their crystallizing tendency, selected borate anions have been originally combined with cations having aliphatic chains functionalized by alkoxy groups and, for the first time, the resulting new ILs have been deeply investigated to possibly correlate their thermal and battery performances. Anyhow, important features, related to their stability and effectiveness for long-term safe applications under an extended temperature range, were not fully assessed.

In this work, two ILs containing the same cation (N-ethoxyethyl-N-methylpiperidinium) and different oxalatoborate anions, bis(oxalato)borate and difluoro(oxalato)borate (BOB and DFOB, respectively), have been considered due to the capability of such anions to form protective layers on both positive, high voltage cathodes and graphite-based anodes [1] of a lithium-ion battery.

The thermal behavior was investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC) and under inert atmosphere, and the kinetics of thermal decomposition was analysed according to two model-free approaches (isoconversional integral and incremental methods in the present study) as in the recent study [2]. The results obtained were used to predict the extent of their degradation at temperature close to their applications.

As a continuation of a previous study [3], the BOB and DFOB ILs were also subjected to Knudsen Effusion Mass Spectrometry (KEMS) experiments in order to investigate their evaporation/decomposition behaviour by studying the nature of the gas phase released as a function of temperature. No detectable release of vapor species was found up to temperatures of 110 °C and 130 °C for BOB and DFOB, respectively. At these temperatures, an intense and rapidly growing peak was observed at $m/z = 98$, which was tentatively assigned to a species where the ether moiety is removed from the ring, most probably formed by thermal decomposition. Simultaneous to the increase of peak 98, a weak peak at $m/z = 172$, corresponding to the mass of the IL cation, was also observed, suggesting that at the temperatures explored in the experiments the evaporation and thermal decomposition processes occur simultaneously, with the latter clearly more abundant.

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Thermal degradation study and evaluation of fire properties of epoxy modified resins

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Keywords: epoxy structural composite, flame behavior, LOI, thermogravimetry, thermal stability

Successful strategies to reduce the flammability of a material are extremely important in the field of aeronautics and aerospace applications. Currently, material scientists have the possibility "to use" the advantages of the nanotechnologies in addition to classical methods to protect the materials. In this field, many researchers are focusing on developing and analyzing nanostructured carbon forms for improving the flame resistance of nanofilled epoxy resins also by using Polyhedral oligomeric silsesquioxane (POSS) compounds. The effects of the incorporation of OctaMethylOligomericSilsesquioxanes (OMPOSS) and carbon nanotubes (CNTs) on the reaction to fire of an epoxy resin containing ammonium polyphosphate (APP) (a conventional intumescent flame retardant) cured with diethylenetriamine (DETA) have been investigated [1]. The combination of APP and CNTs provides no enhancement of the reaction to fire of this system, whereas using OMPOSS in combination with APP, a large synergistic effect via an intumescence phenomenon is observed. In addition, epoxy composite with 2 wt% of octa-aminophenyl polyhedral oligomeric silsesquioxanes-reduced graphene oxide (OapPOSS-rGO) by using as cross-linking agent 4,4′-diamino diphenylmethane (DDM) has also been formulated [2]. It was found that incorporation of 2 wt% of OapPOSS-rGO, causes a significant increase of the onset degradation temperature of the epoxy composite by 43°C. In addition, the peak heat release rate (PHRR), the total heat release (THR) and the production rate of CO were reduced by 49%, 37% and 58%, respectively, compared to what observed with the neat epoxy resin. The positive influence of POSS materials to act as fire retardant was also found for thermoplastic polymers, for example, for a polyether-block-polyamide system (50–70% reduction of the PHRR), for polypropylene (40% reduction of PHRR) and a styrene-butadiene-styrene (SBS) triblock polymer (40–60% reduction of PHRR) [3].

Considering these promising results, we have undertaken a study mainly focused on the thermal properties and fire behavior of a tetrafunctional epoxy resin. Carbon nanotubes and four types of POSS have been dispersed at nanometric and/or molecular level in the matrix. Thermal degradation of POSS was found to be different for the four samples, whereas no significant differences were observed for the epoxy resins containing POSS compounds. Considering that thermal stability is crucial to evaluate the potential applications of the materials [4,5], starting from the best results obtained in our systems [6], our attention has been focused on the study of the thermal degradation behavior of the selected epoxy systems performed by thermogravimetric (TG) analysis using four different heating rates. Flame retardancy tested by the limiting oxygen index (LOI) indicated that glycidyl POSS (GPOSS) has meaningful effects on the flame retardancy of the epoxy mixture. The incorporation of 5 wt% GPOSS into the epoxy matrix resulted in a LOI value of 33 with respect to 27 of the pure epoxy mixture. TG measurements confirmed the trend observed by LOI tests.

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Synthesis and characterization of doped zinc oxide nanoparticles for nanofluids

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ZnO it's one of the most studied oxides due to its nontoxic nature and remarkable properties. It has antibacterial and UV-protection properties, high thermal conductivity and high refractive index. Various ways have been used to synthesize and fabricate doped ZnO, but the sol-gel technique has received a lot of interest because of its safety, low cost, and facile deposition equipment. This paper provides a summary of the synthesis of Cu doped ZnO nanostructures with an emphasis on the sol-gel process and identifies the numerous factors that affect the morphological, structural, and optical properties of the produced materials. CuO is a well-studied metal with unique magnetic, electrical and optical features and has been employed widely in the development and manufacturing of super-capacitors, semiconductors, catalysts, electric and magnetic materials. The samples were synthesized by sol–gel method, and the type of the reactants used, as well as the influence of the copper content on the thermal behaviour of the resulted gels was established by thermogravimetric and differential thermal analysis. Based on the results obtained by thermal analysis, the desired thermal treatment was established in order to obtain the required properties of the resulted powders. The XRD powder measurements revealed that samples had zincite structure. Moreover, the incorporation of doping ions into ZnO lattice was also confirmed by infrared spectroscopy. Copper doped ZnO nanopowders with desired structure and properties were obtained. The main applications being pursued involve nanofluids, photocatalysts, energy storage materials, and microelectronics.

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The micro-hardness of the interfacial transition zone between steel bar and lightweight aggregate concrete with high volume blast furnace slag

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Keywords: blast furnace slag, lightweight aggregates aggregate, interfacial transition zone, micro-hardness

This study aims to investigate the effect of blast furnace slag (BFS) additions on the interfacial transition zone (ITZ) between steel and concrete. In the experiment, normal weight aggregates and lightweight aggregates were used to make concrete specimens with a water-binder ratio of 0.3~0.5. The BFS (Grade 120) was used to replace cement at a weight ratio of 0%, 30%, 60% and 75%, and concrete compressive strength and Vickers hardness tests were carried out at 28 days, 56 days and 91 days respectively. The test results show that the compressive strength of the two kinds of concrete increases with the addition of BFS and age. The strength of normal weight concrete is higher than that of lightweight concrete, but the strength of lightweight concrete containing 75% furnace stone powder is lower than that of 60%; The micro-hardness of ITZ between steel bars and concrete increases with the addition of furnace stone powder and age, and the micro-hardness of normal-weight concrete is higher than that of light-weight concrete. Lightweight concrete is not obvious; the average microhardness of ITZ between steel bar and concrete containing 60% hearth stone powder is higher than that of other concrete, and the effect of improving the quality of ITZ between steel bar and concrete is relatively good.

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Effect of sodium chloride on the oxidation process and properties of nanodiamonds

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Keywords: nanodiamond, NaCl, thermal analysis, DSC, TGA, TMA, Raman spectroscopy, TEM

Nanodiamonds (NDs) are pertinent candidates for different fields of applications: polymer composites, lubricants, sensors, catalysts, and bioapplications [1]. NDs belong to a large family of nanocarbon allotropes that also includes nanographite, nanotubes, fullerenes, graphene, and other varied nanostructural modifications such as carbon onions and semi-crystalline/amorphous carbon. The ND surface often contains varying degrees of non-diamond sp^2 carbon whose minimization is needed for the achievement of predictable and reproducible properties of NDs [2]. In this contribution, we investigate the effect of NaCl on the oxidation process of high-pressure high-temperature NDs (MSY 0-30 nm, Pureon) and compare the properties (size, shape, and sp^2 carbon content) of the oxidized NDs with and without NaCl.

The ND oxidation process was studied by the non-isothermal simultaneous differential scanning calorimetry and thermogravimetry (DSC-TGA) analysis under Ar-O_2 atmosphere (ratio 4:1) coupled with mass spectrometry (MS). ND particles were used either pure or mixed with NaCl powder (ND to NaCl ratio 1:360). The effect of humidity was assessed by calcination of the samples at 300 °C in a nitrogen-filled glovebox with content of moisture and oxygen below 1 ppm as well as by variation of NaCl properties (raw, hydrated, or purified).

The DSC-TGA-MS curves of pure NDs showed the presence of two oxidation processes at 533 °C and 568 °C, respectively. While the second and dominant one clearly corresponds to ND combustion, the origin of the first one is not clear. Interestingly, the addition of NaCl to NDs led to the dominance of the first oxidation peak i.e., NaCl lowers the ND combustion temperature. The lowest oxidation temperature had the ND sample mixed with a humid NaCl which also confirms the role of humidity in the oxidation process of NDs with NaCl. The evolved gas analysis performed by MS confirmed products of combustions or gas consumption (e.g., O_2) matching the effects present in DSC-TGA methods. Apart from that, another set of samples were prepared by interrupted oxidization. These so-called oxidized ND samples were analyzed when the residual mass reached 25%. While Raman spectra showed minimal sp^2-C content in both pure ND (ND-ox) and NDs oxidized with NaCl (NaCl-ND-ox), TEM analysis showed significant differences in the ND shape. While ND-ox particles preserved the sharp and edgy shape of the initial ND particles, the NaCl-ND-ox were significantly round, and their shape became more uniform. The TEM analysis enabled us to tentatively assign the first oxidation process, highlighted by NaCl, to the oxidation of the high aspect ratio parts (e.g., edges, tips) of NDs including the sp^2-C domains. The use of NaCl in the oxidation of NDs thus seems to be a promising strategy towards the control of not only the sp^3-C phase purity but also the shape of the NDs.

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Influence of purity and grain size distribution of powdered NaCl on its thermal properties

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Keywords: NaCl, particle size, thermal analysis, DSC, TMA, stereomicroscopy

Sodium chloride (NaCl), or commonly known as kitchen salt, is one of the most well-known and researched materials in human history. It has a wide range of applications, and it is used in material's research (e.g., for crystal growth, scintillation detectors, medical imaging techniques, homeland security or energy storage technology) [1], in the chemical industry (e.g., brine electrolysis) [2], and also for common household use or as material for sprinkling in winter.

This work continues in our previous study, where an interesting effects of combustion process of nanodiamonds (NDs) by thermal analysis was shown [3] and follows up the current research of the NaCl influence on the combustion process mixed together with the NDs as reported by Zhang et al. [4]. Interestingly, they observed a rounding of ND particles in the mixture of NDs and NaCl, however, the explanation of this phenomenon by changing the combustion mechanism was vague. Thus, deeper analysis of such phenomena is required, and in this work, we focus mainly on the analysis of NaCl properties themselves.

In this study, the raw NaCl (Sigma Aldrich; purity 4N) was divided and treated in various ways. Firstly, one part was stored in the atmosphere-controlled glovebox (filled with N_2 gas and content of oxygen and moisture bellow 1 ppm). Second one was purified from oxidic impurities (O_2, OH^-, H_2O, etc.) with gaseous halogenating agents introduced into its melt according to procedure described in [5]. Third one was purified by a combination of the introduction of halogenating agents and the zone refining method [6]. And fourth NaCl sample was prepared from an ingot of bulk single crystal. All samples were stored in atmosphere-controlled glovebox apart from the raw NaCl, which was kept at ambient atmosphere.

The samples described above were ground in alumina mortar and pestle, then further sieved, and prepared with homogeneous and heterogeneous grain distribution (in size fractions ranging from 90-106 and 200-212 μm).

The aim of this work is to study NaCl samples using thermal analyses in the powder form and single crystal NaCl ingot and to describe the processes that occur in the samples during their thermal treatment. Further, the effect of grain size in NaCl powder samples, the effect of purity and moisture content on its behavior under thermal treatment was characterized. The samples were studied by thermal analyses including non-isothermal differential scanning calorimetry (DSC), thermogravimetry (TGA), thermomechanical analysis (TMA), mass spectrometry (MS), and optical stereomicroscopy (OM). The obtained results of performed characterizations will be discussed. The TMA showed that the smaller the grain size, the earlier the grains are densified and subsequently sintered when heated. On the other hand, the influence of NaCl powder grain size distribution on the course of the TMA curves was recorded and showed a significant influence on the sintering effect.

Acknowledgments

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Metals, alloys, intermetallics

Behaviour of Inconel®625 in CO_2 between 900 and 1000°C

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Keywords: Inconel®625, CO_2, kinetics, oxidation, FIB-SEM

Inconel®625 is a Ni-base chromia-forming superalloy well known for its high creep resistance and dry corrosion at temperatures of 800°C and more. It is used in aerospace and in thermal exchangers where it is exposed to corrosive gases and not only to oxygen. Now, if its behaviour in oxygen at high temperature was widely studied in the 80s and 90s, the effect of other corrosive gases, particularly those produced by combustions (SO_2, $CO_{2\ldots}$) is less known and little studies were devoted to this question.

For the present study [1], the chosen superalloy was one of the most used ones, i.e., Inconel®625, the main applications of which being the turbine shroud rings, the engine thrust-reverser systems or the jet engine exhausts systems. The Inconel®625 studied was a Ni-base alloy containing chromium (21.5 wt.%) molybdenum (9.0 wt.%) and niobium / tantalum (3.65 wt.%). It was heated in a thermobalance, under flowing carbon dioxide (quality N45) containing only very few impurities.

Between 900 and 1000°C, and for reaction times of 10 h, the only product of oxidation was chromia Cr_2O_3, containing traces of titanium dioxide. The surface appeared blistered, and more and more with the reaction advance. The platinum marker test proved that the growth of the chromia layer was due to an external development. In the underlying alloy, under the chromia layer, a zone several µm-deep severely impoverished in chromium was identified. In this zone, many small inclusions containing niobium and molybdenum were observed, together with a dispersed porosity.

The kinetics obtained were parabolic, since the early beginning of the reaction, even when the surface was not yet covered by the continuous layer of chromia, and the associated apparent activation energy comes out at 310 ± 18 kJ/mol. About the influence of the gas pressure, not any effect of the CO_2 pressure was observed on the reaction rate. Even by removing the chromia layer after 10 hours oxidation, and re-oxidizing the samples, the reaction went on such as if the oxide layer was always present, which proves that the chromia layer played not any kinetic role. This special point, rather surprising, is the subject of a specific oral presentation in this JTACC 2023 [2].

These whole results led to determine the reaction mechanism that involves the outward diffusion of chromium, which crosses successively the Cr-depleted zone of the alloy, which then converts into ions Cr^{3+} at the interface alloy/oxide, and which then cross the chromia up to the outer interface, where they finally react with CO_2. The different elementary steps were exhaustively followed in order to determine which of them was the limiting step of the oxidation. The only one able to justify all the experimental findings is the diffusion of the Cr atoms through the Cr-impoverished zone of the alloy, and therefore the conclusion is that this step was the limiting step of the overall reaction of Inconel®625 in CO_2.

This conclusion differs from that usually presented in the studies devoted to the oxidation of chromia-forming alloys in other gases, which considered that oxidation was kinetically governed by the diffusion step inside the oxide layer. The origin of this significant difference has to be found, but it remains currently unknown: we do not know whether this difference is due to the nature of the reacting gas (CO_2 involves very low oxygen pressures) or to another reason.

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Nanofluids

Comparative study on stability, viscosity and thermal conductivity of hydroxyl and carboxyl group functionalized multi walled carbon nanotube nanofluids

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Keywords: nanofluid, stability, thermal conductivity, viscosity, carbon nanotube

Nanofluids are engineered workfluids with increased thermal conductivity, used for heat transport in different applications such as machinery or microelectronic cooling and solar collectors [1,2]. Regarding the nanomaterials used, there are several main types of nanofluids: metal, metal-oxide, carbide and carbon nanomaterial based nanofluids. In direct absorption solar collectors, the photothermal conversion takes place in the bulk of the workfluid [3]. Carbon based nanofluids are advantageous in these applications, as they are completely black due to the small light penetration depth in the nanofluid [4].

We investigated the stability, thermal- and rheological properties and morphology of hydroxyl (-OH) and carboxyl (-COOH) functionalized multi walled carbon nanotubes (MWCNT). We prepared screening samples with different base fluids such as deionised water (DW) with different pH and surfactants, ethylene-glycol (EG) and mixtures of DW and EG. We concluded that nanofluids with added sodium dodecyl benzenesulfonate (DBS) are the most stable. Larger quantities (100 mL) of stable nanofluids with a concentration of 150, 500 and 1000 ppm(v) were prepared with DW as a base fluid and added DBS and ultrasound treatment. Zeta potential measurements confirmed their stability (below -35 mV) and the samples were stable for several months.

These nanofluids showed Bingham plastic flow behaviour. Using the Bingham equation, yield stress (t_0) for the different concentrations is in a 10^{-2} Pa range, while the plastic viscosity (h) is around 1 mPa·s showing that the long MWCNT particles affect the base fluids flow behaviour even in such low concentrations [5].

With low particle concentrations, all nanofluids were completely black, making them suitable for application in direct absorption solar collectors. Also, measurements showed, that nanofluids heat up at higher rate when illuminated with visible light, compared to the base fluid.

The thermal conductivity of nanofluids is higher than the base fluids (DW). Nanofluids showed an average thermal conductivity enhancement of 5.8, 5.5 and 3.5 % (MWCNT (-COOH)) and 6.0, 2.2 and 3.1 % (MWCNT(-OH)) for concentrations of 150, 500 and 1000 ppm(v) respectively at 20 °C. This shows a strange pattern as higher concentrations cause smaller enhancements, most probably due to the increasing interactions between the relatively long MWCNT strings.

In summary we created small concentrations of stable MWCNT nanofluids, with more efficient photothermal conversion and increased thermal conductivity, while the viscosity increase stayed negligible compared to water, making it suitable for applications in flow systems.

Acknowledgments

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Non-linear simulations of nanofluid flow in an MHD convective Moving Flat Plate

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Keywords: boundary layer, magnetic fluid, nanoparticles, heat source, moving plate.

Nanofluids are an innovative class of heat transfer fluids that consist of nanoparticles dispersed in a base fluid. They exhibit improved thermal properties, such as higher thermal conductivity, specific heat capacity, and heat transfer coefficients compared to conventional fluids. These characteristics make them a promising alternative to traditional heat transfer fluids in a wide range of applications, including electronic cooling, refrigeration, and thermal energy storage. However, the thermal behaviour of nanofluids is complex, and it is still not fully understood. Therefore, this study investigates the impact of a magnetic field on the heat transfer and heat source effects of nanofluids flowing over a moving flat plate with second-stage truncation. We used a local non-similarity methodology to obtain numerical solutions for the governing equations. This method involves transforming the partial differential equations into a set of ordinary differential equations that can be solved using numerical techniques. The resulting system of partial differential equations was then solved using the Runge-Kutta method of the fourth order in association with the shooting approach. The effects of several parameters such as magnetic field strength, heat source strength, and nanoparticle volume fraction on velocity and temperature profiles were examined in this study. We found that the presence of a magnetic field had a significant impact on the velocity and temperature profiles of the nanofluid. Increasing the strength of the magnetic field led to a reduction in the velocity of the nanofluid, while increasing the heat source strength resulted in an increase in temperature. The nanoparticle volume fraction was also found to have a significant effect on the behaviour of the nanofluid. Higher nanoparticle concentrations led to a more significant increase in temperature. Furthermore, we found that the presence of the magnetic field significantly altered the nanofluid's velocity and temperature profiles. The magnetic field caused the nanoparticles to align themselves in the direction of the field, which resulted in a decrease in the velocity of the nanofluid. Additionally, the magnetic field generated eddies in the nanofluid that increased the rate of heat transfer. We found that the strength of the magnetic field had a significant impact on the magnitude of these effects. The results of this study have significant implications for the design and optimization of heat transfer systems that utilize nanofluids in the presence of magnetic fields. The findings suggest that the presence of a magnetic field can alter the behaviour of nanofluids in unexpected ways, leading to changes in the rate of heat transfer and the flow characteristics of the fluid. These insights could be used to design more efficient and cost-effective heat transfer systems that utilize nanofluids in the presence of magnetic fields. Overall, this study provides a valuable contribution to the field of nanofluid heat transfer. The results demonstrate the significant impact of a magnetic field on the behaviour of nanofluids and highlight the importance of considering external forces when designing nanofluid-based heat transfer systems. The insights gained from this study could be used to develop more efficient and sustainable energy systems, leading to a reduction in carbon emissions and a more sustainable future. Problem geometry and thermophysical properties of particles as well as base fluid are presented in figure and table respectively.

Table. Properties of nanoparticles and base fluid.

Thermo-physical properties	Base fluid	Reference nano particles			
	H_2O	Cu	Al_2O_3	TiO_2	Ag
Density (kgm^{-3})	997.1	8933	3970	4250	10,500
Specific heat ($J\ kg^{-1}\ K^{-1}$)	4179	385	765	686.2	235
Thermal conductivity ($Wm^{-1}\ K^{-1}$)	0.613	400	40	8.954	429

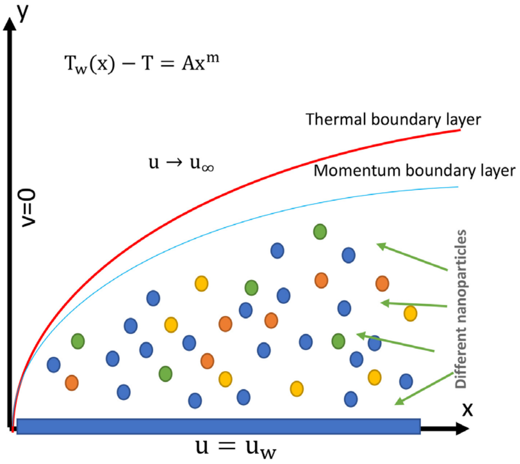

Fig : Geometry of the physical flow problem

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Thermal behaviour and optical properties of silver doped zinc oxide nanoparticles obtained by sol-gel and microwave assisted sol-gel methods

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Keywords: zinc oxide, sol-gel, microwave assisted sol-gel methods

Zinc oxide is a non-toxic oxide used in materials with antibacterial properties, high thermal conductivity and high refractive index [1-3]. Silver oxide is a non-toxic typical metal oxide with a wide range of applications in diverse fields such as antibacterial and electronic materials [4].

In this work different synthesis of silver doped zinc oxide nanostructures were provided, namely sol-gel and microwave (MW) assisted sol-gel methods. Some differences regarding the morphological, structural, thermal and optical properties of the produced materials were noticed. The thermal treatment of the silver doped zinc oxide is established based on thermogravimetric (TG) and differential thermal analysis (DTA). The structure of the powders was determined by X-Ray Diffraction (XRD). The XRD patterns of the thermally treated powders show the crystallization of zincite, belonging to wurtzite-type structure. Moreover, the incorporation of doping Ag-ions into ZnO lattice was also confirmed by infrared spectroscopy. The influence of synthesis parameters on the morphology was studied by field emission scanning electron microscopy (FE-SEM).

The main applications being pursued involve nanofluids, photocatalysts, energy storage materials, and microelectronics [4-7].

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Thermohydraulic analysis of conical annular fins coupled with clove-treated graphene nanoplatelets nanofluids within an annular domain

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Keywords: heat transfer augmentation, geometrical effects, extended surfaces, CGNP nanofluids

Recently, in order to amplify heat transfer rates, geometrical and fluid modification within heat exchangers have been extensively explored. Combined employment of fins and nanofluids have since been subjected to ample investigations, due to their promising heat transfer capabilities. However, the drawback of the current compound method is the penalty in pressure drop. Hence, two variations of streamline conical annular fins are proposed, which allows for lesser blockage and increased streamline flow. The current framework numerically investigates the heat transfer augmentation of two conical fin designs coupled with functionalized clove-treated graphene nanoplatelets nanofluids. Accordingly, the results would then be compared to the thermal capabilities of a smooth conduit and conventional finned conduit under identical working conditions. From the findings, both conical fin designs have proven to obtain enhanced thermal performances, relative to the smooth conduit. Furthermore, the pressure drop exhibited by both conical designs are relatively lower than the conventional fins studied. All factors considered, the steep fin was superior fin design, with enhanced thermal performances and relatively lower pressure drop. Regarding working fluids, the highest concentration of 0.1 wt% of the clove-treated graphene nanoplatelets nanofluids concentration displayed intensified heat transfer coefficients compared to distilled water and 0.075 wt% concentration.

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Investigation of Stability, rheological properitys and Thermal conductivity of Hybrid SiO_2-ZnO nanofluids

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Keywords: SiO_2-ZnO hybrid nanofluid, viscosity, thermal conductivity, surfactant, Zeta potential, TEM

Nanofluids are colloid dispersions where the purpose of particle addition is to produce fluids with enhanced thermal properties, such as thermal conductivity and heath capacity. In our research, SiO_2 nanoparticles were purchased from Sigma-Aldrich and ZnO nanoparticles from Nanografi. The solid particles were characterised by Transmission electron microscopy coupled with energy dispersive X-ray microanalysis (TEM-EDX), Fourier-tranform infrared spectroscopy (FT-IR) and X-ray powder diffraction (XRD). The average diameter of the particles is approximately the same (20-30 nm), but their density is quite different (2.1 g/ml for the SiO_2 particles and 5.5 g/ml for the ZnO particles). Fig 1. shows TEM images of the particles. Vibrations of the ZnO was out of the range of the IR spectrum (4000-450 1/cm), but weak stretching vibrations of the acetate ions were detected so probably $Zn(O_2CCH_3)_2$ was the precursor of these nanoparticles. The SiO_2 nanoparticles are amorphous, and the ZnO nanoparticles are build up from hexagonal crystals. Water has unique thermal properties, so this fluid was set as basefluid. Nanofluids were made in different SiO_2: ZnO ratios (1:0, 3:1, 1:1, 1:3, 0:1) and with 0,5 vol% particle concentration. Nanofluids containing other concentrations of particles are currently under investigation. An ultrasonic homogenizer was used to make stable dispersions. Nanofluids made of only one kind of particles was almost stable, but when two different particles were used, a strong aggregation was observed. Several different surfactants were tried to stabilize the dispersion. Gum arabic was the best because it does not cause foaming and it can prevent the quick aggregation between the different particles. Fig 2. shows the Zeta potential values of the nanoparticles with and without this surfactant. We were able to change the surface charges of the ZnO particles to avoid the quick aggregation. The viscosity of the nanofluids was measured by a rotation viscosimeter. The viscosity of the nanofluids is higher than the viscosity of water, and they also decrease by the increasing temperature as shown in Fig 3. The thermal conductivity of the nanofluids was also measured. Applying 0.5 vol% particles (SiO_2: ZnO 1:1) the thermal conductivity increased by 1.5%.

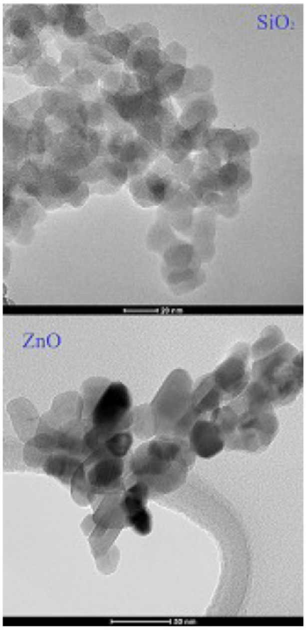

Figure 1.: TEM images of the nanoparticles

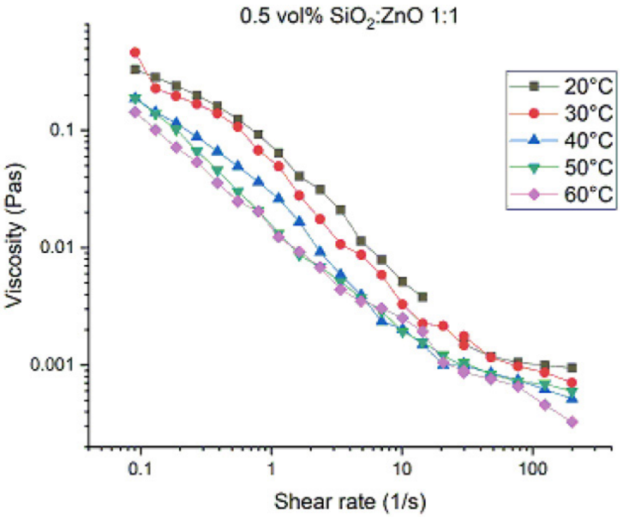

Figure 2.: Zeta potential

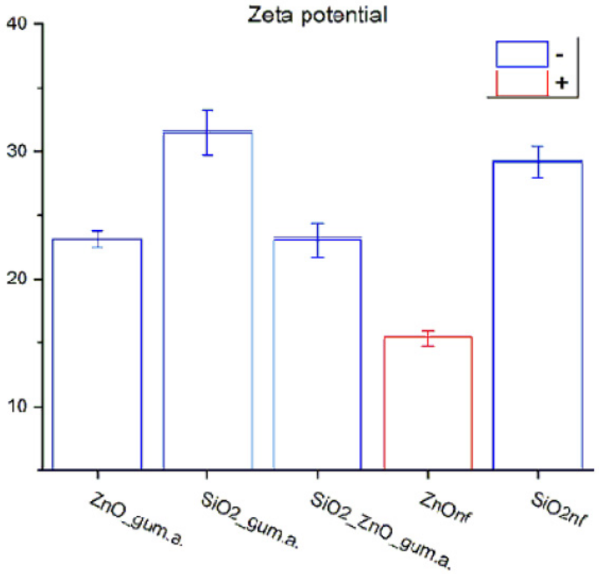

Figure 3.: Viscosity

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Nanomaterials and composites

Thermal and radiation stability of POSS by the presence of hydrocarbon substituents

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Keywords: POSS, thermal stability, hybrid materials

The inorganic structures show appropriate stabilizers for polymers [1,2], because their free space inside polyhedral configuration allows the penetration and tight fixation of fragments. The stability of the substituted compounds was not profoundly investigated [3-5], Accordingly, the details on the energetic transfer especially by high energy irradiation accompanied by structural damaging were not thoroughly reported.

The thermal and radiation stabilities of POSS modified with various hydrocarbon substituents are studied by chemiluminescence and thermogravimetric analysis (TGA). The material answers are different in relation with the electronic densities that exist in the modified structures. The oxidative degradation achieved at four □-doses: 0, 25, 50 and 100 kGy present unlike behaviour, because the substituents interact with the frame of silsesquioxane and the scission of –Si – O – moieties exhibit different levels. The comparison of nonisothermal spectra reveals the generation of hydroperoxides at two different temperatures that demonstrates the induction of degradation by means of the variation of electronic densities. TGA experiments showed the influence of irradation on the stabilisization of the prepared materials.

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Effect of Calcination Temperature on the Phase Composition, Morphology, Thermal proprieties of ternary nanocomposites Mg-Zn-Co oxide by Hydrothermal method for Solid Hydrogen Storage

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Keywords: nanostructure, ternary nanocomposites, kinetic, thermal, and structural properties

Nanocomposites are a class of materials that have gained significant attention due to their unique properties and potential applications. In this study, a simple method for synthesizing efficient ternary nanocomposite samples from Mg-Zn-Co oxide has been developed using the hydrothermal method. The nanocomposite oxide was characterized using structural and thermal methods. The effect of calcination temperature on phase formation and chemical composition of the solid-state products was studied by X-ray diffraction. The results reveal that the synthesized samples had a complex crystalline structure consisting of various crystalline phases of different compositions. Also, it was indicated that varying temperatures had an impact on the average sizes of the nanoparticles. SEM showed the nanoparticle morphology, with different average sizes. Differential Scanning Calorimetry (DSC/ATG) was used to determine the different thermal properties of the samples by measuring the specific heat capacity for investigating the thermal behaviour of materials and understanding their kinetic mechanisms. Also, the DSC thermogram gives the crystallization temperature for the solid materials prepared; specifically, we used three different materials Mg, Zn, and Co with different properties. This information on the kinetic mechanisms of materials is important to determine the optimal processing conditions for a given composite. In this study, we focused on the synthesis and characterisation of ternary nanocomposites, Mg-Zn-Co oxide, with the intention of discovering samples with suitable structural and thermal properties for future solid hydrogen storage applications. As supported by pervious studied, structural properties, including grain size, can affect the storage capacity of hydrogen, with small grains having a better absorption and desorption of hydrogen than large ones [1]. Moreover, it has been shown that an increase in the calcination temperature can significantly increase the hydrogen storage capacity [2]. Therefore, the study of structural and thermal properties is essential to determining the characteristics that provide the best results in hydrogen storage.

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Superparamagnetic cobalt substituted iron oxide nanoparticles as heat source in magnetic hyperthermia: influence cobalt concentration on Specific Loss Power

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Keywords: calorimetry, magnetic hyperthermia, heat generators, co-precipitation, ferrofluids

When magnetic nanoparticles (MNPs) are placed in an alternating (ac) magnetic field, they absorb the energy of the field and convert it into heat, which causes a temperature change in the system. Consequently, it makes them suitable for cancer treatment with magnetic hyperthermia (MH). The efficiency of heat generation by MNPs is expressed through Specific Loss Power (*SLP*). *SLP* dependence on the heat capacity of nanoparticles and the temperature change in the system with time ($\Delta T/\Delta t$), and most often it was estimated from calorimetric heating measurements. For the treatment of malignant diseases by MH, it is necessary to accumulate a sufficient amount of MNPs in the tumor tissue and they should have enough high *SLP*. Nanoparticles $Co_{0.047}Fe_{2.953}O_4$ (S1) and $Co_{0.086}Fe_{2.914}O_4$ (S2) were synthesized by co-precipitation method at 80 °C for 2 hours to be tested for potential application in MH. X-ray diffraction data show that the nanoparticles crystallize in a spinel-type structure (space group Fd3m) and are single-phase. The calculated crystallite size by Scherrer's equation using FWHM of reflection (311) was 9.9 and 11.5 nm, respectively. TEM analysis shows that the particles are quasi-spherical in shape and ~15 nm in size. By measuring the magnetization in different magnetic fields, it was found that the samples are superparamagnetic at room temperature with a value of saturation magnetization of 69.5 emu/g (S1) and 73.4 emu/g (S2), which indicates an incremental influence of incorporating cobalt into the crystal lattice of the host compound (Fe_3O_4) on the magnetism of nanoparticles. Calorimetric curves of S1 and S2 heat generators were measured using a commercial DM100 device (nB Nanoscale Biomagnetics, Zaragoza, Spain) in different external fields and frequencies. The heating curves of studied nanoparticles showed that sample S1 could be potentially used as a heating agent in magnetic hyperthermia applications. The *SLP* values were around 50 W/g (H_{AC} = 15.91 kA/m and f = 252 kHz) for S1, while S2 was significantly lower at ~25 W/g. To be used as heating agent in magnetic hyperthermia, sample S1 was coated with citric acid ($CA@Co_{0.047}Fe_{2.953}O_4$) and poly(acrylic) acid ($PAA@Co_{0.047}Fe_{2.953}O_4$). Further hyperthermia studies, FT-IR, DLS, ζ-potential measurements and TGA analysis are yet to be performed.

Synthesis and thermal characterization of magnetite – based functionalized nanoparticles for forward osmosis

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Keywords: magnetic nanoparticles, magnetite, citric acid, polyacrylic acid, forward osmosis

Forward osmosis (FO) technologies exploit the natural osmotic pressure gradient between two fluids separated by a semipermeable membrane to enable the transport of solvent molecules from the solution of lower osmotic pressure to that of a higher osmotic pressure. The method has gained significant interest in recent years as an alternative to conventional reverse osmosis processes in wastewater treatment and desalination, enabling benefits like lower energy use and less possibility of membrane fouling due to reduced pressure on the membrane [1]. The main challenge in FO remains the re-concentration of the draw solution (DS) used during the process. Iron – based magnetic nanoparticles like magnetite and maghemite could provide ideal candidates since they can easily be recovered using an external magnetic field. Unfortunately, bare magnetic nanoparticles (MNPs) exhibit a low osmotic pressure and tend to aggregate in aqueous solutions, thus they must be functionalized with molecules that generate sufficient osmotic pressure and prevent agglomeration. Various coating molecules have been investigated and reported in literature, including silica, organic acids, lipids, proteins, and polymers [2]. In the present study, magnetite (Fe_3O_4) nanoparticles were synthesized using the coprecipitation method and stabilized using (3-aminopropyl) triethoxysilane (APTES). The amino groups of APTES were further functionalized with citric acid (CA) and polyacrylic acid (PAA) to achieve higher osmotic pressure. The as-prepared nanoparticles were characterized using different methods: Fourier-transform infrared spectroscopy (FTIR) confirmed the binding of APTES and CA/PAA on the surface of the MNPs while the size of the particles was determined by transmission electron microscopy (TEM). The isoelectric point, zeta potential and the particle size in suspension were determined by dynamic light scattering (DLS)/Zeta potential measuring system. The amount of free -COOH groups was determined by conductometric titrations. The amount of organic matter (APTES, CA, and PAA) bound on the surface was determined by thermogravimetric analysis (TGA), giving results between 7.6% for samples functionalized with APTES only to 17.5% for samples with APTES + PAA. The measurements of osmotic pressure provided encouraging results of 28 bar, enabling using the samples as draw solutions in an experimental forward osmosis system.

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Thermal and Plasma-Assisted Atomic Layer Deposition for the synthesis of inverse opal photocatalysts

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Keywords: inverse opals, nanocomposites, thermal ALD, plasma ALD, photocatalysis

The construction of the combined inverse opal (IO) nanostructures can be a promising approach for developing novel materials with enhanced performance. Due to their efficient optical characteristics, and thermal and electrical properties, they have recently been studied for various photocatalysis, solar cells, chemical sensors, electric wires, and highly efficient microwave photonic crystal fiber applications [1,2]. Here, TiO_2, ZnO, TiO_2/Al_2O_3, and ZnO/Al_2O_3 IO structures were grown using thermal and plasma-assisted atomic layer deposition (ALD) in the presence of polystyrene (PS) opals as a sacrificial template. Various characterization techniques were used to investigate their thermal, morphological, structural, and optical properties using TG/DTG/DTA-MS, SEM, XRD, Raman spectroscopy, and UV Visible spectroscopy, and their photocatalytic activity was investigated in decomposing MB under visible light illumination. Subsequent annealing at 500^{o}C burned out the PS nanosphere template, leaving the inverse opal structures behind. SEM, Raman, and XRD results confirmed monodispersed, microporous, well-ordered, and crystalline tetragonal anatase and hexagonal wurtzite phase from TiO_2, ZnO, and their composite IO nanostructures, respectively. UV Vis absorption spectroscopy revealed strong absorption bands found in the UV Vis regions, including increased absorption due to slow photons i.e. light propagation at reduced group velocity, evaluation through electronic transitions, and generating electron-hole pairs necessary for photocatalytic processes The ultra-thin film amorphous Al_2O_3 prepared by thermal ALD has a more ordered IO structure in both (TiO_2/Al_2O_3 thermal and ZnO/Al_2O_3 thermal samples) when compared to Al_2O_3 prepared by plasma-assisted ALD (TiO_2/Al_2O_3 plasma and ZnO/Al_2O_3 plasma samples), which explains its higher photocatalytic activity.

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Synthesis of Co_3O_4/polyaniline nanocomposite: structural, morphological, electrical and electrocatalytic properties

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Keywords: cobalt oxide spinel, XRD, nanocompoaites, conductivity

Polymeric nanocomposites (PNCs) containing metal oxides have attracted lot of interest due to unexpected hybrid properties synergistically derived from both components. Researchers have attempted to enhance the desired properties of PNCs improving their properties by introducing nano metal oxide in them.

PNCs containing nano sized metal oxides have been extensively studied since they exhibit interesting properties with many applications such as quantum electronic devices, magnetic recording materials, sensors, capacitors, smart windows, toners in photocopying, conducting paints and rechargeable batteries.

In this work, Co_3O_4 was prepared by hydrazine based combustion method. Phase formation of Co_3O_4 was confirmed by using XRD. FTIR, TGA/DTA, SEM techniques were used to characterize prepared oxide. Co_3O_4 was incorporated in Polyaniline matrix by weighing appropriate quantity of Co_3O_4 nanoparticles and PANI prepared and grinding it in pestle and mortar for almost two hours. Coded as PANI-5, PANI-10, PANI-20, PANI-30 PANI-40 PANI-50 mass %. The prepared nano composites were characterized by different characterization techniques such as FTIR, Powder XRD, SEM and TG/DTA. The electrical properties of Co_3O_4/Pani hybrid NCs were unique in comparison to the pure phases, PANI and Co_3O_4 nanoparticles (NPs), which were ascribed to the interaction between the PANI and Co_3O_4 nano particles. Room temperature DC conductivity was observed to be enhanced as the Co_3O_4 NPs concentration increased from 10 to 30 wt% in the hybrid NCs but found to decrease from 40 to 50%. The electrocatalytic activity of 30, 40 & 50% Co_3O_4/Pani hybrid NCs for were tested in 2M KOH electrolyte for cathodic reduction of air. Steady state polarisation data shows increase in electrochemical activity on increase in Co_3O_4 conc in PANI matrix.

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Preparation and photocatalytic activity of Halloysite – Ni/Zn-oxide – Magnetite nanocomposites

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Keywords: oxide nanocomposite**,** clay mineral**,** photocatalytic activity, magnetic susceptibility

Clay minerals are particularly promising materials for environmental remediation and technologies. One of the crucial criteria for the environmental application of transition metal-oxide modified clay minerals is their separation from the reagents and products. The efficiency of physical separation in aqueous phase (filtration, centrifugation) can be improved by embedding non-toxic, biocompatible magnetite into the catalyst, rendering it magnetically separable [1].

In this study magnetite modified halloysite–Zn-Ni-oxide composite systems were synthesized and investigated. Zinc-oxide is a well-known photocatalyst, its stability can be improved by adding nickel-oxide to supress photocorrosion [2]. The halloysite clay mineral has multirole in the composites: (i) as carrier could advance the appropriate metal-oxide dispersion and substrate adsorption (ii) could contribute to the photocatalytic activity [3]. The aim was to synthesise magnetite-halloysite-nickel/zink-oxide composites with a sufficient magnetic separability and photocatalytic activity. The optimal Ni:Zn ratio was also investigated. Halloysite-magnetite composites with varying Fe_3O_4 content (10-60 m/m%) were prepared, their structural and magnetic properties investigated (X-ray diffraction (XRD), infrared (FT-IR-ATR) and impedance spectroscopy, N_2-BET). Preparation of metal-oxides was carried out by in-situ synthesis of zinc- and nickel-hydroxide precursors directly on the surface of the halloysite-magnetite composite and their subsequent heat-treatment. Treatment temperatures and the evolution of the oxide composites were followed by means of thermoanalysis (TGA-DSC), nanocomposites with various magnetite (40-48%) and mixed oxide (20-30%) were characterized by XRD, FTIR-ATR, N_2-BET, TEM-EDX and impendence spectroscopy. The synthesis offered a viable oxide preparation by heat-treatment with lower pollutant levels and lower synthesis temperatures.

Photocatalytic activity was probed by measuring the evolution of photogenerated ·OH radicals using the coumarin scavenger compound and the degradation of the aromatic 4-nitrophenol in aqueous phase when the photocatalyst composites were irradiated by λ_{max}=365 nm UV light. The process was followed by UV-Vis spectroscopy.

Acknowledgments

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Organic materials

Photosensitive dendrimers as a good alternative to antimicrobial photodynamic therapy of gram-negative bacteria

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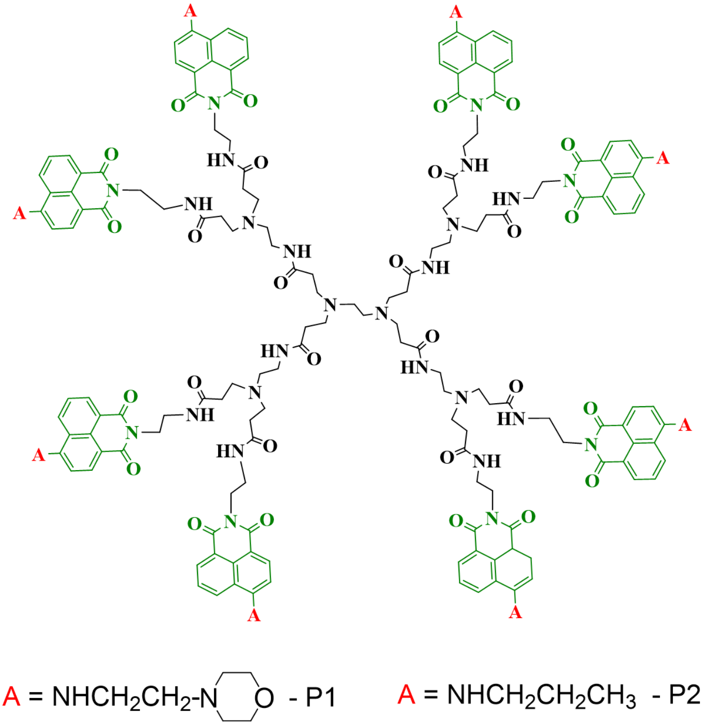
Keywords: 1,8-naphthalimides, dendrimer, bioactivity, photodynamic antibacterial therapy

The spread of multi-resistant bacterial strains has arisen due to the excessive use of antibiotics and has been one of the most worrying threats to public health in recent years. Gram-negative bacteria are responsible for many life-threatening infections in humans, and they are often innately resistant (especially *P. aeruginosa*) to the most commonly used antibiotics. This work describes the antimicrobial activity and cytotoxicity of two photoactive PAMAM dendrimers modified with 1,8-naphthalimides.



Scheme 1. Chemical structure of PAMAM dendrimers modified with 1,8- naphthalimides

Both dendrimers absorb in the visible spectral region and emit yellow-green fluorescence. Their photophysical and color characteristics of cotton fabrics dyed with them have been investigated. It has been found that the dyed cotton fabrics have a brilliant yellow color, which is due to the yellow-green fluorescence emitted by the dendrimers. The antibacterial activity of the dendrimers has been tested *in vitro* against Gram-negative *P. aeruginosa* strain by the broth dilution test. The tests were performed in dark and after irradiation with visible light. The obtained results show the dendrimers to have twice higher activity after irradiation in daylight than in dark. It has also been found that after the dendrimers are deposited on the cotton fabric, its hydrophilicity decreases, which inhibits the deposition of bacteria on its surface. Increased antibacterial activity at light irradiation is due to the generation of singlet oxygen, which attacks the cell membrane of bacterial cells. The formation of singlet oxygen was investigated by the iodometric method, in which I^- was transformed into I_3^-, which was absorbed at 288 nm and 352 nm. The cytotoxicity of the studied dendrimers has been investigated on HEp-2 cells. Low cytotoxicity has been observed after the deposition of dendrimers on cotton fabrics.

Acknowledgments
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Synthesis and optical properties of peri-disubstituted tellurolo-1,8-naphtalimidies

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Keywords: 1,8-naphtalimides, ditellurols, electronic materials

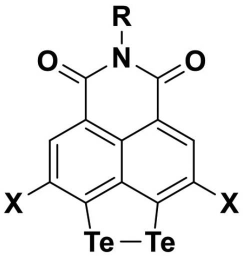
Polyacenes possessing peri-dichalcogen bridges are well documented in the literature and are known for their extremely high electron donating abilities[1,2]. A major problem that arises in such structures is their almost lack of any solubility in organic solvents which makes their characterisation as well as their application in materials science almost impossible.

Substituted 1,8-naphtalimides, on the other hand, have found plenty of applications throughout the years thanks to their exceptionally diverse and rich photophysical properties. This led to many derivatives that were used as fluorescent molecules, anticancer drugs, optical detectors, OLED devices and others.

Thus, combining the great electron donating abilities of tellurium heterocycles as well as the naphthalimide core, novel series of peri-disubstituted ditellurols were synthesised. Contrary to the aforementioned polycyclic aromatics, they show higher degree of solubility and are thus much easier to characterise. The imide group not only enhances the optoelectronic properties of the molecule by acting as an electron sink but also increases the overall solubility by means of controlling the alkyl length of the attached amine. Introducing a strong acceptor lowers the LUMO of the molecule that changes observably the CT excited states. Their facile and straightforward preparation stems from the fact that their synthesis includes few steps starting from the commercially available 1,8-naphtalic anhydride. All synthetic steps require neither harsh/ cryogenic conditions nor the use of air sensitive organometallics, which makes such structures attractive and opens new horizons for their future research.

Ditelluride similar to disulphide bridges are easily reduced in presence of current and reoxidized again since throughout the whole process both tellurium atoms remain in close proximity to each other held tightly by the naphthalene core.

Based on all these facts we suppose that such structures might show better battery capacity and could find applications as potential cathode materials in electronic materials.



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Synthesis of heterocyclic extended 1,8-naphtalimides

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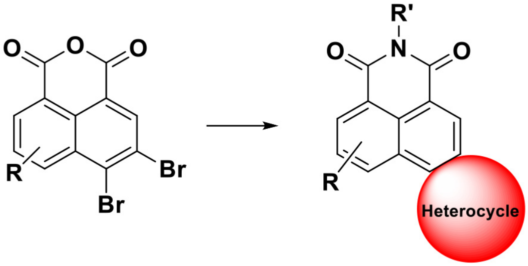
Keywords: 1,8-naphthalimides, anticancer activities, heterocyclic compounds, building block molecules

In the area of anticancer research, the development of small molecules capable of interacting with deoxyribonucleic acid (DNA) and exhibiting anticancer activities has received enormous attention in recent years. Amongst these it has been found that 1,8-naphthalimides and its derivatives possess high anticancer activity towards various human and murine cells. In literature, many examples are known where anticancer activities of naphthalimides have been significantly affected via fusing aromatic or heteroaromatic rings or varying the position and size of side chains.

Consequently, the 1,8-naphthalimide compounds has been extensively used as strongly absorbing and colourful dyes, building block for artificial light harvesting arrays, and fluorescent chemical probes for the sensing of biologically relevant cations and anions.

In our laboratory we have developed several new building block molecules that have found wide application for the synthesis of various naphthalene based fluorophores and chromophores[1,2].



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Enhanced photodynamic efficacy using 1,8-naphthalimides: potential application in antibacterial photodynamic therapy

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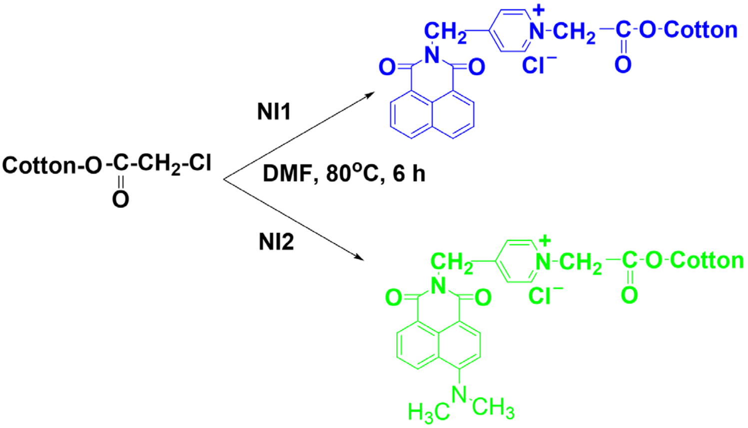
Keywords: 1,8-naphthalimides, photodynamic therapy, antibacterial, textile

In recent years, the resistance of bacteria to the antibiotics used in clinical practice has increased to dangerously high levels in many parts of the world. New mechanisms of resistance have emerged and spread, leading to the inability to treat common infectious diseases since the antibiotics administered are becoming less effective. That necessitates the search for new compounds with good antimicrobial activity as well as inventing new strategies for their usage. In this regard, cyclic imides are of particular interest being as biologically active compounds with well-defined antitumor and microbiological activity. Especial attention has been attracting the 1,8-naphthalimide derivatives, which are a type of cyclic amides with well-defined hydrophobicity and an π-conjugated aromatic skeleton. These compounds of a compact structure and, depending on the type of substituents, can drastically change their functional properties.

In this work, the synthesis and photophysical characterization of two reactive 1,8-naphthalimide derivatives emitting yellow-green (NI1) and blue (NI2) fluorescence were described. The photophysical properties were determined in organic solvents of different polarities. The new compounds were used to dye cotton fabrics which resulted in the covalent bonding of 1,8-naphthalimides to the cotton surface, whereby the resulting fabrics are white and yellow in color with intensive fluorescence (Scheme 1).



Scheme 1. Chemical modification of cotton fabric with NI1 and NI2

The iodometric method has been used to study the generation of singlet oxygen ($^1O_2$) by irradiation of KI in the presence of monomeric 1,8-naphthalimides and of the dyed textile material. The antibacterial activity of both compounds and the dyed cotton fabrics was tested in vitro against Gram-positive *B. cereus* and Gram-negative *P. aeruginosa* in the dark and after light irradiation. Compound NI2 was found to be more active against the studied pathogens compared to NI1. The compounds exhibited better-expressed antimicrobial action against *B. cereus*. The light irradiation enhanced the antimicrobial activity of the compounds and textile fabrics. These results suggest the potential of the novel compounds for use as effective antibacterial agents.

Acknowledgments

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Dioxepine-Peri-Annulated PMIs—synthesis and spectral and sensing properties

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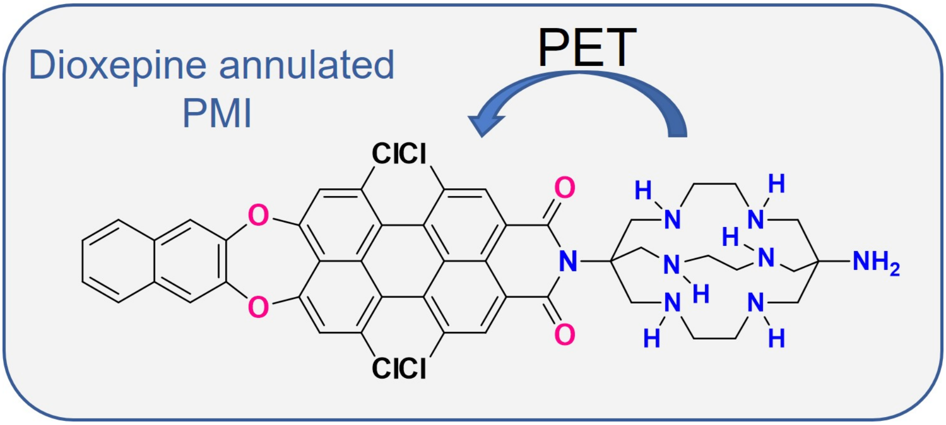
Keywords: perylene monoimides; seven membered ring annulation; DiAmSar; PET sensors; DFT

New perylene monoimide (PMI) derivatives bearing a seven-membered heterocycle and 1,8-diaminosarcophagine (DiAmSar) or N,N-dimethylaminoethyl chelator fragments were synthesized, and their spectroscopic properties in the absence and presence of metal cations were determined to evaluate their potential applications as PET optical sensors for such analytes. DFT and TDDFT calculations were employed to rationalize the observed effects.



Acknowledgments

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New powerful building block molecules in 1,8-naphthalimide chemistry

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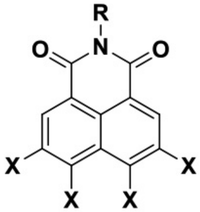
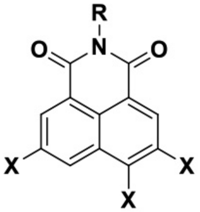
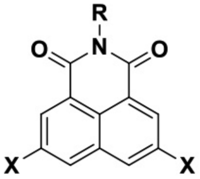
Keywords: 1,8-naphthalimides, building block molecules, anticancer drugs, OLEDs

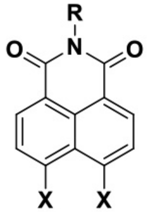
In recent years, much attention has been paid to the design and preparation of new substituted 1,8-naphthalimide architectures and the studies on the properties of materials. Wide possibilities of changing the optical and fluorescence, thermal, electrochemical, electroluminescent, and photoelectrical properties of 1,8-naphthalimide compounds can be materialized by introducing different electron-donating or electron-accepting moieties at the 1,8-naphthalimide core. At the same time, derivatives of substituted 1,8-naphthalimide have found application in other optoelectronic devices, such as organic light emitting diodes, organic solar cells, as well as in memory devices. 1,8-Naphthalimides can have wide energy gaps and low reduction potentials, making them good candidates for use as n-type materials in OLEDs. While many 1,8-naphthalimide derivatives have low luminescent efficiencies at room temperature, due to strong intersystem crossing to their triplet states, 1,8-naphthalimides substituted at the 4 and 5 positions with electron-donating groups can have high fluorescent quantum yields.

In our laboratory we have developed several new building block molecules[1, 2] that have found wide application for the synthesis of various naphthalene based fluorophores and chromophores.









The new dyes are promising candidates for high-tech applications such as OLEDs[1], OFET, visualization of cellular organelles[2], anticancer drugs, bimodal diagnostic imaging, etc.

Acknowledgments
Authors are grateful to the Bulgarian National Science Fund project NSF KP 06-N61/1.

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Pharmaceuticals

Thermal behavior and drug/excipient compatibility studies of antiviral famciclovir

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Keywords: famciclovir, drug-excipient, thermal analysis

Famciclovir is an antiviral prodrug synthetically obtained from the nitrogenous base guanine, with molar mass 321.33 g mol^{-1}[1]. In this work its thermal behaviour was investigated by TG/DTG/DTA and DSC. For compatibility studies, ten excipients frequently used in pharmaceutical formulations were evaluated: stearic acid, carboxymethylcellulose, microcrystalline cellulose, sodium citrate, magnesium stearate, hydroxypropylmethylcellulose, lactose monohydrate, methyl cellulose, methyl paraben, vitamin E were used.

TG/DTG/DTA curves were obtained in a simultaneous SDT Q600 modulus (TA Instruments) using sample mass of *c.a.* 7.0 ± 0.1 mg, heating rate of 10 °C min^{-1}, under dynamic N_2 and air atmospheres (flowing at 50 mL min^{-1}) in open α-alumina sample holders. DSC curves were obtained in a DSC Q10 calorimetric module (TA Instruments), in the heat-cool-heat mode from -40 to 200 °C, at 10 °C min^{-1}, under dynamic N_2 atmosphere (50 mL min^{-1}), in closed aluminum sample holder with a pin hole (ø=0.7mm) in the center of the lid and sample mass of 5.0 mg. DSC curves of excipients and their mixtures with the drug were collected using the same conditions above. For compatibility study, a 1:1 binary mixture of drug:excipient was homogenized in a mortar for 3 minutes using a spatula, then the mixture was placed in a vessel and stirred for another 1 minute at low speed in a vortex until complete homogenization.

According to TG/DTG curves, famciclovir was thermally stable until 206 °C and decomposed in two steps under both air and nitrogen. In nitrogen, 87.6 and 1.62 % of mass losses were observed, while 90.2 and 8.68 % was observed under air atmospheric. Residues of 7.2 and 0.14 % were observed, for nitrogen and air respectively. In the first heating of DSC, two endothermic peaks were observed. The first one at 64.1ºC (T_{onst}) is probably relative to a physical transition, since no water loss is observed in TG curves. This will be detailed latter by collecting samples at this temperature and submitting them to DRX. The second endothermic peak was attributed to famciclovir melting at 105.8 ºC. Only a second order thermodynamic transition was observed on cooling. In the second heating, an exothermic peak at 90.6 ºC represents the cold crystallization of the drug that melted again at 105.8 °C.

TG/DTG/DTA and DSC curves of binary mixtures of famciclovir with each excipient, suggested compatibility of the drug with carboxymethylcellulose, microcrystalline cellulose, sodium citrate, magnesium stearate, hydroxypropylmethylcellulose, lactose monohydrate, methylcellulose. Unlike the mixture of famciclovir with stearic acid, methyl paraben and vitamin E, it was possible to observe changes in the thermal behavior of the drug as shown in the curves. Changes in the melting temperature of the drug were observed in both DSC and DTA, as well as a possible small phase transition seen in the DSC curve. In TG curves of the drug-excipient mixtures it was also possible to perceive changes in the decomposition temperatures of famciclovir, which indicates physical-chemical interactions.

Acknowledgments

LATEQS, IQSC-USP, FAPESP, CAPES e CNPq.

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Compatibility study drug-excipient: an evaluation between hydroquinone and Imidazolidinyl Urea interactions

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Keywords: hydroquinone, Imidazolidinyl Urea, compatibility, thermal analysis, infrared, X-ray diffraction

Hydroquinone (HQ) has been used as a depigmenting in the cosmetics industry for decades. HQ has a similar chemical structure to melanin, being a phenolic compound chemically known as 1,4-dihydroxybenzene. It is known that HQ acts to inhibit the oxidation of tyrosine to 3,4-dihydroxyphenylalanine [1]. The study of the compatibility between drugs and excipients represents a significant phase of the pre-formulation step for the development of all dosage forms. So, it is important to know all excipients and evaluate their possible interactions. In that regard, in a previous study carried out by our research group, a possible interaction was found between HQ and Imidazolidinyl Urea (IMD) [2]. IMD is an excipient used as an antimicrobial preservative, due to the presence of a formaldehyde group denaturing the proteins. Since that, IMD is largely used in pharmaceutical/cosmetic formulations and previous studies reported some interaction between them, these facts motivated the study. Therefore, for this work, it was selected Differential Scanning Calorimetry (DSC) as a thermal technique, and Infrared (FTIR) and X-Ray Diffraction (XRD) as the non-thermal techniques to evaluate the interactions previously mentioned. For that, binary mixtures were prepared in different proportions – 1:1, 1:5, and 5:1 (w/w). Furthermore, each proportion was prepared under 4 different temperatures – room temperature, 50 ºC, 100 ºC, and 200 ºC, totalizing 12 samples. Following that were characterized it. According to the literature, the melting point of HQ is 176 ºC, however, IMD did not show any clear peak referring to the melting point (associated with the polymorphism) [2]. Based on the DSC analysis, the binary mixtures of this work revealed that as the amount of IMD increases, the peak referring to the melting point of the HQ decreases. Besides, the peak shape was also modified, attributing a strong interaction between the substances. The temperature of preparation did not directly influence the interaction capacity between the substances, except for the temperature of 200ºC. The binary mixture prepared at 200ºC does not have any peak because it is already higher than the melting point of the HQ. From the data of non-thermal techniques, it can be inferred that from the increase in the amount of IMD in the mixtures, there is a greater interference in the results. That is, in FTIR there is a disappearance of bands characteristic of HQ, as well as large displacements of these bands. As well as in the XRD analysis, in which there is a disappearance of the peaks that characterize the HQ crystallinity. Finally, it can be concluded that from the thermal and non-thermal techniques carried out in this work, the behavior of the mixtures is observed, which after the discussion carried out, suggests strong interactions between the drug HQ and the excipient IMD. In addition, these interactions are closely linked to both the amount of IMD used and the temperature used (200 ºC).

Acknowledgments

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Compatibility evaluation between Tamsulosin and pharmaceutical excipients

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Keywords: Tamsulosin, compatibility study, solid dosage forms, thermal techniques, FTIR

Tamsulosin hydrochloride (TAM) is an alpha-blocker employed for the treatment of lower urinary tract symptoms associated with Benign Prostatic Hyperplasia (BPH), which is a clinical condition characterized by a benign enlargement of the prostate [1]. Although tamsulosin has been frequently employed for the treatment of BPH, there are few studies available about its thermal behavior and its compatibility with excipients routinely applied in pharmaceutical formulations. The study of drug-excipient compatibility is an important step in the pre-formulation stage for the development of all dosage forms. Therefore, all excipients must be known and evaluated for possible interactions [2]. Therefore, this research aims to characterize and evaluate the thermal compatibility between tamsulosin and the excipients widely applied in solid dosage forms, using thermal techniques (TG/DTG and DTA) and Pearson's correlation applied to FTIR data. For this work, were selected sodium starch glycolate (SSG), starch pregelatinized (PGS), croscarmellose sodium (CCS), magnesium stearate (MS), sodium lauryl sulfate (SLS), mannitol (MA), microcrystalline cellulose (MC) and lactose monohydrate (LAC). After that, binary mixtures were prepared in a proportion 1:1 (w/w) under manual mixing. TG/DTG and DTA curves were obtained using a Shimadzu Thermobalance, model DTG-60H, alumina sample container, under a heating rate of 20 °C/min up to 900 °C. In addition, the spectra of the samples were obtained on a spectrophotometer ATR-FTIR (IRPrestige-21 Shimadzu) between 700 and 4000 cm-1, with 20 scans per sample. Consequently, the spectra were normalized and analyzed by an ad hoc algorithm of spectra comparison, based on Pearson's correlation. It is considered a high correlation when the coefficient is between 0.80 and 1.00. The results obtained from the thermal techniques showed that there are possible physical interactions between TAM and the following excipients: SSG, PGS, MC, LAC, and MA. However, it was confirmed by Pearson's correlation with FTIR data that the binary mixture between TAM and each one of these excipients does not have any interaction or incompatibility that would exclude their application in solid dosage forms containing TAM. Finally, this work shows the importance to associate more than one technique to evaluate compatibilities. Thus, thermal techniques (TG/DTG and DTA) associated with Pearson's correlation by FTIR data confirmed that TAM and excipients above mentioned do not have incompatibilities and may be associated in a solid dosage form.

Acknowledgments

The authors thank Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for financial support and scholarships.

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Preliminary study of polymer-based membrane for Methotrexate drug delivery

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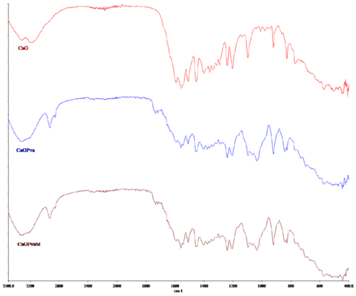
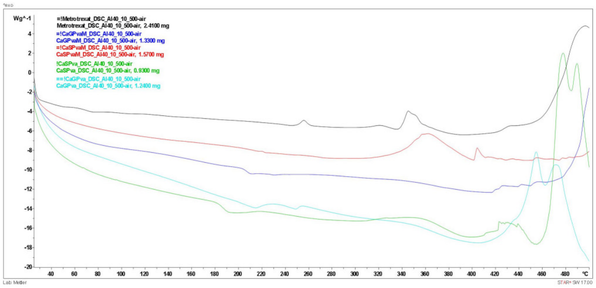
Keywords: drug delivery, biopolymer, thermal analysis, FTIR, UV-Vis

Methotrexate belongs to a class of drugs known as antimetabolites. It is a type of disease-modifying antirheumatic drug (DMARD) commonly used in the treatment of inflammatory arthritis [1].
The efficacy of MTX is related to its cytotoxic and anti-inflammatory effects when administered topically [2,3].

This study follows up on previously published article by our research group in which methotrexate was studied with other different biopolymers to investigate the possible interactions and compatibility of the compounds [4].

The aim of this study is to prepare and characterize membrane based on biopolymers and to select the most suitable type of membrane for the transdermal release of methotrexate. This preliminary study describes the synthesis of new types of membranes based on chitosan and κ-carrageenan to which other copolymers (Span, Glycerol, PVA and PVP). The active ingredient was added in all types of obtained membranes. The membranes and the binary mixtures between the components used in the membrane synthesis and methotrexate are analyzed by thermogravimetric techniques, FTIR, UV spectroscopic techniques and SEM. The analyzes aim to identify the most suitable type of membrane for the controlled release of methotrexate, i.e., those membranes in which there are no interactions that could inactivate the active ingredient.





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Compatibility study for new transdermal leflunomide delivery systems

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Keywords: drug delivery, biopolymer, thermal analysis, FTIR, UV-Vis, leflunomide

Leflunomide is a synthetic isoxazol or, more specific: 5-methyl-N-[4-(trifluoromethyl) phenyl]-4-isoxazolecarboxamide and it is a crystalline solid. [1] Leflunomide is a drug used for the treatment of rheumatoid arthritis, an illness that affects soft tissues and bones and can cause irreversible joint deformities and functional impairment. [2] Leflunomide has an anti-proliferative action. It acts as a dihydroorotate dehydrogenase inhibitor as is has been shown to be selectively inhibited by the active metabolite of leflunomide. [2] This drug is administered orally, and its bioavailability is aprox. 80%. In spite of its rather high bioavailability, leflunomide is practically insoluble in water (less than 40 mg/L), so it belongs to class II of the bio-pharmaceutics classification systems. [2]

TG, DSC (figure) and FT-IR studies have been used to highlight the degree of incorporation of the active substance in the membrane and the possible interactions between the drug and the polymer.

The paper presents a study by spectroscopic and thermoanalytic techniques of membranes in which Leflulomide was incorporated. The study presents the synthesis and characterization of several types of membranes in order to choose the best membrane for controlled release Leflunomide.

The study will be complemented by other techniques that will lead us to the best choice.

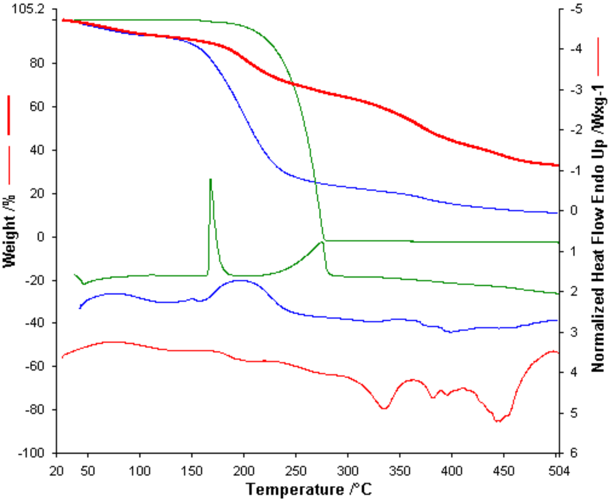

Fig. 1. Thermoanalytic curves for: Leflu, ACGL4, ACG

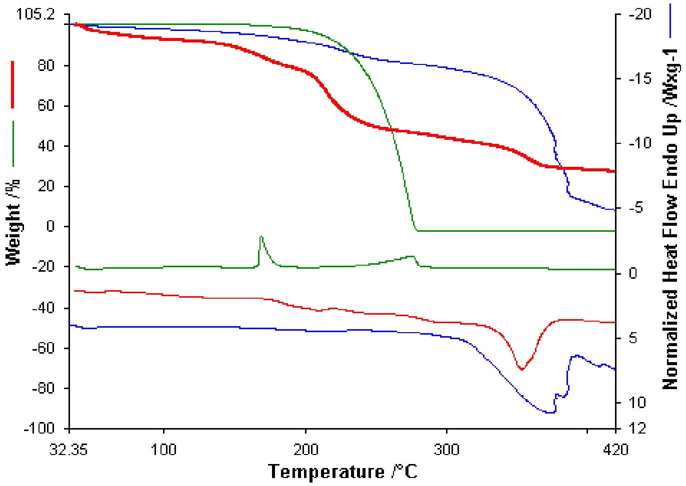

Fig. 2. Thermoanalytic curves for: Leflu, ATGL4, ATG

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Kinetic study and thermal stability of sartan class drugs

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Keywords sartans, thermal analysis, drug delivery, hypertension, kinetic study

Sartans (angiotensin receptor blockers - ARBs) are a group of antihypertensive drugs that functions by blocking the effects of the hormone angiotensin II (Ang II) in the body, thus lowering the blood pressure. [1] [2] These are a class of compounds derived from 2- (1-benzyl-1H-imidazol-5-yl) acetic acid, though the class firstly consisted of an imidazole core, which was substituted differently at certain positions of the heterocyclic nucleus. [3] The purpose of this study is to compare the thermal stability of the studied active substances (Irbesartan, Valsartan, Losartan and Azilsartan) according to their molecular structure, in order to synthesize new materials that will be used for the controlled release of the active principles. In order to compare the stability of the analysed substances, all compounds were analysed at temperatures in a range from 25 up to 400°C, with a heating rate of 10°C/min in a synthetic air atmosphere environment. All samples were analysed on a Perkin-Elmer Diamond thermo-balance in open aluminium crucibles. Kinetic analysis was performed according to ICTAC 2000 protocol, using the isoconversional methods of Friedman, Ozawa–Flynn–Wall, Kissinger–Akahira–Sunose, respectively, the modified nonparametric kinetics method. The aim of this study was to determinate the kinetic triplet without using any approximation, but as well the separation of parallel or successive reaction that occurs at decomposition.

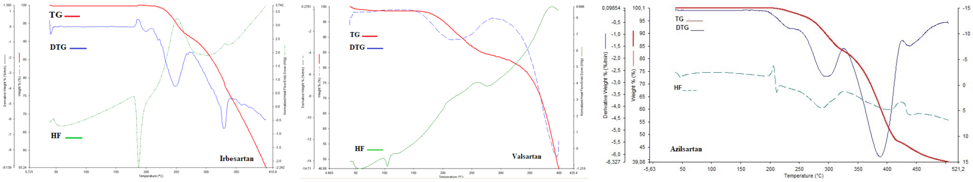

Figure 1. TG/DTG/HF curves for obtained in the range of 25-400° C for Irbesartan, Valsartan and Azilsartan

According to a thermogravimetric study (Figure 1), the variation of the stability of the analysed compounds can be established in the following pattern: Valsartan<Irbesartan< Azilsartan<Losartan.

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Polymers

Utilisation of Phytic Acid as a Reactive Flame Retardant in the Preparation of a Fully Biobased Waterborne Epoxy Coating

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Keywords: phytic acid, reactive flame retardant, fully biobased waterborne epoxy, self-extinguishing system, intumescent flame retardants

Epoxy resins have been used recently in different fields including composites, coatings, electronics, transportation, and many other industries. However, maintaining the outstanding mechanical and thermal properties of their products while adapting the environmentally benign movement in the industry is one of the main challenges for industry and academia [1]. Many studies have been made on bioresources such as cellulose, lignin, isosorbide, plant oils, amino acids, itaconic acid, …etc to produce epoxy resins or curing agents [2]. Currently, flame retardants (FRs) are one of the main components almost in all polymeric materials to reduce fire hazards. They can be added to the polymer by direct physical blending, or chemically incorporated into the polymer structure. Intumescent FR coatings have been widely used to protect steel structures against fire, and recently it's reported they can be applied to protect polymer substrates [3].

By using biobased flame retardants, a fully biobased flame retardant epoxy system can be prepared. The waterborne epoxy systems are also preferred compared to the solvent-borne systems from the green chemistry point of view [4].

A fully biobased waterborne flame retarded epoxy system was prepared using sorbitol polyglycidyl ether epoxy resin (SPE) and phytic acid (PA) which was used as a reactive flame retardant (FR). Ammonium polyphosphate (APP) and melamine (MEL) were added to the system to improve the intumescence effect and as a result, decrease the flammability of the bioepoxy resin. The results of limiting oxygen index (LOI) and UL-94 flammability tests showed better flame retardant (FR) properties and higher LOI via the addition of APP and MEL. PA presents around 1% of phosphorous content to the system, and by the addition of 2% phosphorous from APP, the self-extinguishing V0 UL-94 rating was presented. The thermogravimetric analysis (TGA) measurements showed a relatively high residual char weight which increased by using 5% of melamine and increasing APP content. The charring effect of PA was confirmed further by mass loss calorimetry (MLC), and the intumescent effect was improved by using MEL and APP. The sample MEL(5%)+APP3 showed the lowest heat release HRR values, pHRR decreased by 66.7% compared to the reference and 8.4% compared to the APP3 sample, THR decreased by 55.5% and 27.3%, respectively. The thermal insulation of the char was discussed by measuring the temperature on the back surface of coated steel plates, after one hour, using 3%P of APP decreased the temperature by 108°C compared to the reference sample. These results obtained by the activity of the intumescent FR system were supported also by the char morphology studied by scanning electron microscopy. For a better understanding of the flame retardant mechanism of the different systems, infrared spectra were investigated for the char residues and the pyrolysis gaseous products.

Acknowledgments

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Intermolecular interactions in controlled release systems

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Keywords: responsive polymers, poly(N-isopropylacrylamide) gel, indole, calorimetry, host-guest interactions, controlled drug delivery

The research and use of controlled drug delivery systems is one of the most dynamically developing areas of research today. These complex systems consist of a carrier matrix and an active drug substance [1]. The temperature-sensitive (thermoresponsive) hydrogel poly(N-isopropylacrylamide) (PNIPA) has reversible conformability and high absorption capacity, making it potentially suitable for applications in the fields of separation technology, sensing and microfluidics, among others. Its advantageous properties make it a promising matrix material for pharmaceutical drug delivery systems. Its biocompatibility and the fact that its phase transition temperature in pure water is close to the temperature of the human body (34 °C), contribute to its biomedical applications [2].

The second-order interactions between the gel matrix and the drug molecules are governing factors in the development of drug delivery systems, as both their nature and strength have a fundamental impact on the structure and properties of the system [3].

Indole derivatives have a broad spectrum of biological activity, making them important building blocks for drug research due to their analgesic, anti-inflammatory and antidepressant activity [4]. In the present work, the interactions of PNIPA hydrogel with different test molecules, indole, 5-aminoindole and 5-hydroxyindole, have been investigated.

By swelling the gel in an aqueous solution of the active ingredients, the changes in its mechanical and swelling properties can be investigated. Scanning microcalorimetry can be used to follow the effect of the active ingredient on the phase transition of the gel, which is one of the markers of the interactions between the gel and the active molecules. Deconvolution of the phase transition curves provides additional information on the sub-processes involved in the transition [5]. The interactions between the gel and the active molecules can be localised by magnetic resonance spectroscopy (NMR) in the swollen state and by Fourier transform infrared spectroscopy (FT-IR) in the dry state. The successful amorphisation of the active substance within the gel matrix (formation of an amorphous solid dispersion) was investigated by powder X-ray diffraction (XRD). The different interactions can explain the different delivery profiles of the tested active substances.

Acknowledgments

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Stability effects of Microalgae extracts in the SBS substrate

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Keywords: SBS, algal extract powders, stabilization, chemiluminescence, thermal degradation

The polymer durability may be achieved by an appropriate presence of protection compounds. One efficient class of antioxidants is natural extracts, where the algal solid products are included. The stability assays are the practical proofs by which the efficiencies are evaluated. The chemiluminescence procedure which provide accurate processing picture is selected for the kinetic analysis of hindering oxidation. The studied samples consisting of styrene-butadiene-styrene matrices where are various algal extract (*Chlorella vulgaris* and *Arthrospira platensis*) loadings are included were subjected to a thermal degradation at three temperatures. The delay of oxidation is qualified by the evaluation of some kinetic parameters of ageing through which oxidation induction time and oxidation rate are the main illustrative. The consequences of the concentration of stabilizers, structural ratios of styrene/butadiene moieties are discussed in relation with the evolution of oxidation states. The protection ability of added powders is highlighted by the comparison between the different values of activation energies required for the conservation of initial stability degrees. The interferences of active compounds contained in the studied algal extracts are discussed starting from the activity of chain breaking that characterizes the antioxidant efficiency of natural polyphenols. The comparison of stabilization levels provided by these products in SBS is presented in relation with other polymer structures that are recommended for the manufacture of ecological packaging materials. The degradation mechanism of polymer, as well as the involvement of stabilization activity of additives in the ageing polymers is taken into consideration for the extended application in the area of engineering polymer materials. The accelerated ageing is attentively explained based on the antioxidant potentials of studied algal extracts, which are reliable products for the improvement of durabilities for a large category of polymers including the most usual material like polyolefins. However, the presence of benzene ring in the SBS structures, as well as the initial unsaturation is the main factors that must be considered as the determining elements in the propagation of oxidation. The mechanistic approach is called for the illustration of stabilization contribution of algal biomasses in the extension of polymer durability.

Acknowledgments

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Influence of biogenic material content on biodegradability of styrene-butadiene composites with *Chlorella vulgaris* biomass

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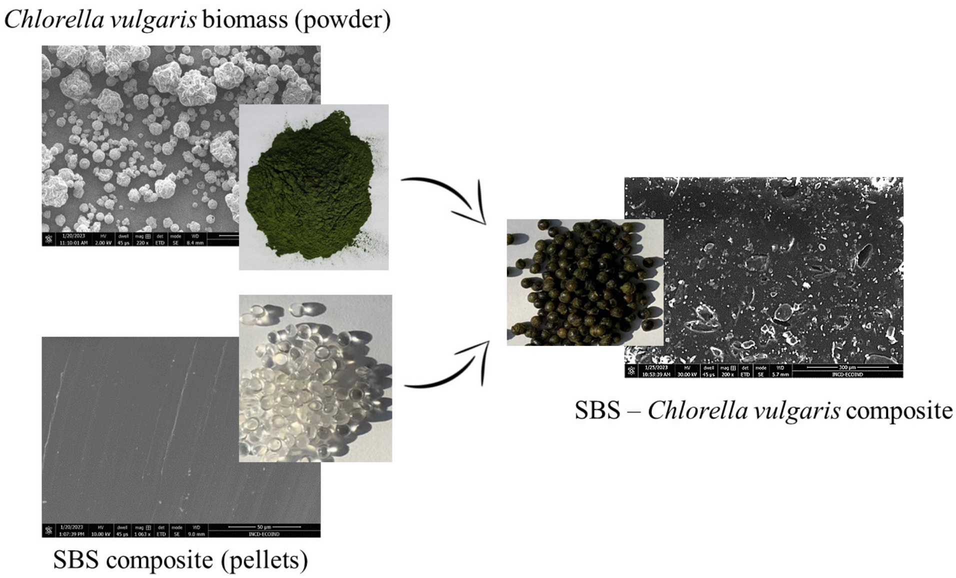
Keywords: microalgae biomass, *Chlorella vulgaris*, styrene butadiene rubber, biodegradation

Biofillers are increasingly used as fillers for polymer composites. In this context, the algal biomass may be considered an important resource, as it can be obtained at a relatively low cost, as harvested as a by-product from wastewater treatment plants. The algal species *Chlorella vulgaris* biomass is characterized by a macroconstituents composition (w/w) of 15-25 % carbohydrates, 10-20 % lipids, and 50-60 % proteins. Poly (styrene-butadiene-styrene) (SBS) copolymers have a matrix that is composed of glassy polystyrene domains connected by polybutadiene segments. Although the physical-mechanical properties of SBS copolymers recommend them for many industrial applications, they are characterized by low biodegradability degree. Thus, adding biogenic material to a polymer composite may lead to a better biodegradability degree when comparing with the SBS polymer. In this study, the variation of the biodegradability of bio-polymer composite was performed using the procedure described by ISO 14855-1:2012(E), modified according to experimental setup.

The study focused on the influence of the biomass content of *Chlorella vulgaris* in a SBS polymer composite. For the present study, a base SBS composite was prepared with the following composition: 25% (w/w) copolymer SBS1 (linear copolymer 30% styrene, and 70% butadiene), 50% (w/w) copolymer SBS2 (linear copolymer 40% styrene 60% butadiene), and 25% (w/w) paraffin oil. Then, the microalgal of *Chlorella vulgaris* biomass (powder with moisture 5 ± 0.5%) was incorporated in the base-polymer-composite so that the biogenic content in the final bio-composite polymer was of 5, 10, 20 % (w/w).

The structural changes of studied materials were evaluated by Fourier Transform infrared spectroscopy (FTIR) and Raman spectroscopy, while morphological differences were evaluated by scanning electronic microscopy (SEM) and confocal microscopy. Potential correlations between the quantity of carbon dioxide released under the degradation conditions and the percentage ratio of biomass added to the base-polymer matrix were followed.



Acknowledgments

The research leading to these results has received funding from the NO Grants 2014-2021, under Project contract no. 27/2020 - GRAALrecovery, and from project “Excellence and Performance to increase the RDI Institutional Capacity (Pro Excelence)”, financed by the Romanian Ministry of Research, Innovation and Digitization under the contract no 43 PFE/30.12.2021.

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The influence of specific nucleation and branching on the properties of blends of polypropylene

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Keywords: blends, long-chain branched polypropylene, specific nucleation, thermal properties,

Isotactic polypropylene (iPP) occupies a privileged position among semi-crystalline polymers due to its excellent mechanical properties. However, iPP has relatively low melt strength and elongation viscosity, which introduces complications in processing technologies that require these properties, such as blow moulding or thermoforming. These problems can be avoided by using long-chain branched polypropylene (LCB-PP), but its higher price hinders its widespread use. Hence, by using blends of linear and branched polypropylene, the desired melt properties can be achieved at an affordable cost [1, 2]. The aim of this work is to study the influence of branching and specific nucleation on the thermal and mechanical properties of polypropylene blends using differential scanning calorimetry, tensile testing and Charpy impact test. Blends of linear and branched polypropylene were prepared in different proportions (LCB-PP content 0, 1, 2, 5, 10, 20, 50 or 100 wt. %) with the addition of a specific β-nucleating agent *N,N´*-dicyclohexyl-2,6-napthalene dicarboxamide (0 or 0.03 wt. %). Melting thermograms (Figure 1) clearly showed that β-phase formation is significantly suppressed with the addition of LCB-PP to the blends. The presence of only 5 wt. % of LCB-PP in the blend resulted in the almost complete disappearance of the trigonal β-phase. The findings of the melting experiments indicate that blends primarily composed of α-phase, possibly γ-phases, show greater thermodynamic stability than the blends containing mainly β-phase. As shown in Figure 2 Young's modulus significantly rises with increasing content of LCB-PP in blends, the addition of only 1 wt. % of LCB-PP (BL1) leads to an 18 % increase in modulus compared to L-PP. The highest modulus values can be found in BL20 and BL50, over 30 % increase as compared to L-PP. In the case of pure LCB-PP the small drop can be seen.

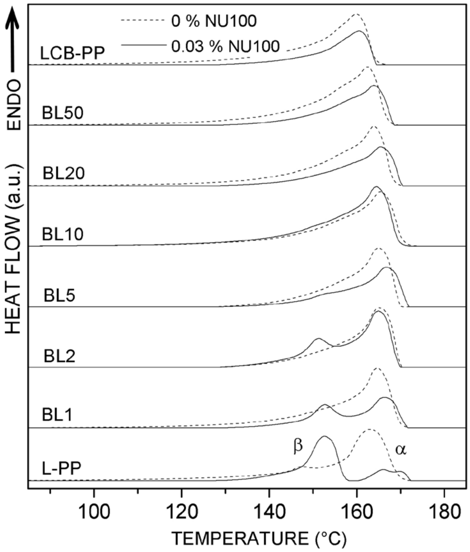

Figure 1: Melting thermograms of the blends

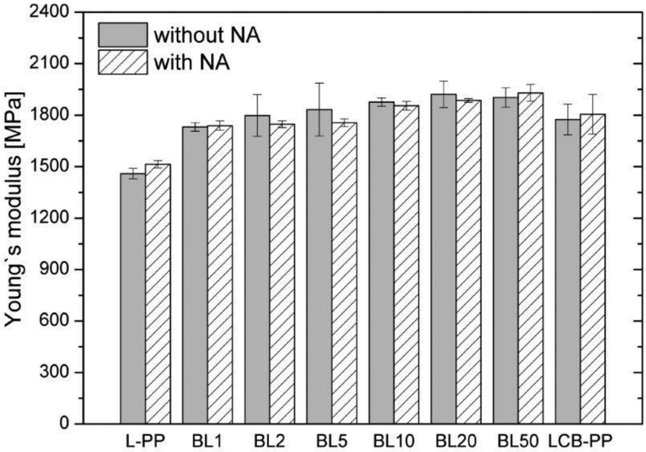

Figure 2: Comparison of Young’s modulus

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Flame retardancy of recycled pet foams produced by batch foaming

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Keywords: flame retardant, foams, recycled, thermal analysis, poly(ethylene terephthalate)

The management and recycling of short-life packaging waste, such as poly(ethylene terephthalate) (PET) bottles, are serious issues and provide the basis for sustainable development. In our work, CO_2-assisted batch foaming was used to manufacture low-density (ρ = 200-350 kg/m^3) microcellular foams from bottle-grade recycled poly(ethylene terephthalate) (rPET) in flame retarded form. A reactive, epoxy functionalized chain extender was used to enhance the foamability of the PET regrind by improving the melt strength, while 6 % aluminium-tris-(diethylphosphinate) flame retardant (FR) was used to reduce combustibility and improve the flame retardant properties of the rPET foams. The effects of adding 1% natural montmorillonite (MMT) and polytetrafluoroethylene (PTFE) powder as potential cell nucleating agent and flame retardant synergist were also investigated. The final foam products were subjected to morphological, thermoanalytical, flammability and mechanical tests. Thanks to the FR addition, charring of the foams was effectively promoted, was evinced by thermogravimetric analysis (TGA) and pyrolysis combustion flow calorimetry (PCFC). Only moderate increase in flammability was observed for the high-porosity (>75 %) foams compared to the corresponding bulk materials, as characterized by similar limited oxygen index (LOI) values. In cone calorimeter tests, for the flame retarded foams a 50 % reduction in peak heat release rate (pkHRR) and a 30 % reduction in total heat release (THR) values were measured compared to the FR-free reference. The addition of PTFE to the FR formulation was found to increase the time-to-ignition (TTI) and reduce the pkHRR, while MMT was mostly efficient in char promotion and THR reduction. The mechanical performance of the flame retarded rPET foams was found to be primarily determined by the apparent density and less affected by the presence of FR additives. Due to strain-induced crystallization occurring during cell growth, the rPET foams are highly crystalline ($\chi > 25$ %) which leads to increased thermomechanical resistance compared to unfoamed references.

Acknowledgments

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The effect of various β-nucleating agents on the morphology of polypropylene

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Keywords: isotactic polypropylene, nucleation, non-isothermal crystallization, injection moulding, compression moulding

Isotactic linear polypropylene (iPP) is a semi-crystalline polymer with versatile applications, excellent mechanical properties, and cost-effectiveness. It is distinguished by its low density, high melting point, and exceptional chemical resistance, making it an essential material in modern times. Isotactic linear polypropylene displays a polymorphic structure, exhibiting well-defined distinct phases, including α, β, γ, and smectic phases, which are formed during high undercooling [1]. The monoclinic α-phase is formed during regular processing conditions and presents two variants, α_1 with random down-up directions of methyl groups, and α_2, a more stable form with ordered methyl groups. The β-phase can be achieved by creating favourable crystallization conditions, such as high temperature gradient, the presence of shear forces, or using heterogeneous β-nucleating agents (NA), resulting in a trigonal lattice. The β-phase displays improved toughness and ductility but is less stable than the α-phase and can recrystallize into the latter upon stretching at high temperatures [2, 3]. In this study, the effect of β-nucleation using various nucleating agents on the crystallization, thermal properties and supermolecular structure of iPP were studied with comparison to non-nucleated iPP. Additionally, the effect of shear-induced crystallization is studied. The three β-nucleating agents, namely, calcium pimelate (*PP+CaPim*), zinc phthalate (*PP+ZnPht*) and γ-quinacridone (*PP+γ*), were mixed into the iPP and then injection moulded or compressed moulded. The morphology was analysed using differential scanning calorimetry including flesh type, wide-angle X-ray scattering, microscopy techniques and mechanical testing. Figure 1 shows the photos of supermolecular structure taken from scanning electron microscopy (SEM): the effect of nucleating agent can be seen. All nucleating agents used significantly affected the process of crystallization. When material undergoes injection moulding, the amount of β-phase increases, in this case, the highest amount of β-phase has the material containing NA calcium pimelate, the lowest γ-quinacridone. This study shows that the most effective β-nucleating agent is calcium pimelate in samples processed by injection moulding.

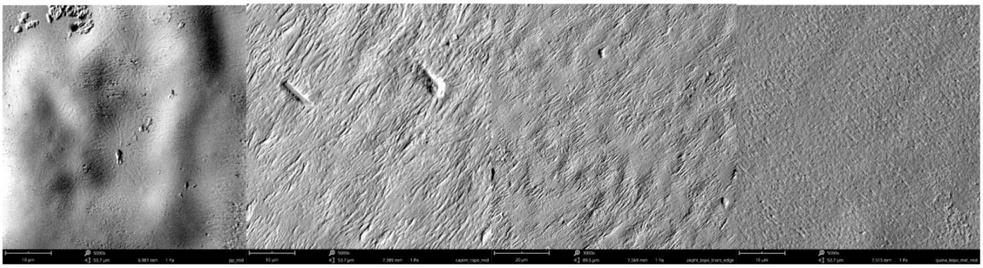

Figure 1: SEM of non-nucleated iPP, PP+CaPim, PP+ZnPht, PP+γ (from left)

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On the structural consequences in the thermal degradation of styrene block copolymers

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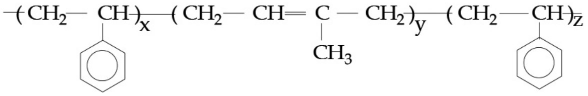
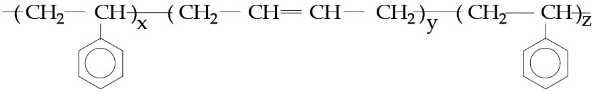
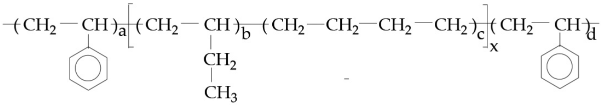
Keywords: styrene block copolymers, thermal degradation, kinetics, chemiluminescence

The material qualification based on their behaviours during thermal degradation represents an important study subject, when useful information is provided in relation with material durability under severe operation conditions. A series of block copolymers consisting of styrene-isoprene styrene (SIS), styrene-butadiene-styrene (SBS) and styrene-ethylene-butadiene-styrene (SEBS) was characterized by chemiluminescence during their thermal degradation at superior temperatures around 170 ºC. Two methods, isothermal and nonisothermal measurements, were preferred for the kinetic assay of polymers stability. The main parameters: oxidation induction time and onset oxidation temperatures were determined. The activation energies required for oxidation ageing were calculated based on the measured data. The structural composition influence on the progress of thermal oxidation is discussed. The mechanistic approach showed that structural features are correlated with different thermal durability when these materials are subjected to accelerated degradation. The energetic consequences of oxidation are analyzed starting from the problem of polymer waste recycling, which is an acute matter. The present results are the start points for the evaluation of the durability of the products manufactures by these block copolymers. The comparative evaluation of oxidation rates, as well as the description of oxidation start conditions that are taken into consideration for industrial warranties is conceptually included into the technical features of safety products. The influence of the different molecular fragments that contain unsaturation may be identified due to the unlike shapes of isothermal chemiluminescence spectra, while the modification of thermal strength is demonstrated by the changes in the values of onset oxidation temperatures obtained from the nonisothermal chemiluminescence spectra.

Table. Structures of the investigated styrene block copolymers

Styrene-isoprene-styrene (SIS)	
Styrene-butadiene-styrene (SBS)	
Styrene-ethylene-butadiene-styrene (SEBS)	

Acknowledgments

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Biodegradation study of Styrene-butadiene Composites with *Arthrospira platensis* Biomass

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Keywords: microalgae biomass, *Arthrospira platensis*, styrene butadiene rubber, biodegradation

The use of biodegradable polymers has emerged as a response to the problem of microplastics increasing volume in the environment and reoriented industrial capacities and sales strategies of polymer composite manufacturers towards this direction. Poly (Styrene-Butadiene-Styrene) copolymers (SBS) are hard rubbers used for elements capable of maintaining their tensile shape, as they are wear-resistant with low biodegradability. SBS polymers consist of glassy polystyrene domains connected by polybutadiene segments, thus having a two-phase morphology. The preparation of polymer composites that incorporate material of a biogenic nature in the polymer matrices may lead to reduction of fossil polymer consumption and a potentially higher biodegradability. Furthermore, microalgae biomass as biogenic filler has the advantage of fast growing and high tolerance to different types of culture media with higher production yields than those provided by the biomass of terrestrial crops. On the other hand, algal biomass can be a secondary product in wastewater treatment processes. In last decade new technologies were developed for the recovery and dewatering of algal biomass resulting microalgae biomass with relatively low production cost. The biomass of *Arthrospira platensis* (spirulina), mainly, contains carbohydrates (10-15%), lipids (5-10%), proteins (55-70%) and pigments. This composition makes spirulina biomass as a high protein content biogenic material for polymer composites. For the present study, an SBS polymer composite (SBSC) containing 25% (w/w) copolymer SBS1 (linear copolymer 30% styrene 70% butadiene), 50% (w/w) copolymer SBS2 (linear copolymer 40% styrene 60% butadiene) and 25% (w/w) paraffin oil was prepared. *Arthrospira platensis* biomass (moisture content 6.0 ± 0.5 %) was incorporated into the SBSC in 5, 10, 20 and 30 % (w/w) ratios to obtain polymer composites with spirulina biomass. For the biodegradation studies, the ISO 14855-1:2012(E) standard was applied, with slight changes, as per the specificity of our experiments. Degradation of the studied materials was followed by quantitatively monitoring the CO_2 resulted in the degradation process, and captured by absorption in NaOH solution 0.5 mol/L. The morphological changes of the material were also monitored by SEM and confocal microscopy. It was found that the volume of carbon dioxide released under degradation conditions at 58 ºC is influenced by the percentage of biomass added to the polymer matrix. The polymers resulting from the biodegradation test are compared with the initial composites in terms of swelling and pigments transfer in methanol, ethanol and acetone solutions.

Acknowledgments

The research leading to these results has received funding from the NO Grants 2014-2021, under Project contract no. 27/2020 - GRAALrecovery, and from the Romanian Ministry of Research, Innovation and Digitization under the Project contract no 43 PFE/30.12.2021 – Pro-Excellence.

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Poly(ε-caprolactone)/Hydroxyapatite composites – Thermal and ir studies on the modified material

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Keywords: hydroxyapatite, polycaprolactone, DSC, structural analysis

The regenerative medicine uses various materials for the restoration and defect elements replacement. However, the metallic implants have serious disadvantages that concern more or less mechanical stress in the implant area, possible inflammatory or foreign body reaction, and the need for additional surgical procedure to remove metallic implants. On the other hand, bioactive composites offer several features, such as a porous 3D structure, biocompatibility and bioresorbability (controlled degradation), appropriate surface chemistry for cell activity, and sufficient mechanical performance comparable with those for host tissues. Regarding these aspects, promising materials are composites based on non-toxic, tissue compatible polymers with bioactive fillers, for example poly(ε-caprolactone) (PCL) filled with hydroxyapatite (HAP). Poly(e-caprolactone), one of the most commonly used polymers for bio-applications, has proper processability, biocompatibility and mechanical strength, as well as approval for use in medical devices. Despite these advantages, it was also found that PCL-based materials show relatively slow degradation rate after implantation that may restrict the process of bone regeneration [1, 2] and lacks bioactivity [3]. To tackle these drawbacks preparation of functionalized composites containing bioactive ingredients, such as HAP, β-tricalcium phosphates (β-TCP), or bio-glass particles, is a most proper choice.

On the other point of view, hydroxyapatite in the form of nanoparticles and collagen fibers are the two main constituents of bone tissues. Their mutual relation (synergism) with the hierarchical structure are responsible for unique mechanical performance of bones.

In our study, biocomposites made of PCL and hydroxyapatites were produced by melt processing to investigate the impact of HAP addition and its modification on the physicochemical properties of PCL. Hydroxyapatite whiskers were produced by the hydrothermal method using dihydrogen phosphate, calcium nitrate tetrahydrate, and zinc nitrate hexahydrate as a source if ions. The effect of HAP loading on overall properties of PCL was assessed by thermogravimetry (TG) and differential scanning calorimetry (DSC), and the structure and morphology of composites was investigated by scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR). Besides, the material was subjected to the hydrolytic degradation in phosphate buffered saline (PBS) for up to 12 weeks, to assess the polymer composite's resorbability.

The obtained results indicate that both ceramic fillers affect the PCL properties, such as crystallinity, melting, and thermal stability.

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Non-isocyanate polyurethane hydrogels modified physically with POSS – thermal study

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Keywords: non-isocyanate polyurethanes, hydrogels, POSS, thermal properties

The influence of physical modification of non-isocyanate hydrophilic networks with polyhedral oligomeric silsesquioxanes (POSS) molecules was studied in regard to materials' thermal stability, mobility (glass transition), and mechanical performance. Non-isocyanate polyurethane copolymeric hydrogels were synthesized using two hydrophilic monomers: poly(ethylene oxide)-based biscyclic carbonate (PEO-CC, M_w~650 g/mol) and polyethyleneimine (PEI, M_w~ g/mol), a multifunctional amine. Polymeric networks were obtained via single-step aminolysis of PEO-CC in the presence of 1,5,7 triazabicyklo(4.4.0)dek-5-en (TBD) as a catalyst, and dimethylacetamide (DMAc) as a solvent. The reaction was carried out at 55°C in inert atmosphere (argon). Upon viscosity increase, the reaction mixture was transferred into a polypropylene mold and conditioned at 90°C. Hybrid composites NIPU/POSS were synthesized analogously, with octaPOSS introduced into the reactor alongside all other components. This variant of POSS bears eight hydroxyl groups, which do not participate in any reactions but improve solubility in the matrix. A series of modified hydrogels was synthesized with varying POSS content (1-10 wt%). The reaction progress was monitored with Fourier-transform infrared spectroscopy (FTIR). Studied hydrogels were dried for 3 days under vacuum at 90°C, and then conditioned over phosphorus pentoxide until equilibration of mass. Drying of the materials was carried out to eliminate the influence of water on the thermal and thermo-mechanical properties (e.g. plasticization), since polyhydroxyurethanes exhibit high water absorption capacity [1]. Subsequently, the dried materials were studied by: X-ray diffraction analysis (XRD) to determine POSS dispersion in the matrix, thermogravimetric analysis (TGA) to determine influence of POSS on thermal stability, and by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) to determine POSS influence on glass transition temperature and thermomechanical performance. FTIR analysis confirmed formation of hydroxy urethanes in expense of cyclic carbonate rings. XRD analysis showed excellent POSS dissolution and dispersion with only one amorphous halo present on the diffractograms even for the highest POSS loading, which is not usually the case in polyurethane/POSS composites [2]. TGA revealed that with increasing POSS content thermal stability increases in both inert and oxidative atmosphere, rendering octaPOSS suitable for application as thermal stabilizer [3]. POSS introduction into the matrix resulted in plasticization seen as decrease of calorimetric glass transition temperature (T_g) [4]. Composite with 5 wt% POSS loading showed superior mechanical properties in the broad temperature range in comparison to the unmodified matrix. All composites with POSS content up to 8 wt% showed increased mechanical stability at high temperatures. The highest POSS loading (10 wt%) resulted in high brittleness and deterioration of mechanical performance at temperatures above 30°C.

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Influence of functional comonomers in the polymer additive on the low-temperature properties of diesel fuel

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Keywords: low-temperature properties, diesel fuel, polymer additives, paraffin crystallization

A variety of chemical additives are added to modern fuels to improve their performance and meet desired specifications. [1] By combining these additives in carefully measured amounts, they can impart properties that cannot be achieved by the refining process alone. One important function of these additives is to improve the flow properties of diesel fuel. [2] Several classes of polymers and copolymers with varying degrees of polymerization and molecular weights are used as flow improvers in diesel. The effectiveness of these flow improvers and pour point depressants is determined by several factors, including the nature of the paraffins present in the diesel, the amount of additive used, the molecular weight of the additive, and the chemical structure of the polymer. [3] The chemical structure can affect the solubility of the additive in the fuel, its ability to interact with paraffins, and its thermal stability. By carefully selecting the right type of polymer for a particular fuel, producers can achieve optimal performance and reduce overall fuel costs. In our research, we have synthesized polymeric additives with functional methacrylic comonomers (2-(diethylamino)ethyl, 2-(diisopropylamino)ethyl, and 2-(*tert*-butylamino)ethyl methacrylate) and studied their influence on the low-temperature properties of diesel fuel. Differential scanning calorimetry (DSC) and optical microscopy with polarization were used to determine the influence of the additives on the crystallization behavior of diesel. The standard ASTM D5950 pour point (PP) test showed a large improvement of more than 30 °C compared to non-additivated diesel.

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Thermo-mechanical effect on Niti ribbon with pmma polymer

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Keywords: thermal behaviour, mechanical behaviour, dynamical behaviour, shape memory alloy, polymer

Thermo-mechanical behavior of composite made of metal-polymer interface displays significant behavior towards the actuation effect. Both poly (methyl methacrylate) (PMMA) and NiTi possess shape memory and biocompatibility behavior. The macroscale properties of PMMA–NiTi composites depend immensely on the quality of the interaction between the two components. The interface plays a significant role in the final mechanical and thermal behaviour of the composite overall. NiTi shape memory alloy (SMA) and superelastic (SE) sheets were spin-coated on one side with PMMA. The composite was prepared by the spin coating method with an alloy-to-polymer-thickness ratio of 1:3. The physical, thermal, structural, and mechanical properties of PMMA foils cast from solutions of toluene were investigated by differential scanning calorimetry, optical microscope, Fourier infrared spectroscopy, and dynamical mechanical analysis. The PMMA foils were prepared from a different ratio of PMMA powder with toluene solvent by the solution cast method. The surface features, glass transition temperature, and C-H bonds of foils were investigated and compared with commercial PMMA foil. The mechanical characterization of foils was examined by using static and dynamic loads in axial and transverse modes. The tensile behaviors of the commercial and as-prepared foils were investigated by using a strain rate of 0.01/s. The dynamical behavior of the foils was tested in tensile mode using 0.1 N of stress with a frequency of 1 Hz for the determination of storage, loss modulus, and damping values of the tan delta. Integrating both structures will open the flexibility in bistable actuators in composite structures as a function of thermal cycles. The bending stiffness and radius of curvature were calculated by using numerical and experimental methods during thermal cycles. The experimental radius curvatures in actuation have good agreement with the model. The change in shape results from the difference in coefficients of thermal expansion between PMMA and NiTi. Actuation temperatures were between 0 and 100 °C for the SMA–PMMA composite with a change in curvature from 10 to 120 mm with fixed Young's modulus of PMMA at 3 GPa, and a change in Young's modulus of NiTi from 30 to 70 GPa. PMMA–NiTi composites are useful as actuators and sensor elements. Simultaneously we performed an elasto caloric effect on the sample. The strain percentage was mapped as the function of temperature for various iso-stress conditions for both SE and SMA NiTi samples. The phase distribution for martensite and austenite phases was plotted as the function of stress with temperature. The change in displacement as strain percentage was investigated for the alloy with polymer interface in the composite material.

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Balanced improvement of mechanical properties and thermal resistance of recycled PET by additives and post-crystallization

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Keywords: recycled PET, EBA-GMA, impact modification, thermal annealing

Poly (ethylene terephthalate) (PET) is one of the most widely used commodity plastics: in 2020, 70 million tonnes were produced globally [1]. One of the main application areas of PET is the packaging industry, where plastic bottles are produced, which after a short life cycle becomes waste. In Hungary, 1.4 - 1.6 billion PET bottle waste is generated annually, and only 35% is recycled. However, its application as engineering plastic is limited, which can be explained by the poor heat resistance and fragility of the injection moulded parts.

The focus of the research is to increase the impact strength and heat resistance of the recycled material. For this, recycled PET was compounded with different ethylene-butyl acrylate-glycidyl methacrylate terpolymer (PTW elastomer) contents (0-5-10-15 %) and then the samples were crystallized at 150°C for 0-20-40-60-180 s. The morphological changes caused by PTW elastomer and thermal annealing were monitored with differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), while the mechanical properties and heat resistance were analysed by dynamic mechanical analysis (DMA).

Based on the tests, the impact strength of non-crystallized samples increases sharply above a critical PTW content, which is lower in the case of recycled PET, in accordance with the literature [2]. After crystallization, however, the impact strength increased gradually with the additive content.

The DSC measurements analysed by the three-phase model revealed important connections. It was proved that with increasing PTW content, the ratio of rigid and mobile amorphous phase (RAF/MAF) rises. This indicates that some segments of PET chains attached to the PTW particles are immobile. Before crystallization, the polymer chains covalently linked to PTW molecules contribute to the RAF. During annealing, first the compulsion of PTW molecules disappear due to the melting of the elastomer, then, the PET segments are restricted again because of their crystallization, and the rigid amorphous phase thickens around the growing crystallites. It is also crucial that the quantity of RAF and MAF do not change evenly during crystallization: the relaxation of segments and crystallization have a complex effect and their resultant determines the ratio of the three phases and indirectly the mechanical and thermal properties of the polymer blends.

The significance of the research is that by blending recycled PET with relatively low amount of elastomer, high stiffness, impact resistance and improved thermal resistance can be achieved. The notched impact resistance of toughened (15 % PTW) and crystallized RPET blend is approximately 5-times higher than that of uncrystallized pure RPET, and in the thermal resistance values (E90') a 50-fold increase was reached. This approach not only enables the cut of production costs of engineering plastics, but the requirements of circular economy are also fulfilled by applying recycled material.

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Isothermal crystallization kinetics of two polyamides

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Keywords: nylon, crystallization, kinetics, DSC

Nylon 66 and Nylon 11 are two polyamides of industrial application. Due to its low water absorption and chemical resistance, combined with other properties, nylon 11 is used for tubing and wire sheating in anumber of applications. [1,2] Nylon 6,6 is one of the most common polyamides used for textile and plastic industries. This study aims to investigate the crystallization behaviour of two commonly used polyamides, Nylon 6,6, and Nylon 11, using differential scanning calorimetry (DSC) and a logistic-based model fitting approach [3]. In addition to previos studies, a relative new model based on logistic functions is used in this work. This method allows for very good fittings of the crystallization exotherms obtained at all temperatures. The DSC thermograms of both polymers, corresponding to the isothermal crystallization obtained under different temperatures, will be analysed to determine the crystallization kinetics. One of the most insightful parameters of the model is the crystallization rate. Its dependence on temperature is analyzed for both polymers and compared to others. The other parameters can also help to better understand some of the crystallization features of these polyumers. In addition, the information retrieved from this study can be useful to adjust processing conditions.

Acknowledgments

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Pyrolysis

Environmentally friendly production of electricity, heat and cold energy with a CHP pyrolysis small power plant

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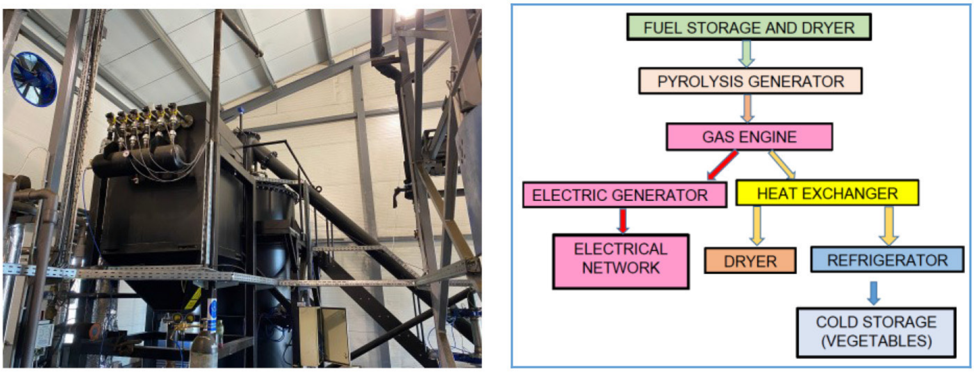
Keywords: biomass, pyrolysis, gas generator, waste heat, cold energy, CHP

In our study, we present an environmentally friendly CHP system that produces electricity and heat using primary or waste biomass. In the case of the developed pyrolysis (heat decomposition) equipment, 0.9-1.15 kg of wood (containing 15-20% moisture) is required to produce 1.0 kWh of electricity. During operation, compared to electricity, 1.1-1.3 times more useful thermal energy can be obtained, which can be used (recovered) in its entirety. In this research, waste heat is used to produce cold energy, namely to drive an absorption chiller.

The entire system has a peak electrical output of 120kW, which can also be used for feeding into the network, depending on the usage demand.

The authors have been dealing with the practical development and implementation of systems for several years, while also conducting numerous theoretical research. In today's increasing energy crisis, the solution can be beneficial, as a more favorable efficiency can be achieved in the conversion of materials rich in cellulose into energy than with traditional combustion technologies (boilers or stoves). The system is perfectly suited to produce electricity and thermal energy in rural settlements. Especially where these biological materials are available on site or nearby. It can be suitable, for example, for the heating of community buildings in village centers and can be sold or produce own electricity, but in the summer season when heat energy can only be used in a smaller proportion, recovered heat energy is used to drive heat pumps, so the cooling of buildings can be solved, which is increasingly necessary in the current warming period.



The gas purifier of the system and the schematic diagram

Acknowledgments

The research and development topic number GINOP-2.1.2-8-1-4-16 entitled "Development of a complex energy system, with the aim of realizing circular-circulation decentralized energy production with approximately 95% efficiency", the processing of which provided content support.

Experimental analysis and numerical simulation of biomass pyrolysis

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Keywords: pyrolysis, biomass, biochar yield, simulation, biofuel

Biomass residues are a viable source of clean, and renewable energy. The pyrolysis of agricultural waste was assessed experimentally and numerically with Aspen Plus software. Optimization of the pyrolysis conditions and parameters was conducted to maximize bio-oil production and improve its quality. The pyrolysis process was studied using a fixed bed reactor at a temperature ranging from 250 to 480 °C. Elemental analysis of biochar was determined using EDX. It was found that the biochar yield decreased with increasing temperature. Bio-oil was rich in phenolics (54.03%), acid (3.54%), alcohols (2.63%), aldehyde ketones (1.9%), and other aromatic compounds. At 450°C the gaseous byproducts with compositions (mol) of 46.6% CO, 34.8% CO_2, 6.7% H_2, and 11.9% CH_4. The high heating value (HHV) of pyrolytic gas was 8.437 MJ/kg with the raw gaseous product. Aspen Plus simulation was carried out and the primary constituents of the biomass were estimated from the proximate and ultimate analyses. The simulation results showed minimal variation in the yield of pyrolysis products at high temperatures.

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Biofuels production from camel thorn biomass using pyrolysis process

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Keywords: pyrolysis, biomass, characterization, camel thorn, fixed bed reactor

Pyrolysis of camel thorn biomass offers several benefits, including the reduction of greenhouse gas emissions, the production of renewable energy and fuels, and the creation of a value-added product from waste. In this study, the pyrolysis of the camel thorn process was conducted at 250°C, 300°C, and 350°C under uniform pressure of 10 bar using a fixed bed reactor. The pyrolysis products were bio-oil, biogas, and biochar. Products were characterized using Fourier Transform Infrared (FTIR), gas analyzer, GC-MS, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). In pyrolysis, cellulose and hemicellulose was converted into bio-oil, a complex mixture of oxygenated hydrocarbons, while lignin decomposed into biochar, a carbon-rich solid material. Phenol was produced up to 21% at 300 °C.

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Thermogravimetric Analysis and Kinetic Modeling of the AAEM-Catalyzed Pyrolysis of spruce wood, wheat straw, switchgrass, miscanthus and swine manure

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Keywords: biomass, catalyst; alkali and alkaline earth metals, kinetic modeling, model-free methods

In today's carbon-constrained world, renewable energy carrier development is a key component of the strategies adopted to tackle ever-growing energy needs while meeting overarching greenhouse gas emission reduction goals. In this context, the use of low-emission and carbon-neutral renewable energy resources, such as biomass, has attracted interest, with a view to gradually substituting conventional fossil fuels. When being pyrolyzed under an inert atmosphere, the biopolymers composing biomass typically decompose into biochar, bio-oil and incondensable biogas. Pyrolysis products obtained directly from raw biomass, however, usually present certain disadvantages due to their high oxygen content, leading to high corrosiveness and a low heating value. To address this, an interesting option is to implement a catalytic treatment of biomass to optimize selectivity and remove oxygenated groups to produce upgraded pyrolysis products. Among the catalysts currently considered, specific attention is devoted to alkali and alkaline earth metals (AAEMs) due to their low toxicity, affordability and catalytic efficiency. Notwithstanding the findings reported in recent studies aimed at elucidating the impact of AAEMs on the catalytic conversion of biomass, further research, based on a systematic comparison of the impact of AAEMs added to the same feedstocks under the same conditions, are more than ever required to determine the respective catalytic efficiency of these additives, notably from a kinetic perspective. To contribute to such a research effort, the present work aims at characterizing the catalytic pyrolysis of 5 different feedstocks (spruce wood, wheat straw, switchgrass, miscanthus and swine manure) impregnated with 4 additives containing AAEMs (NaCl, KCl, $CaCl_2$ and $MgCl_2$). To that end, thermogravimetric analyses (TGA) were carried out with raw and catalysed samples prepared by wet impregnation. Measurements were carried out with 4 different heating rates (5, 10, 15 and 30 K/min). The results obtained were then processed by means of 3 isoconversional models (namely, Kissinger–Akahira–Sunose (KAS), Flynn-Wall-Ozawa (FWO), and Friedman). Based on the obtained rate constant parameters, the variation of the fuel conversion degree as a function of the temperature was simulated while considering different reaction models commonly employed in the literature. As highlights, this work in progress showed that the computed conversion profiles derived from the implementation of each tested modeling approach allowed properly reproducing the TGA results. Furthermore, the existence of catalytic effects was exemplified by a shift of the decomposition process to lower temperatures when the tested feedstocks were impregnated with the AAEM additives. On the other hand, a promotion of char formation has also been evidenced, thus prompting the need for additional works conducted while considering different catalyst concentrations to better rule on the impact of AAEM catalysts over a wide range of operating conditions.

Research on the pyrolysis mechanism of waste wood using modified distributed activation energy model

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Keywords: discrete flame spread, flame front shape, wooden dowel, heat transfer

Thermal decomposition conversion of waste wood into combustible fuels or chemical feedstocks has been realized as an ideal approach for refuse handling [1], which can convert wasted wood into valuable raw materials or fuels without generating toxic gaseous emissions from the process itself, meanwhile the thermal kinetics can help to conclude submodels for related recycling problems. Therefore, it is unreasonable to describe the entire process with a single reaction mechanism. Distributed activation energy model (DAEM) can be well adapted to the complex pyrolysis reaction and accurately describe the pyrolysis process in a wide range of temperature and heating rates [2].

In this study, waste fir wood was selected to perform TGA test, based on which we determined the proper number of parallel independent sub-reactions. It was assumed that the ensemble pyrolysis process was a sum of the corresponding number of pseudo-components decomposition. From previous studies [3], A strong linear correlation exists between the activation energy and the natural logarithm of the pre-exponential factor, i.e., the kinetic compensation effect (KCE). Therefore, the KCE factors has been calculated based on the thermal kinetic methods in this work. Different with the previous DAEM studies, the pre-exponential factor was determined by employing the actual KEC factors instead of a constant value. Then, two distribution modes with two types of reaction orders including first-order and *n*th-order were developed and fitted to the pyrolysis behaviors to search the best models. A multi-parameter optimization program was developed to solve the DAEM questions. The important characteristics and relationships of different models were discussed, with guidance in how to select the proper model.

The results also have implications for the study of kinetic mechanism, waste recycle, combustion model constructed, and simulations of more complicated solid decomposition.

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Nitrogen distribution analysis during the devolatilization process of various feedstocks using TG-DTG-MS analysis

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Keywords: TG-DTG-MS, nitrogen distribution, NO_x emissions, devolatilization, feedstock

The fuel-NO_x emissions during the conversion of carbon-based feedstock into energy and chemicals are on a global level in focus last decades due to environmental issues. The emission of nitrogen oxides is recognized among the other pollutants, as one of the key environmental problems related to energy production by various types of feedstocks. In this paper, the effect of fuel-based nitrogen delivery on the development of NO_x precursors (HCN and NH_3) during the devolatilization process of properly selected samples (coal, sawdust, wheat straw, and ground coffee waste) has been examined. TG-DTG thermal analysis techniques, coupled with mass spectrometry (MS) were used for the assessment of nitrogen distribution for HCN and NH_3 gases, as intermediate species during feedstocks devolatilization, which directly influences the NO_x emission during thermochemical conversion processes (pyrolysis and combustion). The mass balance of nitrogen together with performed EGA (evolved gas analysis), and the distribution of nitrogen between volatiles and formed char were also determined. The obtained data for investigated samples could be exploited for further thermochemical process optimization, in regard to NO_x emissions. The presented results could be used as the experimentally determined input parameters for the mathematical modeling of indicated processes, and with further analysis can be transferred to large-scale industrial plant applications.

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Theory and instrumentation

Heat: from caloric to entropy and interpretation of Boltzmann constant

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Knowledge of heat accompanied the development of civilization. Black's discovery of conjugated variables at the turn of the nineteenth century opened the door of understanding heat in terms of an intensive (intensity of heat) and extensive (matter of heat) thermal phenomena. Within the internal energy, U, providing the equivalence of input heat, Q, and work done on the basis of volume, V, and pressure, P, i.e., $dU = dQ - PdV$, the energy, E, is given as $E = \phi \, x \, T$ where ϕ has an extensive meaning of heat (like Comenius' caloric), and T is the hotness level (temperature). Within the Clausius' dynamic (substitutional) theory it was altered by the normalization via entropy, $S = Q/T$, which factually mixed extensiveness with intensiveness thus introducing subsequent discrepancies in the understanding of heat. The result was the necessarily definition of Boltzmann's constant, K, in the static state now re-reconsidered as noncontact under a moving system, which exhibits a specific meaning in relativistic transfer. Thermodynamics based on the efficiency treaties of a steam engine as an information transducer, can also provide a re-understanding of its moving force involved being thus unconnected with the consumptions (of entropy) but with the caloric transfer from hotter body to colder one without its internal change. It provides the struggle of temperature depiction within its phenomenological (macroscopically measurable) mode and its statically weight together with it measurability under rapid extreme changes. Supported by the institutional research program No. RVO: 1100 and NETZSCH-Gerätebau GmbH in Selb.

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Thermal hazards, lifetime prediction

Examination of possible inhibitors of ammonium nitrate decomposition under limited mass transfer conditions

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Keywords: ammonium nitrate, exothermic decomposition inhibitors, thermal analysis

Ammonium nitrate (AN) is known to be an extremely dangerous compound. It is also extremely important in various branches of chemical industry, as its use ranges from fertilizers to explosive materials used in mining [1, 2]. Due to numerous documented explosions caused by systems containing AN, the topic of its stability in the presence of various additives has been extensively studied with the use of thermal analysis [3-5]. Inhibitors and catalysts of ammonium nitrate decomposition have been verified in binary or multicomponent systems over the years; however, many studies only defined the influence of studied additives on the endothermic dissociation of ammonium nitrate [6-8]. Such results, especially for compounds defined as stabilizers, should be further assessed under conditions that allow the dangerous exothermic decomposition process to occur in analyzed systems. The present work focuses on determining the thermal stability of ammonium nitrate in systems with additives that are considered or were previously defined as inhibitors of the thermal decomposition process of AN. The presented research has been conducted with the use of differential thermal analysis coupled with thermogravimetry and mass spectrometry (DTA-TG-MS). Samples containing AN in appropriate proportions with selected additives were heated to a temperature of 450°C in air atmosphere. Obtained results allowed to verify the influence of every compound on the thermal stability of ammonium nitrate and some potential inhibitors either exhibited a negative effect on the overall thermal stability of AN or did not meaningfully impact the exothermic decomposition process. Additionally, small amounts of substances that are generally considered as inhibitors worsened the thermal stability of AN.

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Study on the connection between fire/explosion limit and the gas components released after thermal runaway of lithium-ion batteries under different SOC levels

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Keywords: thermal risk, overheat method, thermal runaway reaction, gas chromatography-mass spectrometry, thermal runaway gases

The use of lithium-ion batteries (LIBs) has increased saliently, but so has the incidence of fires and explosions. The fire/explosion triggered by thermal runaway are thought to be highly linked to the emission of gas components, making gas analysis critical for identifying potential thermal hazards and evaluating the level of thermal risk posed by such an event. The fire/explosion of gases can worsen the thermal runaway process, posing a severe danger to people and property. Therefore, it is crucial to study the composition of these gases and their effect on fire/explosion limits. In this research, we used the overheat method to trigger the thermal runaway reaction and collected two steps of emission gas samples for analysis. Gas chromatography-mass spectrometry (GC-MS) was used to analyze the gas composition. The results showed that the emission gas was mainly composed of CO, CO_2, alkanes, and alkenes. Additionally, the complexity of the gas increased with the state of charge (SOC). The study highlights the importance of considering the SOC level when evaluating the thermal risks associated with thermal runaway of LIBs. It also emphasized the need to incorporate the gas composition and explosion limits of thermal runaway gases into safety measures for LIBs at different SOC levels.

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Components and thermal hazard characteristics of spark fireworks and cold light fireworks

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Keywords: nitrocellulose, thermal hazard, thermal analysis, simultaneous thermogravimetric analysis, thermodynamic analysis

The "Regulations on the Administration of Pyrotechnics" classifies pyrotechnics into nine categories, with spark type being the third largest category imported into Taiwan. Spark-type pyrotechnics were commonly used in festivals and public events. Both professional stage pyrotechnics (cold light fireworks) and normal spark light fireworks had a similar discharge pattern. However, normal spark light fireworks produce dense smoke and temperatures when discharged due to potassium perchlorate and Al-Mg metal powder composition. In contrast, cold light fireworks were primarily composed of nitrocellulose and titanium metal powder, which had a low ignition point, without dense smoke, and lower discharge temperatures.

Cold light fireworks had a discharge temperature that was safer than normal spark light fireworks, averaging 201.49 °C compared to 503.38 °C for the latter, producing less smoke. However, it was necessary to note that the presence of nitrocellulose in fireworks results in higher energy content and nitrating properties than normal spark light fireworks, with an average enthalpy of 2389.64 J g^{-1}, compared to 567.42 J g^{-1} for the latter. This can pose potential thermal hazards, as both fireworks have different apparent activation energies, measured using the ASTM E698 method. The former has lower apparent activation energy and was more reactive than the latter, emphasizing the need for careful management of the amount of nitrocellulose used and stored during production and storage.

This study used commercially available normal spark light fireworks and cold light fireworks, produced a relatively simple spark eruption, and the gunpowder was sampled directly without grinding or additional sieving. To ensure the accuracy of the experimental results, laterite fixtures on the cylindrical launch port and lime fixtures on the base would be excluded as much as possible to avoid contamination of the sampling samples. The observation of the microstructure using field emission scanning electron microscope/energy-dispersive X-ray spectroscopy, observed thermal analysis by using laser particle sizer and simultaneous thermogravimetric analysis and using advanced thermodynamic analysis software to compare and discuss the thermal hazard of the two types of firework.

Thermal Inhibition analysis on ammonium nitrate mixed with dry extinguishing agent

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Keywords: ammonium nitrate (AN), DSC, ARSST, dry extinguishing agents, kinetic parameters

There are many accidents induced by ammonium nitrate (AN) in manufacturing process, which have caused the serious loss of property and human being. Therefore, we used AN as our main topic material for discussing its thermal characteristics, such as kinetic parameters by DSC and ARSST. Beside, Dry extinguishing agents also was applied in this study for deeply evaluating the inhibition effectiveness and inhibition reaction mechanism. Meanwhile, kinetic parameters were also be researched for these complex reactions. Results by this study will benefit to the process of AN and the relevant staff, which also have the safety protection in the working environment.

Thermochemistry

Experimental evaluation on pyrolysis and gasification characteristics of simulated waste cation exchange resin

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Keywords: cation exchange resin, pyrolysis, gasification, kinetics, products, nuclides

The safe disposal of large irradiated cation exchange resin waste in nuclear power plant has attracted worldwide attention. Thermal cracking including pyrolysis and gasification, through the degradation of waste resin could be favourable to get high volume reduction of the radioactive resin with safe treatment of radionuclides [14-16], which is a promising treatment method. In this work, the kinetic characteristics and product characteristics of the simulated waste resin in the pyrolysis and gasification were evaluated based on thermogravimetric analysis as well as TG-FTIR and TG-GC/MS. In nitrogen atmosphere, metal elements combine with sulfur elements in the resin to form compounds, which would hinder the reaction of waste resin in the first stage and promote the reaction in the second stage. The gasification process of waste resin in 10% oxygen and 10% steam of atmosphere has three weightlessness stages. The average weight loss rate of waste resin in 10% oxygen atmosphere was 90%, which could be attributed by the stronger oxidation of oxygen. The main reactions of the waste resin in the first stage were the same in different atmospheres. Under the 10% oxygen atmosphere, the copolymer matrix of waste resin in the third stage of the reaction at 500 °C would be oxidized to carbon dioxide, which could be related to that the sulfur bond breaks, resulting in increasing the weight loss rate. Under the nitrogen atmosphere, the sulfur bond breaks at 700 °C, which makes the copolymer matrix difficult to decompose and the weight loss rate is low. The work can provide basic data for the thermochemical integrated treatment technology of waste resin in nuclear power plants.

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Predicting and optimizing on decontamination performance of metallic radionuclides in irradiated graphite in a fluidized bed reactor

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Keywords: irradiated graphite waste, bubbling fluidised bed reactor, chlorination roasting, metallic radionuclides, machine learning

Chlorination roasting is an effective method for removing metallic radionuclides from irradiated graphite waste [1]. Fluidized bed reactors have been widely used in the field of solid waste treatment due to their excellent heat and mass transfer capabilities [2]. Therefore, a 2D semi-continuous bubbling fluidised bed reactor CPFD (computational particle fluid dynamics) model was considered in the present study to remove metallic radionuclides by chlorination roasting method with NH_4Cl as chlorination agent. The proposed model used a Lagrangian-Eulerian approach to describe flow patterns, local particle velocities, particle solid fractions, and gas composition. Chlorination process was continuously monitored by measuring the amount of produced metal chloride with time. The effects of different boundary conditions including operating temperature, irradiated graphite flow rate, feedstock particle size and size distribution, injector location, and carrier gas velocity on the decontamination efficiency were systematically investigated. Machine learning algorithms (MLA) were then applied to predict the optimised conditions that led to the maximum decontamination efficiency. Support vector regression with particle swarm optimisation algorithm [3] was developed and applied to the CPFD datasets to predict the optimum values of boundary condition. The CPFD simulation was also carried out using the optimum parameters obtained by the MLA. The CPFD results and the values predicted by the MLA for the maximum decontamination efficiency were finally compared where a good agreement was achieved. This research would be beneficial to the industrial application of chlorination roasting in irradiated graphite treatment.

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