BOOK OF ABSTRACTS

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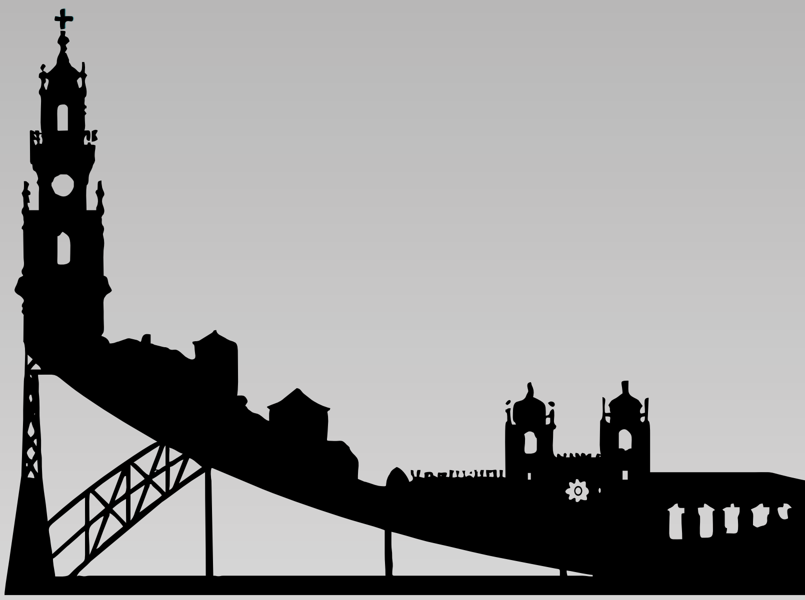
ANA R. R. P. ALMEIDA
JORGE M. GONÇALVES



19-21 July 2023

Porto

MEDICTA2023

Mediterranean Conference on Calorimetry and Thermal Analysis

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DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY
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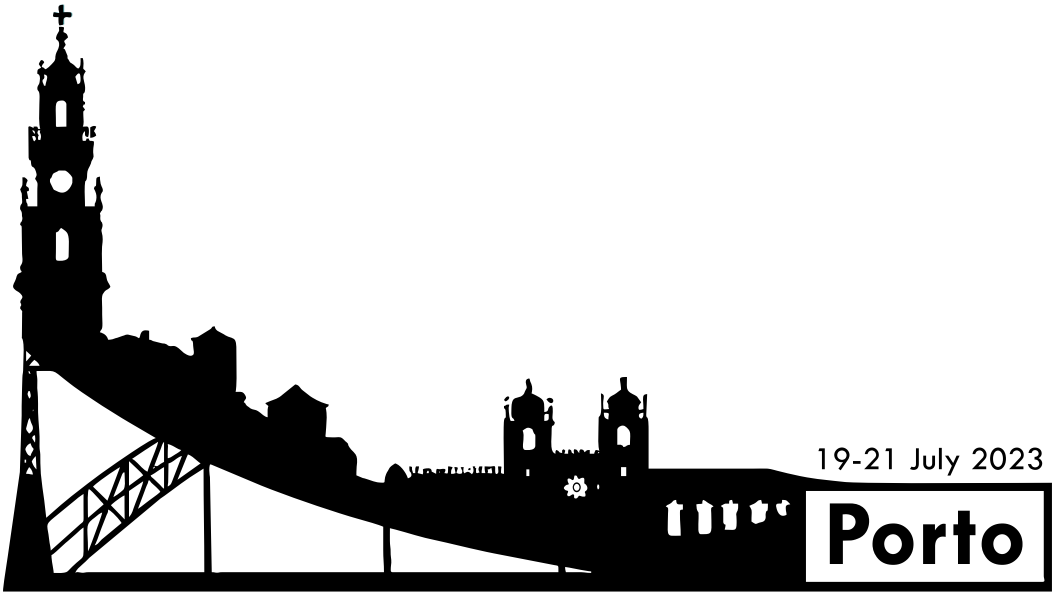

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Book of Abstracts of the 16th Mediterranean Conference on Calorimetry and Thermal Analysis
MEDICTA 2023
16th Mediterranean Conference on Calorimetry and Thermal Analysis – 19-21 July 2023
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FOREWORD

The 16th Mediterranean Conference on Calorimetry and Thermal Analysis (MEDICTA 2023) is jointly organized by the Calorimetry and Thermal Analysis Group of Porto (CATPOR) and five National Associations for Thermal Analysis and Calorimetry operating in Italy (AICAT and GICAT), Spain (GECAT), Greece (HSTA), France (AFCAT) and Croatia (CCTAC- CSCE).

The preceding fifteen conferences took place every two years, from 1993 to 2021, in several countries, namely: Corte (Corsiga, France, 1993), Cagliari (Sardinia, Italy, 1995, Palma de Maiorca (Spain, 1997), Patras (Greece, 1999), Santiago de Compostela (Spain, 2001), Porto (Portugal, 2003), Thessaloniki (Greece, 2005), Palermo (Italy, 2007), Marseille (France, 2009), Porto (Portugal, 2011), Athens (Greece, 2013), Girona (Spain, 2015), Loano (Italy, 2017), Roma (Italy, 2019, jointly with CEEC-TAC5), Split (Croatia, 2021, jointly with CEEC-TAC6, partially on-line).

As one more MEDICTA Conference, MEDICTA 2023 intends to provide a forum for scientists interested in the materials' thermal properties and the various thermal analysis and calorimetry techniques. Its Program includes sessions on several topics of Calorimetry and Thermal Analysis, covering the most recent findings and applications, to provide opportunities for exchange ideas and opinions on industry and relevant subjects.

The scope of MEDICTA 2023 is wide enough to attract the interest of scientists from academy and from industry. We did our best to give the opportunity to all researchers, interested in thermal analysis and calorimetry, to meet and to discuss the results of their latest research works. A special attention has been devoted to young researchers, offering them an intensive school, Porto MEDICTA School, lectured by recognized experts in the field.

The present Book of Abstracts contains the abstracts of all the contributions submitted to the Conference (5 Plenary Lectures, 5 Key Lectures, 50 Oral Communications and 61 Poster Communications) by 122 Authors of 17 countries (13 from Europe, 3 from America and 1 from Asia).

We hope to provide a very fruitful Conference to all the participants, believing that MEDICTA 2023 will be strengthened with their high scientific impact contributions.

The contributions from all the authors, sponsors and exhibitors are gratefully acknowledged.

University of Porto, July 2023

Maria das Dores Ribeiro da Silva
Conference Chair

GENERAL INFORMATION

The scientific programme includes Plenary Lectures, Key Lectures, Oral Communications and Poster Communications. The programme starts every morning at 9:00 am and at 2:00 pm every afternoon.

Information on the location of Lecture Theatres as well as the day, time and theatre for the presentations is given in the Programme.

This book includes the following abstracts and codes:

Plenary Lectures (**PL**)
Key Lectures (**KL**)
Oral Communications (**O**)
Poster Communications (**P**)

As a rule, oral and poster communications were assigned to the appropriate Section as and when indicated by the author(s). Only in a very few cases did the Committee decide on a different assignment.

Authors are solely responsible for the contents, style, and quality of their abstracts, which were reproduced from their originals.

PLENARY LECTURES

Mechanisms and physico-geometrical modeling for kinetic description of solid-gas reactions

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Solid-gas reactions are heterogeneous chemical reactions, including thermal decomposition of solids and reactions between a solid and a gas to produce a new solid phase such as high temperature corrosion for example.

Kinetic analysis of these solid-state processes aims to quantitatively describe the temporal evolution of the system. Kinetics of such heterogeneous reactions can be influenced by numerous factors. Indeed, temperature and partial pressure of gases (reactant or product) can obviously have great importance on the reaction rate [1]. Nevertheless, other characteristics of the system can also play a primordial role on the course of the reaction: solid sample geometry (including the shape of the initial particles [2] and their size [3]), the presence of alloying elements or impurities in the solid phase, the surface state, and the porosity are some factors that can influence the kinetics.

In order to express the rate equation of a solid-state reaction, one must remind that such an heterogeneous solid-gas reaction results from the combination of two successive processes: surface nucleation and nuclei growth. Each processes obey the same balance equation but occur according to its own mechanism, i.e. its own succession of elementary steps. These elementary steps can be adsorption, desorption, an interfacial reaction, or a diffusion, and involve the creation and the destruction of intermediate species such as point defects or adsorbed species.

Due to kinetic assumptions of pseudo-steady state and rate-determining step approximations, a general equation of the rate may be established [4]. The reaction rate is then a product of two functions, one depending of the thermodynamic variables and the other one of the geometric variables and time. According to the various possibilities of geometry, growth direction, rate-determining step localization, nucleation and/or growth processes, adapted physico-geometrical models may be obtained for the variations of the kinetic rate with time. Mechanism decomposition in elementary steps is shown to get the calculation of the function that governs the effect of the thermodynamic variables on the kinetic rate.

In the present talk, the general concepts of both kinetic analysis and reaction mechanism will be briefly recalled and some examples of physico-geometrical modelling for solid-gas reactions will be shown.

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POSS, a very thermally stable nanoparticle: state of the art and future developments

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Polymer was the defining material of the twentieth century whilst, both for the considerable increase in articles published in literature and for the growth of applications over the last fifteen years the defining material plat-form of the twenty-first century could very well be the hybrid material. The design of an hybrid material is related with the combination of two or more components in a single material to give new and previously unattainable combinations of useful properties [1]. For the preparation of these materials are required building blocks like carbon nanotubes, graphene and polyhedral oligomeric silsesquioxanes (POSSs). The set of knowledge regarding these latter expanded rapidly over a very short period of time as highly efficient synthesis methodologies were developed. Efforts to develop practical applications for discrete POSS frameworks gained a major champion in the early 1990's when Joseph D. Lichtenhan initiated a research program at Edwards Air Force Base (California, USA) to use POSS-containing polymers as precursors to hybrid inorganic/organic materials [2]. The interest observed for these nanomaterials since the nineties, was probably due to an increased focus on mechanistic studies involving POSS frameworks, and the deliberate use of POSS as pre-cursors to more complex Si/O and Si/O/M frameworks. Since the existence of reports consistent with silsesquioxane formation back as far as the 1870s [3], we can consider this new development as a real rebirth of POSS. Today POSSs, due to their thermal and chemical stability, cover with their use various fields, ranging from high-performance materials to flame-resistant materials, novel homogeneous POSS-supported catalyst and applications in proton exchange membranes [4]. POSS molecule has been considered a next generation material in several biological fields, due to its excellent mechanical properties and biodegradability provided by Si–O–Si bonds. Accordingly, POSSs have been used as tissue engineering and biomedical materials and to improve the efficiency and pathway of delivery in drug delivery systems [4].

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Calorimetry: a powerful methodology for studying the stability of G-quadruplexes and their interaction with anticancer drugs

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DNA G-quadruplexes (G4s) form in relevant genomic regions and intervene in key cellular processes, including telomere upkeep and modulation of oncogene expression [1]. Many studies have been focused on searching for small organic molecules able to stabilize G4s within gene regulatory elements. This has been shown to be effective to some extent and there is an ever-growing library of G4-binding compounds able to inhibit tumor cells growth [2]. However, the physicochemical basis of such stabilization is still largely to be explored. The role of calorimetry is crucial in studying the thermodynamic stability of G4s and the energetics of their interaction with molecules of therapeutic interest. Differential scanning calorimetry (DSC) and isothermal titration calorimetry (ITC) are important complementary methodologies. DSC is very useful to acquire thermodynamic parameters on G4 stability and to reveal the formation of multiple conformations or the presence of intermediate states along the folding/unfolding pathway. In addition, DSC allows to estimate the impact of chemical modifications on the stability of bio-macromolecules [3]. ITC can be applied to obtain the thermodynamic properties of drug-G4 interactions to screening among various potential ligands and to address drug design [4].

Here, some results on the stability of G4s and their drug binding, obtained using DSC and ITC in combination with other physicochemical methodologies, are discussed.

Acknowledgements: These studies are supported by the Italian Association of Cancer Research (AIRC), through grant IG 23198.

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Thermal analysis of solid-state transformations: metallic alloys and compounds

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Solid-state transformations include a wide variety of processes: eutectoid, peritectoid, martensitic, allotropy, oden-disorder transitions, crystallization of an amorphous, spinodal decomposition, precipitate formation, recrystallization, and more. Thermal analysis techniques have been widely used to characterize these transformations.

This presentation will focus mainly on the solid-state transformations of metal compounds and alloys, emphasizing crystallization and martensitic transformation [1-2]. Thermal analysis techniques allow both the determination of the characteristic temperatures and the obtaining of the associated thermodynamic parameters. It is also discussed the complementarity of thermal analysis techniques with those of microstructural or functional characterization.

Acknowledgements: I appreciate the collaboration of senior and junior researchers throughout these more than 30 years, as shown in the research articles (orcid: 0000-0002-7653-3415).

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Thermodynamic and transport properties of ionic liquids

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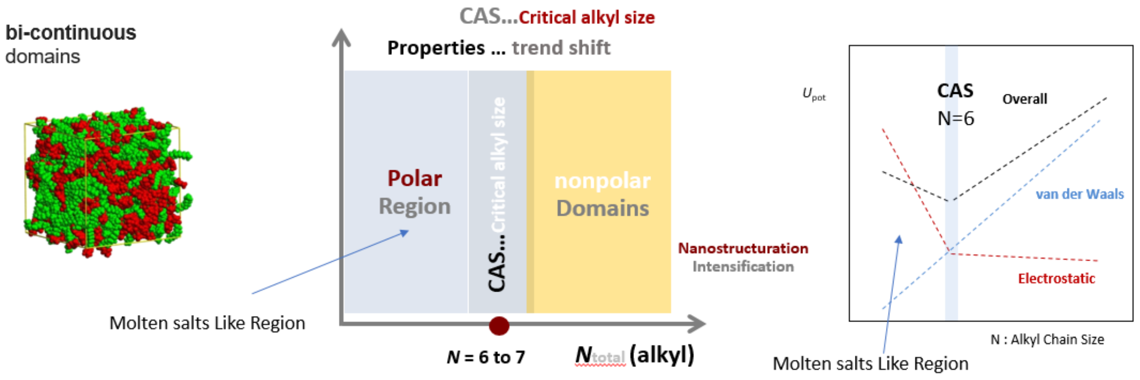
Over the last few years the study of thermodynamic and transport properties of ionic liquids, [1-5] has proven the existence of a significant differentiation in the trend of thermodynamic property series before and after CAS (critical alkyl size of n=6) due to the change of the cohesive electrostatic potential that rules the network packing both in solid and liquid phases. The trend change of thermodynamic and transport properties was associated with intensification of the nanostructuration in the ionic fluids and the formation of bi-continuous domains. Further studies allowed us to unravel the role of IL nanostructuration and acidity on the preferential interactions established between the alcohol and the IL, the speciation and cohesive energy of protic ionic liquids [6] as their nucleation and growth of micro droplets of ILs deposited by physical vapor method onto different surfaces [7] and more recently the interpretation of their phase behavior, mixing properties and transport properties.



Scheme 1. Nanostructuration effect on the properties of ionic fluids

We were able to give additional support to the nanostructuration effect on the thermodynamic and transport properties on several ionic liquids families. Ionic liquids form nanoaggregates constituted by anions and cations giving rise to a network of highly polar areas ruled by coulombic forces and nonpolar ones corresponding to regions of alkyl chains dominated by van der Waals interactions.

Acknowledgements: This work was supported by the Fundação para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020), IMS-Institute of Molecular Sciences (LA/P/0056/2020).

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KEY LECTURES

Solid-state of active pharmaceutical ingredients: The role of thermal analysis

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Pre-formulation studies are one of the pharmaceutical development phases during which the physicochemical properties of the drug substance are characterised and established. Investigation of the solid-state landscape of active pharmaceutical ingredients is one the most important points in these studies. In fact, different solid forms, like polymorphs, salts, cocrystals, amorphous phases, may have different physicochemical and biopharmaceutical properties and it is important to select the most appropriate solid form for formulation. Some examples have already shown that the lack of control of the solid form in drug formulations can have serious consequences both financial and societal. [1,2]

Thermal analysis, with emphasis on differential scanning calorimetry, thermomicroscopy and thermogravimetry, plays a relevant role in screening polymorphs and stablishing their relative stability, and also in the investigation of salts, cocrystals and amorphous phases. In this communication, several case studies that we have come across in recent years will be presented. These examples will show the relevance of thermal analysis in the study of the solid state of active pharmaceutical ingredients.

Acknowledgements: CQC-IMS is funded by national funds through FCT, project UIDB/00313/2020.

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Implementation of spark discharge methodology into fast scanning calorimetry for the case of nanoscale homogeneous alloy materials

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Lately, the development of lasers with high and precise energies as well as sensors with ultra-fast response times has given rise to fast scanning calorimetry (FSC) as a potential method which can demystify and expand the knowledge on thermal and energy transitions taking place during non-controlled high energy fast processes such as laser and plasma sintering, combustion synthesis etc. To achieve huge heating (~50 kKs^{-1}) and cooling (~5 kKs^{-1}) rates, the method is confined to minute samples, below a milligram of material, that need to be precisely positioned on a measuring chip (typically multichannel 25×25 mm chip with 100×100 µm active surface).

Small sample sizes usually come as an advantage, but for studies of some systems, such as soft amorphous metals and alloys as well as glasses, where often micrometer sized particles are mixed together and thermally treated, this is a problem because of great inhomogeneity which leads to poor measurement repeatability and reproducibility making the results non representable. So-called soft metals are actually solid-state materials, typically alloys, with reduced level of the ordering at the atomic scale. To prepare such glass-like formations, very fast cooling rates are necessary to prevent the crystallization, typical for thermodynamic cooling of molten metals. A few ways exist to approach these issues and given the inherent size of the measuring system, all of them fall under a physical deposition category type.

The question is how to prepare such minute sample homogeneous in any way. Here we try to offer between a methodology for homogeneous and precise preparing of soft metals onto FSC chips, and a methodology for preparing of soft metals in the first place. Spark plasma ablation deposition (SPAD) is a powerful tool that sparks the electrode materials into a plasma cloud that rapidly condensates into nanoparticles that can be streamed for deposition through a nozzle. Here we demonstrate the potential of spark ablation, as a green, effective and cost-efficient method of metallic nanoparticle production for preparation of various nanocomposite materials. It is a method where nanoparticles are produced through disintegration of an electrode made from the desired material, by plasma which is induced by a spark at high voltage in a controlled setting. This process needs only a carrier gas, an electrode and electricity to produce a wide range of clean metallic nanocomposites of multiple constituents. The cooling of particles by mixing with the gas leads to vapour condensation, producing atomic clusters, which further coagulate to form larger particles. If this coagulation is induced between multiple materials, a homogeneous mixture of precursor metals on a nanoscale can be obtained.

Samples were prepared directly on chips for FSC by coating them with the precursor mixtures in-situ prior to nanoparticle synthesis. Obviously, the thermodynamics of the method inherently suits the soft metal envelope. With our configuration of to 4 different elements can be combined having in mind a pure electrode approach. However, we want to use mixed metal electrodes, prepared in different ways, from compacted metal powders to alloys from melts.

This investigation basically confirmed that SPAD is indeed capable of depositing suitable amount and that SPAD is indeed capable of creating the materials in a form of amorphous metals. Much more vas revealed by the comparison of the thermal properties between several approaches: (i) conventional attempts to put the samples on FLASH DSC chips, vs. (ii) SPAD-based attempts via pure electrode approach, vs. (iii) several SPAD-based attempts via several mixed electrode approaches. We comment and discuss in depth on the importance of structural similarity of measured vs. real systems as well as on the extent of the improvement SPAD has on FSC as a measuring technique.

Acknowledgements: This work has been funded by the project KK.01.2.1.02.0316 by the European Regional Development Fund and UIP-2019-04-2367 and PZS-2019-02-1555 by the Croatian Science Foundation

Molecular recognition by nano-containers and aggregates: determining species and driving forces in solution

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Non-covalent, weak interactions are major tools in supramolecular and coordination chemistry to oversee molecular recognition and self-assembly processes for the design and synthesis of molecular capsules, cages, flasks and nano-containers [1]. By mimicking the active sites of enzymes, synthetic assemblies are able to isolate proper guest molecules from the surrounding media and promote chemical reactions in a controlled fashion. The dramatic differences between the bulk solvent and the inner space of a molecular container provide the "thermodynamic boost" to guest complexation which cannot be driven only by structural complementarity or fitting between host and guest. Consequently, the determination of species and thermodynamic parameters for molecular recognition, self-assembling, host-guest encapsulation and micellar aggregation phenomena is a key point for the rational design and application of nano-containers in solution.

The entropic and enthalpic driving forces for guest binding to supramolecular receptors in solution are very different, which significantly complicates their determination. The advantageous use of complementary techniques, such as NMR, UV−vis/fluorescence and isothermal titration calorimetry (ITC), enables the disentanglement of multiple host-guest interactions. Data collected by each technique measure different components of the host−guest equilibria and together provide a complete picture of the solution thermodynamics. We developed a procedure for the simultaneous refinement of multiple parameters (ΔG, ΔH and ΔS) by handling different observables through a weighted non-linear least-squares analysis [2]. By applying this procedure to different sets of observables, each looking at different components of multiple equilibria, the binding constants as well as the enthalpy and entropy change for the interior and multiple exterior guest binding to a supramolecular receptor were determined.

Furthermore, a general-purpose computer program for the simultaneous determination of both standard enthalpy of reaction and binding constant values from data obtained by ITC was recently developed [3]. The program does not impose limits on the complexity of the chemical systems that can be treated or on the quantity of experimental data to be analyzed. The chemical system is defined in terms of species of given stoichiometry rather than in terms of binding models. Many titration curves may be treated simultaneously. The software can also be used as a simulation program for experimental design.

These data refinement tools have been successfully applied for the molecular recognition of charged guests by a metal-ligand cluster [2], calixarene receptors [4] as well as the formation of anion-templated capsules/compartments [5] or micellar aggregates in aqueous solution [6]. The suitable combination of ITC with other techniques allowed for the deconvolution of the host-guest equilibria and the determination of the species formed in solution thus unveiling the different and often opposing forces driving guest recognition and self-assembly processes.

Acknowledgements: MIUR (PRIN 2015MP34H3) and University of Catania (Piaceri 2020-22, Linea 2) are kindly acknowledged for supporting this research.

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Synthesis, structure, energetics and conformational dynamics of polyphenyl polycyclic aromatic hydrocarbons

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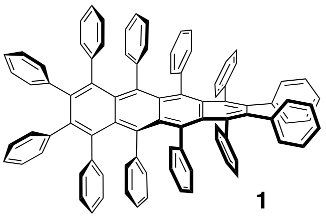
The synthesis and crystallographic characterization of several extremely crowded polyphenyl polycyclic aromatic hydrocarbons—dodecaphenyltetracene (**1**), decaphenylphenanthrene (**2**), 1,2,3,4,5,6,7,8-octaphenylphenanthrene (**3**), and 1,2-bis(pentaphenylphenyl)benzene (**4**)—are described.[1-3] All these molecules adopt chiral conformations in the solid state, often with severe distortions of the central aromatic rings due to steric conflict among the many peripheral phenyl groups. Would these chiral molecules be configurationally stable if resolved? Dispersion-corrected DFT calculations and conventional (uncorrected) DFT methods give very different estimates of the barriers to racemization. In the most extreme case, compound **4**, the former methods yield racemization barriers greater than 29 kcal/mol ($t_{1/2}$ = 7 years) but the latter give barriers on the order of 18 kcal/mol ($t_{1/2}$ = 2 sec). Experimentally, the barrier, determined by dynamic NMR spectroscopy, is only 20.3 kcal/mol ($t_{1/2}$ = 86 sec).[3] The differences are due to the large areas of interacting hydrocarbon surfaces and the varying computational treatment of London dispersion in these molecules. One must ask: is there a problem with dispersion-corrected DFT methods in large, crowded, polyphenyl aromatic compounds? To address this question, the experimental gas-phase enthalpies of formation of several very crowded polyphenyl biphenyls, including decaphenylbiphenyl (**5**), were determined.[4] The results, when compared with the enthalpies of formation of less crowded polyphenyl aromatics, indicate that dispersion-corrected DFT methods are essentially correct (and perhaps even underestimate the magnitude of the attractive force). The gross errors in the estimates of the racemization barriers by dispersion-corrected DFT methods must be due to the failure of these calculations to include intermolecular dispersion from the solvent. As a practical matter, if chemists wish to calculate the dynamic properties of such large molecules in condensed phases, it is better to ignore dispersion than to include only intramolecular dispersion in the calculations.



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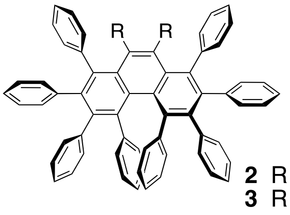
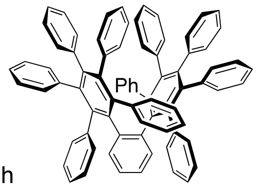


2 R = Ph
3 R = H



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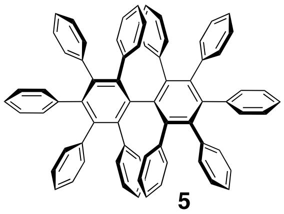

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Acknowledgements: The authors thank the U.S. National Science Foundation (grants CHE-1762452 and MRI-1228232) and the Portuguese Foundation for Science and Technology for financial support.

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New methods for an old problem: fast-scanning nanocalorimetry for a microscopic description of glass transformation

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Understanding the physics of glass formation and devitrification is still a challenge despite the intense experimental and theoretical research of the last 100 years. Two main practical obstacles hinder the study of non-equilibrium dynamics: i) the difficulty to access low temperatures in the equilibrated system, due to the exponential growth of relaxation times as the temperature is lowered and ii) the difficulty to observe dynamic and static variations at a molecular level in the non-equilibrium glass structure. The formation of ultrastable glasses, being equivalent to ordinary glasses equilibrated very down in the energy landscape, not reachable by ordinary cooling rates or aging times, showed a way to overcome the first obstacle[1]. In this talk, we show how fast scanning nanocalorimetry offers an efficient and promising way to overcome the second obstacle and shed new light about the transformation and equilibration process of glasses.

Fast scanning membrane-based nanocalorimetry gives access to the heat capacity and transitions of nanometric thin films, thanks to the low mass of the cell, the lack of thermal loses towards the surroundings and the large heating rates employed (of the order of 10^5 K/s), fundamental to access temperature ranges not able to be explored by other means. Here, we show how this is a suitable tool to characterize and extract valuable information about the transformation of glasses. First, we show how to identify the transformation mechanism of glasses from the calorimetric trace. In uncapped vapour deposited glasses – ultrastable but also less stable –the surface mobility is inherently larger than in the bulk, which triggers the transformation, manifested via a liquid front propagating into the bulk at a given growth front velocity[2], a value that can be accessed from the calorimetric trace. Second, and when such a surface-mediated mechanism is suppressed, we can access bulk transformation and their relaxation dynamics. In this context, we observe how the bulk relaxation of glasses proceeds via a nucleation and growth-like mechanism, regardless of the thermodynamic state of the system, providing a microscopic view of the relaxation process[3]. All this is possible thanks to the fast-scanning rates of this technique, that allows to explore temperature and time regimes not accessible by other means. The nanostructure of a glass can also be affected by mixing, either at a molecular or mesoscopic scale, and by interfaces. Nanocalorimetry offers a fast tool to provide information about the impact of such a structure in the dynamics of glasses.

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ORAL COMMUNICATIONS

A physical-chemical study on oil-protein mixtures used as paint binders

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The 15th century was a great period of innovation in Italy, known as Italian Renaissance. During this time, the great Old Masters started to turn from traditional egg based tempera to oil painting which was widespread in the Flanders. Nowadays, there are several proofs [1,2] of the presence of both drying oils and proteinaceous binders in the same painting, but how this was done and why, is still not understood today.

Tempera and oil paints are very different systems from a chemical, physical and rheological point of view. Tempera paint dries very quickly by water evaporation: proteins – which are polymers – are the paint binder. Oil paint dries very slowly through an autoxidative radical chain process: the paint binder is the polymer produced upon cross-linking of polyunsaturated triglycerides.

There are several ways to combine oil and protein in the same paint layer. In this study, two different painting techniques have been investigated:

- tempera grassa, an emulsion of oil in water, in which the pigment particles are dispersed;
- protein coated pigment, an oil paint in which the pigment particles are coated with a thin layer of proteins.

Recent research [1] showed how the addition of egg yolk to oil paints, and the addition of oil to tempera paint influence the flow behavior, the drying kinetics and the chemistry of the paint binder. Starting from this point, we investigated the physical-chemical behavior of these paints, introducing egg white as proteinaceous medium.

Tempera grassa- and protein coated pigment- model paints were prepared using either egg yolk or egg white as proteinaceous media, linseed oil as drying oil, and synthetic ultramarine blue as pigment. Model paint layers were also prepared, by casting the model paints on glass and metal supports. The behavior of these model paints and paint layers were compared with that of egg yolk tempera, egg white tempera and oil paint, prepared mixing the single binders with ultramarine blue.

The model paint layers were monitored with Differential Scanning Calorimetry (DSC), to investigate the curing of the paints, and the model paints were analysed with ThermoGravimetrical Analysis (TGA) under air flow at constant temperature, to monitor the mass changes due to oxidation and to oxidative degradation. The natural oxygen uptake and the dry to the touch state of the model paints were also recorded. Data were compared with those obtained by monitoring the molecular composition of the volatile products of oxidative degradation of model paint layers using solid phase micro-extraction - gas chromatography - mass spectrometry (SPME-GC-MS).

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Measurement of sublimation and vaporization enthalpies of two aza crown ethers and two cryptands by isothermal thermogravimetry methodology

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The aza crown ethers are macrocycles with a molecular structure similar to that of the crown ethers [1] but in which some of the oxygen atoms are replaced by nitrogen atoms [2]. Other aza derivatives of the crown ethers but with a bicyclic structure are the cryptands that, compared with the crown ethers and aza crown ethers, can complex metal ions in a more efficient way due to such ions are easily trapped into the cavity formed by the bicyclic structure [3]. Although the aza crown ethers and cryptands are very well known and studied for their great ability of complexing other molecules, there is no thermochemical study that help us to understand the role of the nitrogen atoms or the bridged structure in the molecular stability of these compounds. As the first part of a large thermochemical study, in this work we report the vaporization and sublimation enthalpies of the 1-aza-18-crown-6; the 1,10-diaza-18-crown-6; the cryptand [2.2.2] and the cryptand [2.2.1] — whose molecular structures are shown in figure 1— measured by isothermal thermogravimetric analysis (TGA) applying combined Pieterse-Fock and Clausius-Clapeyron equations. In this methodology the enthalpies of vaporization and/or sublimation are derived from the slope of the rate of mass loss as function of the inverse of the temperature, as described in figure 2. The results of enthalpy of sublimation are related with intermolecular interactions into the crystal arrangement of each compound.

Figure 1. Molecular structure of compounds in study.

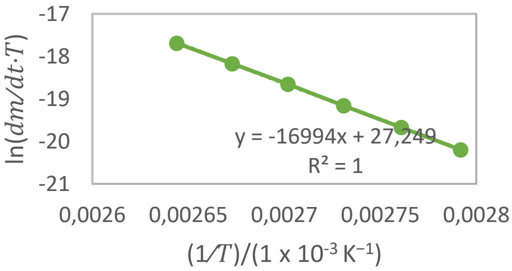

Figure 2. Representative graph ln[(dm/dt)·T] vs 1/T for a thermogravimetric experiment of 1,10DA18C6

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Thermochemistry and reactivity of aminothiadiazoles

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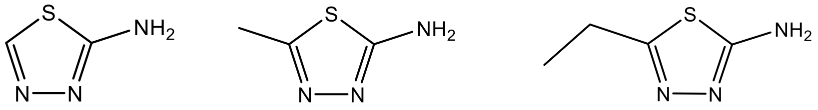
Thiadiazoles are pentacyclic compounds containing one sulphur and two nitrogen atoms that can present different structural isomers, depending on the relative positions of the three heteroatoms (1,2,3-, 1,2,4-, 1,2,5- and 1,3,4-thiadiazole). 1,3,4-Thiadiazole derivatives play an important role in medicinal chemistry, as they have physicochemical and pharmacokinetic properties suitable for the development of new drugs.[1,2] Moreover, the characterization of this class of compounds provides also relevant information for their application as metal ligands and as inhibitors of metal corrosion.[3,4]

Despite the large interest in the synthesis of this type of functionalized compounds, the corresponding thermodynamic properties are not well established, as well as the existence of energetic-structural correlations and the evaluation of the respective reactivity. In this context, our Research Group has been involved for the last few years in a systematic study of this class of five membered heterocyclic compounds, being our main goal the determination of the corresponding thermochemical and thermophysical properties. The present work reports an experimental and computational study on three aminothiadiazoles, 2-amino-1,3,4-thiadiazole (2AT), 2-amino-5-methyl-1,3,4-thiadiazole (2A5MT) and 2-amino-5-ethyl-1,3,4-thiadazole (2A5ET) (Figure 1). The enthalpies of combustion and sublimation of the compounds were determined, respectively, by rotating bomb calorimetry and two independent methods, high temperature Calvet microcalorimetry and mass-loss effusion method. The standard molar enthalpies of formation of the three compounds in the gaseous phase were derived from the experimental results and from computational studies. The corresponding standard Gibbs energies of formation in the crystalline and gaseous phases were also determined, to assess the relative thermodynamic stability of each one of the compounds. Additionally, a tautomeric analysis of these compounds was also performed allowing the establishment of the relation energy *versus* structure of the respective tautomeric forms.



(a) **(b)** **(c)**

Figure 1: Molecular structure of the compounds studied: (a) 2AT, (b) 2A5MT and (c) 2A5ET

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Quantification of π-electron correlation in polyaromatic hydrocarbons

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Electron correlation has been extensively studied in the last decades due to its central role in physical and quantum chemistry. The nature of this energy still eludes the chemists, being frequently distinguished in various forms, such as dynamic and static correlation.[1]

This work is a combined energetic and structural study of a series of polyaromatic hydrocarbons, including naphthalene and anthracene derivatives, which can serve as a molecular set to evaluate π-electron correlation in aromatic systems.[2] The experimental approach is based on the study of phase equilibria and analysis of molecular energetics with the help of combustion calorimetry. The π-electron correlation is discussed focusing on its optical, structural, and energetic manifestations.

With the use of the homodesmotic reaction schemes, the π conjugation energy in the molecules studied was experimentally quantified, and its dependence on molecular structure (type of spacer and position of phenyl rings) analyzed. The main objective is to understand the influence of molecular size and the presence and position of substituents on the π–electronic conjugation. Additionally, through the comparison of experimental results with the theoretical predictions, the nature of this conjugation is evaluated in terms of electron correlation energy (static vs dynamic).

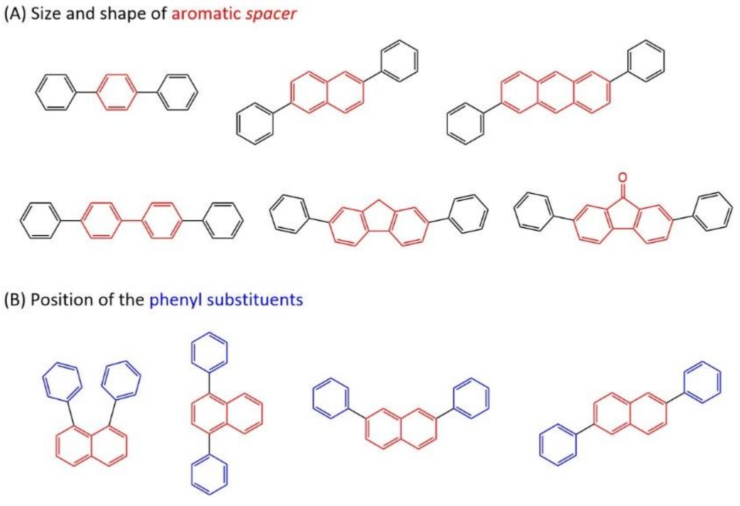

Figure 1. Effect of the size and shape of the aromatic spacer and position of the phenyl substituents on π-electron conjugation in aromatic molecules.

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Simulation of crystalline morphology from a simple calorimetric crystallization curve under isothermal or non-isothermal conditions

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This work presents a novel approach, which provides a probabilistic simulation crystallization process and modelling method of crystalline structure, based on the calorimetric crystallization curve recorded both under isothermal and non-isothermal conditions. The present approach describes the crystallization by random nucleation and subsequent growth of nuclei similarly to the conventional kinetic models, but it provides real structural data, like average spherulite size and size distribution as well as nucleus density data. The model is based on our earlier methods [1, 2], but a new program code was developed and consequently, the simulation in its present form can handle both isothermal and non-isothermal crystallization processes as well. The approach was validated using isotactic polypropylene homopolymer and random copolymer supplied by MOL Petrochemicals Ltd. (Hungary). Two nucleating agents were used to modify the crystalline structure within a wide range of nucleus density. One of them was a conventional heterogeneous nucleating agent marketed as NA-21E by ADK stab. The other nucleator was a fourth generation of sorbitol based organogelator called as Millad NX8000 supplied by Milliken. The crystallization curves were recorded using a Perkin Elmer DSC apparatus under constant cooling rate of 10 °C/min or at different isothermal temperatures. The simulation environment as well as the starting parameter set of simulation runs were studied in details in order to check the reliability of the simulation results. In addition the simulated results were compared to the spherulitic structure determined by optical microscopic studies under isothermal temperatures and good agreement was found between the simulated and measured structure. The presence of nucleating agent accelerated the crystallization process and resulted in much larger nucleus density, which was supported by the simulation results clearly.

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Phase behaviour of binary mixtures of imidazolium ionic liquids: anion and alkyl chain effects

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This works presents a study on the phase behavior and heat capacity of seven binary mixtures of 1-alkyl-3-methylimidazolium ionic liquids. The work strategy was divided in three parts (Figure 1): a) the study of anion effect while maintaining the cation, mixtures $[C_2C_1im][NTf_2]/[C_2C_1im][OTf]$, $[C_2C_1im][OTf]/[C_2C_1im][FAP]$ and $[C_2C_1im][PF_6]/[C_2C_1im][FAP]$; b) the study of the effect the alkyl chain while maintaining the anion, mixtures $[C_2C_1im][NTf_2]/[C_8C_1im][NTf_2]$ and $[C_2C_1im][NTf_2]/[C_{16}C_1im][NTf_2]$; c) the study of a system with two different cations and two different anions, mixture $[C_{12}C_1im][PF_6]/[C_2C_1im][FAP]$. The phase behavior of the pure ionic liquids and binary mixtures at different composition was studied by differential scanning calorimetry. The isobaric heat capacities at T = 298.15 K for the neat compounds and the equimolar mixtures were measured using a high precision drop calorimeter [1].

Throughout the studied systems different types of behavior were found, such as, absence of crystallization, immiscible liquid phases, solid precipitation, and regular eutectic behavior. This differentiation highlights the impact of the nature and composition of the system on the phase behavior. Relative to the anion effects the obtained results support that the presence of more spherical anions seems to favor the crystallization process. Based on the results, $[C_2C_1im][PF_6]/[C_2C_1im][FAP]$ was found to be the most crystallizable system, as the crystallization process was observed in the entire composition range. The results with different alkyl chain lengths highlighted that a large size unbalance can lead to phase separation. The system $[C_{16}C_1im][NTf_2]/[C_2C_1im][NTf_2]$ presented a large range of immiscibility that appeared to be overlapped with the solid-liquid equilibrium region. The $[C_{12}C_1im][PF_6]/[C_2C_1im][FAP]$ was found to present a complex phase behavior due to the interchangeability of the ion pairs resulting in the presence of multiple phase equilibria.

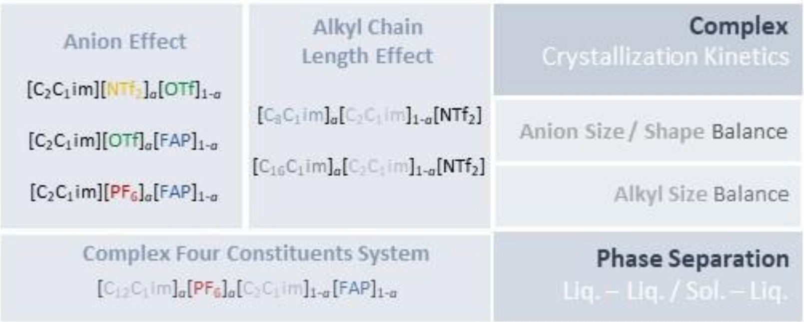

Figure 1: Schematic representation of the studied ionic liquid mixtures.

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Study of the kinetics and thermodynamics governing O_3 dissolution in concentrated nitric acid

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To secure sufficient supply in key materials, such as platinum group metals (PGMs), alternative supplying routes are sought after [1]. One of the ways considered is to treat industrial waste containing PGMs *via* oxidative dissolution [2]. This can be achieved by adding a highly oxidizing species, such as ozone gas, to a nitric acid solution. For applications to the oxidative dissolution of PGMs, knowledge of the kinetics and thermodynamics governing O_3/HNO_3 interactions is required.

This study focuses on the dissolution of O_3 in concentrated nitric acid. Ozone dissolution kinetics were monitored *in situ* by UV-Vis spectroscopy on-line measurements [3, 4]. The following parameters were studied: ozone partial pressure (pO_3) from 2.81×10^{-2} to 8.06×10^{-2} bar, temperature (T) between 9.0 and 30.0°C, reactor stirring rate (v), gas flow rate (Q), bubble residence time and HNO_3 concentration. Stirring rate and bubble residence time do not seem to have an impact on the dissolution of O_3. The duration of the transient regime decreases as gas flow rate increases. For $Q \geq 10$ L.h^{-1}, solubility equilibrium is reached after a few minutes (Fig. 1). The solubility of ozone in nitric acid verifies Henry's law. The Henry coefficient K_H at (24.8 ± 0.2) °C was found to be equal to $(1.02 \pm 0.05)\times10^{-2}$. The enthalpy of dissolution $\Delta_{sol}H^0$ for O_3 in 4.0 mol.L^{-1} HNO_3 solution was evaluated at $\approx$ -13.6 kJ.mol^{-1} (Fig.1).

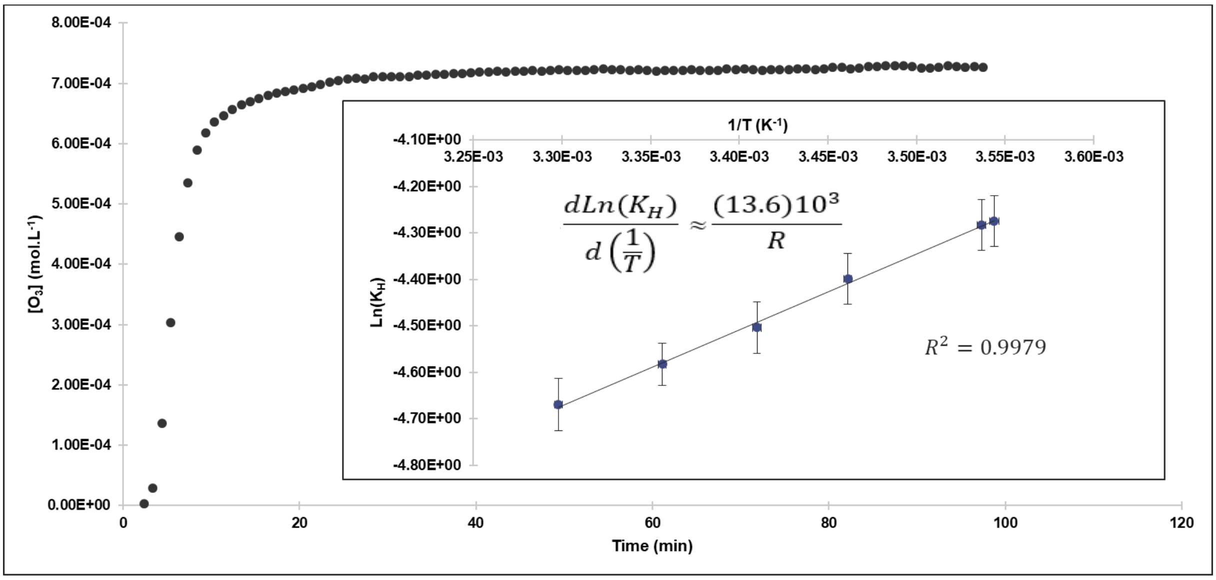

Figure 1: Evolution of $[O_3]$ dissolved in nitric acid as a function of time ($[HNO_3]$ = 4.0 mol.L^{-1}, Q = 20.0 L.h^{-1}, v = 400 rpm, T = 24.9°C, $pO_3 = 7.09\times10^{-2}$ bar; in insert: evolution of Henry's coefficient as a function of temperature for $[HNO_3]$ = 4.0 mol.L^{-1}.

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Evaluation of thermal and physicochemical properties for type-II Deep Eutectic Solvents

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Deep Eutectic Solvents (DESs) are mixtures of two or more salts among which a strong network of hydrogen or halogen bond is formed, resulting in a melting point strongly lower respect to their precursors [1]. They have attracted a lot of interest in the recent years due to their green features and to the wide range of applications in which they can be used, e.g. for the trapping of CO_2, for extraction processes from biomasses, as reaction solvents etc. [2]

Here, we present the preparation and the evaluation of the physicochemical properties of type-II DESs made by choline chloride and calcium (or magnesium) hydrated chloride, proposed in recent works as cheap and not-toxic green solvents for the solubilization of lignin in the pretreatment of lignin-cellulosic biomasses [3]. Samples were prepared using a coaxial microwave antenna as an energy- and time-saving method to heat the precursors. In a second step, we performed an overall evaluation of their thermal and physicochemical properties, useful for orienting the applications and having more information on the sample nanostructure. More in detail, the density, viscosity, and conductivity of the samples at different temperatures were measured, and their thermal degradation and thermal properties were evaluated by thermogravimetry coupled with FTIR spectroscopy and Differential Scanning Calorimetry. The addition of water as cosolvent, and its effect on the system properties, was also evaluated.

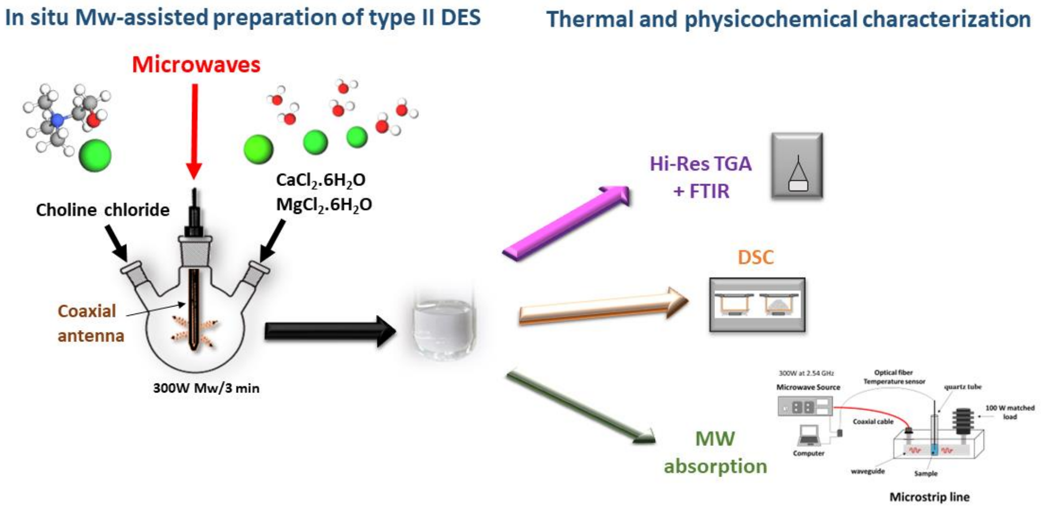

Figure 1: Scheme of the DES preparation and characterization.

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Measurement of sublimation enthalpies of organic compounds using isothermal thermogravimetry

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Compared with conventional techniques of sublimation, the thermogravimetry (TG) offers advantages such as the use of small amounts of sample, the ease in the sample preparation and the relatively short duration of the experiments. In this kind of measurements the Langmuir equation, derived for a solid sublimating in vacuum [1], is frequently used despite thermogravimetric experiments are performed under atmospheric pressure and a constant nitrogen gas flow. To solve this problem in this work an isothermal thermogravimetric method was developed to determine the sublimation enthalpies of solid organic compounds with a TA Instruments® SDTQ600 equipment. Considering that the rate of mass loss (dm/dt) is limited by the diffusion of the gas of the sample that sublimates into the inert gas, we made use of the Pieterse and Focke equation [2], $\frac{dm}{dt} = P\left(\frac{MS}{RT}\right)D$, which is valid under atmospheric pressure and applies for isothermal procedures. Combining such equation with the integrated Clausius-Clapeyron equation, we obtain the expression $\ln\left(\frac{dm}{dt}T\right) = B' - \frac{\Delta_{cr}^{g}H}{RT}$ [3], useful to determine the sublimation enthalpy from the slope of the graph of $\ln\left(\frac{dm}{dt}T\right)$ vs $\frac{1}{T}$. To assure the accuracy of the results we determined the sublimation enthalpies of the reference compounds [4] benzoic acid, phenanthrene and pyrene. We also determine the sublimation enthalpies of three carboxy pyridine acids isomers the picolinic acid, nicotinic acid and isonicotinic acid, this in order to demonstrate that the isothermal methodology was accurate enough to account differences in the heat of sublimation due to small changes in the molecular structure of the organic compound.

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The rapid method to evaluate the thermooxidative stability of organic materials using DSC

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Polymers are sensitive to changes in chemical structure caused by external conditions. Especially the changes caused during the ageing or degradation are more significant under the factors from nuclear facilities. Most important factors influence the material stability at this type of facilities are radiation and heat. Therefore, is important to try to predict the lifetime of new kind of material. This is possible to predict by induction period (IP) which is frequently taken as a measure of a material stability.

In this work, the aim of the study was to develop a predictive model for stability of coaxial cable insulations used in nuclear power plants. Under study was several types of samples as unaged cable and cables aged by various degradation doses of heat, radiation and combination of heat and radiation. Non-isothermal DSC measurements was used to study the stability of cables and isoconversional kinetic analysis was carried out using non-Arrhenian temperature function. From the values of kinetic parameters IPs and residual stabilities were calculated. A predictive model for the cable service life was developed based on the thermal and radiation stress tests. The model allows to predict the degree of insulation damage in a wide range of environmental conditions.

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Relationship between phase behavior and thermal history in ionic liquid [C_4mim][PF_6]

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Substances exhibiting polymorphism transition from the metastable phase to the stable phase via supercooling below the melting point, known as Ostwald's rule of stages [1]. According to Ostwald, the metastable phase is often observed as the initially selected crystalline phase in the supercooled state, but this is not always the case. Thermodynamically, the problem of crystal selection can be regarded as a matter of the nucleation and growth rates of different crystalline phases, although details remain unclear. Understanding how nucleation and growth change depending on thermal history is essential in non-equilibrium thermodynamics.

A representative ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate (referred to as [C_4mim][PF_6]), exhibits crystalline polymorphism and shows three crystalline phases α, β, and γ at low temperatures [2]. Thermally, the α phase is the least stable, while the γ phase is the most stable. It is known that the β phase adopts the most stable trans conformation of the butyl group, but the crystallization dynamics, such as nucleation rates of each phase, are not well understood. DTA measurements by Endo et al. reported the occurrence of exothermic heat release due to the generation of the unstable α phase, followed by a crystalline phase transition to the β phase and the appearance of the γ phase in accordance with Ostwald's rule of stages. On the other hand, thermal measurements by Triolo et al. observed exothermic heat release attributed to crystallization into the β phase without passing through the α phase, deviating from Ostwald's rule of stages [3]. In this study, we investigated the variations in phase sequence by altering the thermal history.

The sample used in this study was [C_4mim][PF_6] (manufactured by Merck, 99.9% purity). The sample was vacuum-dried at room temperature for approximately 48 hours to remove moisture. After drying, the moisture content was measured using the Karl Fischer method, which was confirmed to be 131.1 ppm. The obtained sample was then sealed in a glass cell under a helium atmosphere, and its thermal behavior was examined using differential thermal analysis (DTA).

According to Ostwald's rule, the nucleation rate of the metastable α phase is expected to be higher than that of the β phase. However, contrary to this expectation, the results exhibit non-Ostwald behavior that classical crystallization theories cannot explain under specific conditions. The infrared (IR) study and density functional theory (DFT) calculations suggest that the α phase exhibits a strong stabilization tendency due to Coulombic forces. In contrast, the β phase shows a strong stabilization tendency based on the conformation of the butyl group at low temperatures [4]. Considering this, the stabilization of the α phase during rapid cooling can be attributed to an ion liquid structure dominated by Coulombic forces near room temperature. The traces of this structure remain pronounced during rapid cooling. Consequently, in the low-temperature regime, the stabilization of the butyl group requires more time, resulting in a decrease in the nucleation rate of the β phase during rapid cooling.

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Thermal degradation kinetics of virgin and recycled polymers and polymer blends using the random chain-scission model

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Thermal degradation of polymers is a complex, highly stochastic process that yields a variety of products. Kinetic modeling is an essential tool in this context since it allows for the tracking of the progress of thermal degradation. As a result, numerous kinetic modeling studies for the simulation of the thermal degradation of polymers have been carried out in the literature [1-3]. Usually, thermogravimetric analysis is used to record the total mass loss of the polymer as a function of temperature. Isoconversional models, which were derived from several heating-rate experiments, are recommended for representing the kinetics of the process [1]. The variation of the overall activation energy of the degradation with the extent of conversion is predicted using differential or integral methods. In model-fitting approaches, global models are used to depict the variation of the overall polymer conversion with time or temperature providing the kinetic triplet, which consists of the pre-exponential factor, activation energy, and the reaction model. However, models usually used are coming from solid-state physics and sometimes predict very well the experimental data though without any physical meaning. Recently, Sánchez-Jiménez et al. [4] developed a model based on the original idea of bond breakage by random scission of Simha and Wall [5] to simulate the thermal degradation of polymers. Our group to describe the thermal degradation kinetics of several polymers further used this model [6].

In this research, we propose a method for the thermal degradation kinetics of several polymers and polymer blends being a combination of the random scission model and isoconversional analysis for calculating activation energy. A system of differential equations was set and solved using the random-scission model without any adjustable parameters. The activation energy was estimated from isoconversional approaches and the only parameter left to fit the data was the pre-exponential factor. It was found that this approach could be applied with good results in several different either virgin or recycled polymers and in a wide range of conversions. Moreover, the thermal degradation kinetics of blends of biodegradable and non-biodegradable recycled polymers was investigated using non-isothermal thermogravimetric data. It seems that this model describes fairly well the thermal degradation of several PET/PLA blends in a large conversion range based only on the kinetic parameters obtained from the neat polymers and without any additional adjustable parameter.

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Study of UO_2 oxidation at high temperature under an Ar–O_2 atmosphere

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The widespread use of Mixed Oxide (MOX) fuel in Pressurized Water Reactor associated with a plutonium multi-recycling is an option currently studied in France. Such strategy has gained increasing attention as a way to stabilize the plutonium inventory. However, an upgrade of the La Hague reprocessing facility (France) would facilitate the MOX treatment at industrial rates. In this context, the development of innovative processes is studied, including the fuel extraction from its cladding upstream the dissolution in order to improve the fuel accessibility and to facilitate dissolution. The most promising studied solution to overcome this technological issue lies on the oxidation of the irradiated MOX fuels. It involves an oxidizing heat treatment, which induces phase transformations leading to the collapse of the ceramic and a better fuel separation from cladding.

However, the microstructure of such MOX MIMAS fuel is made up of three phases: U-rich agglomerates, Pu-rich agglomerates and a coating phase [1]. Due to their different plutonium content, these phases present different behaviours during oxidation. Thus, the understanding of the mechanisms occurring during MOX fuel oxidation implies first studying the oxidation of the different phases constituting its microstructure.

The present study is focused on the oxidation of UO_2, which is supposed to be representative of U-rich agglomerates present in the MOX microstructure. Most of the previous studies [2] were focused on the phases formed during oxidation in dry storage conditions of spent fuels (<400°C and oxygen content close to that of air). This work investigates UO_2 oxidation from 350 to 600°C under Ar-O_2 atmospheres (pO_2 varying from 20 kPa to 72 kPa). The oxidation kinetics were *in situ* monitored by thermogravimetric analysis and the newly formed phases were characterized by XRD, Raman and SEM. At 350°C and $pO_2 \approx 20$ kPa the kinetic curve shows a pseudo-plateau that can be interpreted by a two-step reaction. This assumption is supported by the rate of weight gain curve and the heat flow versus time curve. However, for the same pO_2 and for temperature of 400°C and above, the kinetic curve is in favor of a one-step reaction. Moreover, the results obtained at 350°C show that the higher the pO_2 the faster the oxidation rate. This effect is more pronounced at lower pO_2. Partial oxidation experiments were also carried out on UO_2 discs whose surface has been marked by Au sputtering. The results show an internal growth of the oxide scale. From all these results, a mechanism is proposed to describe the oxidation of UO_2 under temperature and pO_2 investigated.

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Kinetic analysis of the thermal decomposition of $BaCO_3$ in YBCO precursor films

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The energy transition towards a drastic reduction of CO_2 emissions is one of humanity's most important challenges; by 2050 the use of renewable energy should account for 80 to100% of the total energy [1]. To this end, high-temperature superconductivity (HTS) is identified as a crucial technology [2, 3]. In particular, $REBa_2Cu_3O_7$ (REBCO) coated conductors (CCs) are foreseen for a wide market implementation [4]. However, nowadays REBCO CCs are not competitive, so it is of utmost importance to reduce the manufacturing cost while achieving a high current density. Thus, new methodologies are required to synthesize thick films (beyond 1 µm) in a single step with a critical current density above 4 MA/cm^2 at 77 K and a high yield.

We have demonstrated that it is possible to grow YBCO films at fast rates as high as 100 nm/s through the so-called transient liquid-assisted growth (TLAG) process [5]. TLAG is based on the eutectic reaction between $BaCuO_2$ and CuO to form a transient liquid in the region of the phase diagram where solid YBCO is the equilibrium phase. The fast atomic diffusion and high atomic density of the liquid phase concerning the solid phase allow for achieving ultrafast growth of YBCO.

The limiting step for YBCO growth is the decomposition of $BaCO_3$. In this communication, we analyze the decomposition of $BaCO_3$ in the form of films and under the conditions to achieve the TLAG process. In particular, we analyze the effect of the presence of Cu and Y oxides, the presence of metastable $BaCO_3$ phases [6], the role of the film thickness on the kinetics, and the composition of the surrounding atmosphere. We will show that in-situ kinetic analysis of the decomposition of $BaCO_3$ allows us to disclose the controlling mechanisms and a deep understanding of the process decomposition. Therefore, in-situ kinetic analysis is a powerful tool to tailor the synthesis process of REBCO CCs.

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Crystallization kinetics of polyethylene: An application of the NPK method

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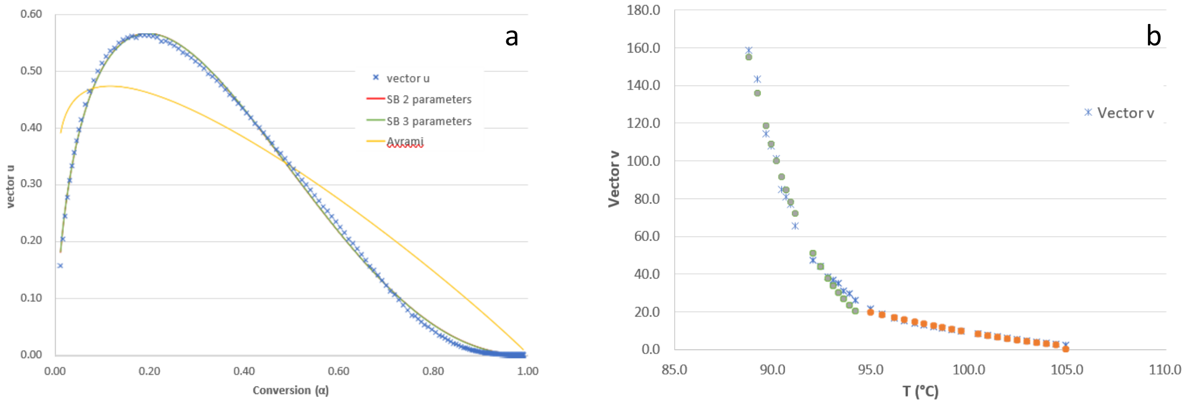
From its inception in 1998 [1], the NPK method [2] has been a popular tool for analyzing thermal behavior, degradation reactions, and stability in compounds. However, it wasn't until 2021 that the method was first applied to study the crystallization kinetics of polypropylene during cooling, after nearly 25 years since its launch [3]. The NPK method offers the advantage of not relying on any predefined models for describing temperature or conversion functions in analyzing crystallization kinetics. Through a mathematical process, the method generates two vectors: the **u** vector containing information on the kinetic model, and the **v** vector containing information on the temperature function. In a recent study on polypropylene [3], the **u** vector fitted well with both the Avrami and Šesták-Berggren models with 2 and 3 parameters, while the **v** vector fitted well with the Lauritzen and Hoffman equation. However, it was not possible to detect any change in the crystallization regime. The objective of this study is to investigate the applicability of the NPK method in simulating the crystallization kinetics of the three most used types of polyethylene: high-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE).

The Figure shows the results obtained in the adjustment of vectors **u** and **v** to LLDPE. The results show a highly accurate fit of the kinetic model. However, the fit of the temperature function indicates that the Lauritzen and Hoffman model is only suitable for lower temperatures, highlighting the need for improved modeling. Notably, the linearization of the L-H model reveals a significant change in slope at around 95°C. Further analysis using the L-H equation to adjust each segment independently (Figure 4) demonstrates an improved fit of vector v, revealing a change in the crystallization regime for LLDPE. The numerical values of the parameters of the equations studied are very similar to those reported in the bibliography [4].



(a) Function of conversion. (b) Function of temperature, including L-H fitting.

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The use of TGA to study the degradation of polymers

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Thermogravimetric analysis (TGA) is used to analyze polyurethanes synthesized in the lab to study their thermal stability and investigate the kinetics of thermal degradation. In addition to studying the polyurethane (PUR) degradation in an air environment, these measurements are often performed under inert conditions, using N_2 (Nitrogen) as the purge gas. Although it is known that even a small amount of oxygen can affect the degradation process and render measurements in inert conditions irreproducible, the inertness of the TGA instrument is rarely checked. This work explores the thermal and thermo-oxidative degradation of linear and network polyurethanes by conducting TGA measurements with the combination of diverse temperature programs and atmospheric conditions. To verify the instrument's inertness when nitrogen is used as a purge gas, copper oxalate (CuC_2O_4) was employed to detect the presence of O_2 and potential air leaks in the TGA instrument [1]. The measurements detected an increase in the sample mass, indicating the formation of copper oxide (CuO) rather than the reduction of CuC_2O_4 to elemental copper (Cu), which suggests that the instrument is not entirely inert [2]. Changes in nitrogen supply and adaptions to the equipment conditioning performed prior to the start of heating resulted in an improvement in the instrument inertness and significantly enhanced measurement reproducibility. The developed method has been applied to the series of polyurethanes yielding reproducible measurements under both non-isothermal and isothermal conditions. Model-free kinetics methods were applied to the obtained TGA results, providing initial insights for the development of a comprehensive degradation model and the estimations of kinetics parameters, such as activation energy (Ea) [3]. Taking a step further, mass spectrometry was performed on selected PURs to analyze the evolved gases during the degradation process and propose a degradation mechanism.

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Kinetic parameters of the decomposition process of commonly used explosive compositions based on secondary explosives

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Explosives are considered metastable substances. It is possible to initiate an exothermic transformation in them through the action of a series of initiating external stimuli. It is necessary to have appropriate experimental data to describe the kinetics of a given reaction, including those leading to thermal decomposition. The methods used to study the kinetic parameters of the decomposition process include, among others: Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG). These tests enable determining the activation energy and pre-exponential Arrhenius factor of explosive samples from a series of measurements using different heating rates. This paper presents the results of analyses of samples of explosive compositions based on classic explosives such as 2,4,6-Trinitrotoluene (TNT), 1,3,5-Trinitro-1,3,5-triazinane (hexogen, RDX), 1,3,5,7-Tetranitro-1,3,5,7-tetrazocane (octogen, HMX) and other inert additives. Explosive compositions intended for testing were taken from ammunition after long-term storage in military warehouses. Kissinger, Ozawa, Friedman and Ozawa-Flynn-Wall methods will be used to determine the kinetic parameters. The research will be summarized and discussed regarding the safety of using explosive compositions in ammunition subjected to the natural ageing process to determine the maximum safe temperatures of the testing and disposal processes used ADT24 rule and rule 100.

Integration of the Sestak-Berggren conversion function and perspectives on new generalized kinetic models for heterogeneous processes

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Kinetic models are relevant to describe heterogeneous kinetic processes; a number of kinetic models and their mathematical expressions have been reported in the literature, many of these based on idealistic conditions in terms of geometrical constrain and driving forces [1].

Alternatively, the semi-empirical Sestak-Berggren (SB) logistic-type conversion function, which was proposed as a general equation, encompass a large variety of equations corresponding to different kinetic models $h(\alpha) = \alpha^m \cdot (1-\alpha)^n \cdot (-ln(1-\alpha))^p$ [2]. Despite the fact that the SB equation does not provide any physical meaning, it is extremely useful for kinetic analysis as it offers a good fit to experimental data even when they do not follow the ideal conditions assumed for the conventional kinetic models [3,4]. One limitation of the SB kinetic model is the fact that its conversion function cannot be analytically integrated to provide an exact solution; thus, it cannot be directly applied in kinetic integral methods [5-7].

The objective of this study aims finding a solution for some specific cases, while the mathematical limits for the values of the kinetic exponents *m*, *n*, *p* of the SB model and their validity are also explored [7]. Important proofs obtained are indicating that independent members or parts of the SB conversion function are interrelated: when we derive with respect to one parameter, it can be observed that the other parameter will decrease with one unit. This is valid also for the emergent $(-\ln(1-\alpha))^p$ after the differentiation in the case when the logarithmic part was not explicitly present ($p = 0$), and it is a consequence of the logistic part of the function. Such a result may be pointing out the likelihood to have a number of elementary/basic kinetic models co-existing, all embedded in a master kinetic model. Therefore, multifaceted heterogeneous processes may occur by means of unitary master kinetic models encompassing several inseparable kinetic models conjointly acting. Also, it was observed that the role of the function $(-\ln(1-\alpha))^p$ has a low rate of relevance within the model. When we established the convergence, it was emphasized that this function may be eliminated and transfer the power coefficient p to the $(1-\alpha)^n$. Moreover, the function $(-\ln(1-\alpha))^p$ is extremely awkward from the point of precision estimate of the integrals [7].

Hence, we strongly conclude that the term $(-\ln(1-\alpha))^p$ should be replaced with a better term in the Sestak-Berggren equation, or even another logistic expression for the general differential conversion function may be needed to allow for accurate estimates of the integrals; thus, a new generalized kinetic model shall be proposed [7].

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Analyzing protein gelation: Insights into thermal behavior and kinetics

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Proteins have the ability to aggregate and form gels, which is a critical phenomenon in many contexts such as food preparation and living organisms. This process occurs when the attractive forces between proteins become stronger than the repulsive forces. As a protein solution cools, the aggregates interact further, forming a three-dimensional network structure that traps water and other small molecules within it. This network of proteins gives the gel its unique properties, such as its ability to maintain its shape and resist flow. The objective of this study is to investigate the gelation behavior of a protein solution using differential scanning calorimetry (DSC) and determine parameters to optimize its industrial processing.

Solutions of Gelatine from porcine skin, gel strength Bloom, type A, in water were prepared and their cooling ang heating behaviour was investigated using DSC. Unexpectedly, the integrals of the DSC curves were found to be non-constant [1][2]. Nevertheless, the curves demonstrated a clear trend in relation to the heating rate, indicating a possible correlation between heating rate and gelation behaviour. A deeper investigation of this connection could yield valuable insights into the underlying mechanisms of gelation in the protein solutions being studied. A generic kinetic equation as $\dot{\alpha} = f(T) \cdot g(\alpha) \cdot h(\beta)$ could be considered. Where $f(T)$ represents the function of temperature, $g(\alpha)$ is the functionality with conversion, and $h(\beta)$ is the “limit conversion” at each heating rate. Taking $\dot{\alpha}/h(\beta) = f(T) \cdot g(\alpha)$, the non-parametric kinetics (NPK) method [3] is applied. Just focussing on $g(\alpha)$, several models could be adjusted, i.e., the Šesták–Berggren (SB) empirical model: $g(\alpha) = \alpha^m \cdot (1-\alpha)^n \cdot [-ln(1-\alpha)]^p$. The model exhibits a satisfactory agreement with the data, suggesting a second-order transformation. Nevertheless, we are currently exploring more precise models that may provide better insights into the gelation of proteins, ultimately leading to improved processing conditions.

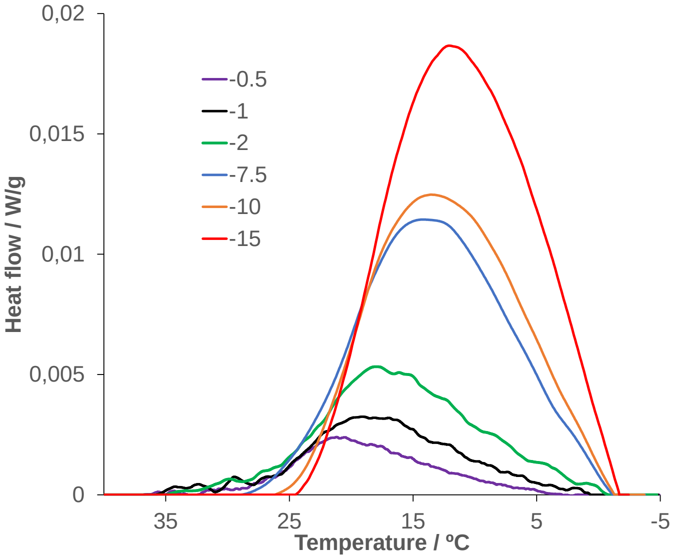

Figure 1. Raw DSC records of Solution C #5. Heating rates are in K/min.

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Features of the general rate equation and the consequences

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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]

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

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].

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

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. 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.

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

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Investigation of crystallization kinetics in PBSu/Biochar composites through isoconversional and model fitting approaches

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Poly(butylene succinate) (PBSu) is a biobased polymer that can be synthesized in significant quantities from plants using CO_2 and water through photosynthesis. It is produced through a two-stage melt polycondensation process using biobased succinic acid and butanediol. Biochar, a solid material created by heating biomass at high temperatures in the absence of oxygen, is being investigated as an environmentally friendly and cost-effective alternative to traditional carbon fillers in polymer-based composites. The growing interest in PBSu/biochar composites stems from their potential applications, including water pollutant removal and biofuel production. This study focused on examining the influence of different concentrations of biochar on the crystallization and melting behavior of PBSu. Biochar was incorporated into the PBSu matrix using an in-situ polymerization method at concentrations of 1%, 2.5%, and 5% wt.%. The non-isothermal crystallization kinetics of the composites were analyzed using differential scanning calorimetry (DSC) at various cooling rates. Nucleation activity and half time of crystallization were calculated to evaluate the effect of biochar on the PBSu matrix. Both isoconversional and model fitting methods were employed to determine kinetic parameters such as activation energy, pre-exponential factor, and reaction model. Isoconversional methods, namely Friedman and Vyazovkin analyses, were utilized to estimate crystallization energy. Model fitting analyses involved the Avrami-Erofeev equation, Nakamura/Hoffman-Lauritzen model, and Sbirrazzuoli crystallization model. Results showed that the inclusion of biochar raised the energy barrier for crystal formation, leading to a slower crystallization rate at higher biochar concentrations. The presence of biochar also influenced the shape of the crystalline structures and impacted the kinetic parameters. The calculated Kg parameter for neat PBSu closely matched literature values, confirming the accuracy of the analysis. The glass transition temperature and melting temperature of neat PBSu were consistent with experimental measurements. However, the 5% biochar composition acted as both a nucleating agent, promoting nucleation, and a physical hindrance, impeding chain segment transport during non-isothermal crystallization. The Avrami equation had limitations in accurately predicting the crystallization behavior, while the Nakamura/Hoffman-Lauritzen model performed well but potentially underestimated the final stage of crystallization. The Sbirrazzuoli crystallization model successfully described the complex crystallization mechanism involving nucleation and growth in PBSu/biochar composites. In conclusion, the incorporation of biochar had a complex impact on the crystallization behavior of PBSu, emphasizing the importance of employing multiple methods to fully understand the underlying mechanisms. This study contributes to a deeper understanding of non-isothermal crystallization and presents a comprehensive approach to modeling the crystallization of PBSu/biochar composites, aiming to optimize their production and enhance their thermal and mechanical properties.

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Unambiguous identification of different API crystalline phases: thermal analysis to the rescue - two case studies

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Active pharmaceutical ingredients (API) may often give rise to different solid forms, single component (polymorphs) or multicomponent ones (solvates, salts, cocrystals), which may also have different polymorphs. These solid forms differ in physicochemical and often in biopharmaceutical properties and, as a consequence, they are both a challenge and an opportunity in pharmaceutical development. Therefore, a thorough knowledge of a target API solid form landscape is a crucial factor for the pharmaceutical industry[1].

In this work, two case studies are presented highlighting the role of thermal analysis methods in the unambiguous identification of new solid forms of two APIs: probucol (PROB), an antihyperlipidemic drug, and pyrimethamine (PMA), a dihydrofolate reductase inhibitor used as an anti-malarial.

Screening of polymorphic forms of PROB was carried out by crystallization from different solvents. Thermal analysis methods were crucial for the identification and distinction between form II of PROB and two new isostructural solvates (Fig. 1), which also allowed the interpretation of unexpected slurry equilibrium results.

The other case study concerns the investigation of PMA cocrystals. Cocrystal screening, with theophylline and caffein as coformers, was carried out by the common mechanochemical approach. The new cocrystals were identified by infrared spectroscopy and X-ray powder diffraction (XRPD), but thermal analysis methods gave the first clue for the existence of other cocrystal polymorphic forms[2]. These findings prompted new screening approaches leading to the unambiguous identification of two pairs of polymorphic cocrystals and the discovery of reproducible preparation methods.

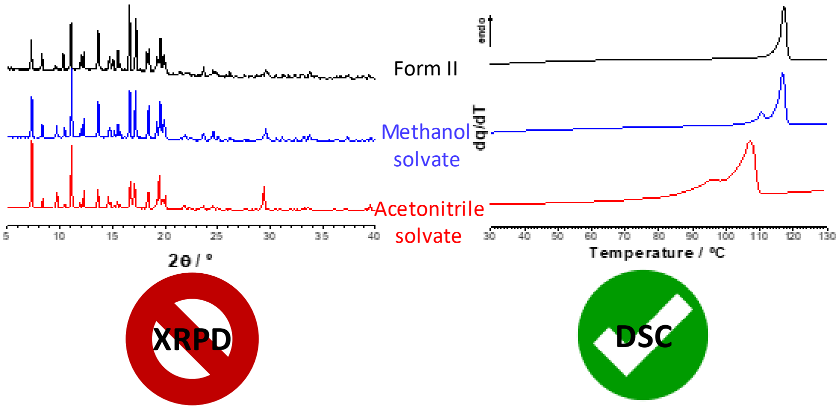

Fig. 1: The identification of different PROB solid forms can be very difficult (or even impossible) without the use of thermal methods (XRPD vs DSC-differential scanning calorimetry).

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Physico-chemical studies of inclusion complex between natural products and cyclodextrins

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Cyclodextrins (CDs) comprise a family of cyclic oligosaccharides, and several members of this family are used in the pharmaceutical industry for their capability of improving the stability, apparent solubility and bioavailability of numerous molecules of interest, including drugs and nutraceuticals [1]. CDs have low toxicity and, for this reason, have been employed for different routes of administration, including oral, ocular, nasal and parenteral [2]. The CD that has received the most attention in recent years is hydroxypropyl-β-cyclodextrin (HPβCD), mainly because of its cheapness, suitable dimension of the lipophilic cavity and ease of availability [3]. Several physicochemical methodologies have been employed for studying cyclodextrin/guest interaction, i.e. phase solubility, isothermal titration calorimetry (ITC) and differential scanning calorimetry (DSC). Here we describe a physicochemical characterization of complexes between cyclodextrins and natural products and how the combination of the appropriate pH, solvent, temperature, and mixing time can improve the complexation [4-6].

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Thermal analysis as a tool to prospect novel nimesulide dual-drug solid forms

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The low aqueous solubility of the active pharmaceutical ingredients (APIs) compromises the desired plasmatic concentration and, consequently, limits their oral bioavailability and clinical efficacy and security. Several strategies have been used to overcome these obstacles by e. g., the synthesis of multicomponent solid forms, like salts, cocrystals, eutectic mixtures and co-amorphous systems [1, 2]. Furthermore, a dual-drug perspective may result in enhanced synergistic action, therapeutic combination, and reduced adverse effects [3]. In this regard, considering that nimesulide (NMS) is a widely used and prescribed drug, but has low aqueous solubility being classified as BCS-class II [3], the present work aimed to prospect new NMS multicomponent solid systems.

Initially, thirty molecules were preselected through a virtual-experimental screening. Some of the parameters for choosing the coformers were the compatible functional groups and/or the desired combination of therapeutic action. Nimesulide multicomponent solid forms were synthesized through several approaches such as liquid assisted grinding, quench cooling and cryomilling, and characterized by Differential Scanning Calorimetry (DSC), X-ray powder diffraction (XRPD) and infrared spectroscopy (FTIR).

Thermal analysis enabled the identification of eutectic mixtures, as well as the confirmation of the composition through the construction of the binary phase diagram and Tammann's triangle. Drug-drug co-amorphous systems were also identified, produced both by quench cooling and by cryomilling. Quench cooling, that is more prone to promoting total crystallinity breakdown, produced co-amorphous materials with higher physical stability than those obtained by cryomilling [1]. Other techniques complemented the characterization and supported the results.

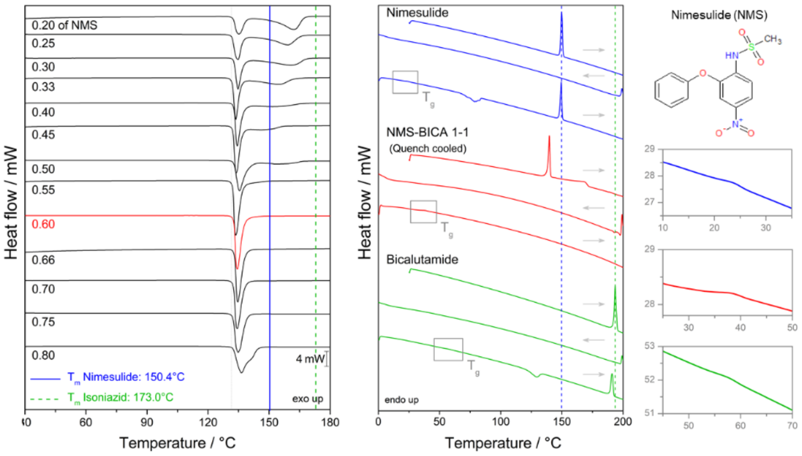

Figure 1: Thermal analysis of some nimesulide multicomponent solid systems.

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Dissecting the effects of low-molecular-weight heparins on antithrombin III thermodynamic stability

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Heparin (also referred to as unfractionated heparin, UFH) is a naturally occurring drug produced by mast cells exhibiting anticoagulant properties that has been widely used in the prevention and treatment of venous thrombosis and acute myocardial ischemia [1]. From a chemical standpoint, heparin is a glycosaminoglycan, a linear and anionic polysaccharide made up of 1 → 4 linked disaccharide repeating units consisting of a α-d-glucosamine (A) and a hexuronic acid, namely either α-l-iduronic (I) or β-d-glucuronic (G) acid. However, some substitutions such as O-sulfation, N-sulfation or N-acetylation randomly occur along the polymer chain [2]. Some of the heparin chains embed a distinctive pentasaccharide sequence, $–A_{NAc,6S}–G–A_{NS,3S,6S}–I_{2S}–A_{NS,6S}–$ (AGA*IA), which is characterised by a rare central trisulfated glucosamine (A*) and is responsible for the anticoagulant activity of heparin upon its interaction with the protein antithrombin III (ATIII), a physiological inhibitor of the coagulation process. Nevertheless, UFH has exhibited some pharmacokinetic limitations as well as some undesired side effects [3], which are not shared by the low-molecular-weight heparins (LMWHs), a class of molecules derived from UFH by controlled depolymerization processes, fractionation methods, or both [4], and differ from their parent heparins for the molecular weight and oligosaccharide sequence.

In this study, the effects produced by the interaction of LMWHs with ATIII protein were investigated. Specifically, the ATIII thermal stability modifications in the presence of Enoxaparin, Tinzaparin and Dalteparin were assessed by micro-DSC, in comparison with UFH and a synthetic pentasaccharide, this latter being an α-methylated structural analogue of the ATIII binding sequence (AGA*IA_{M}) [5]. Furthermore, in order to dissect the effects due the heparin chains peculiarities on the thermal stability of ATIII, two type of further fractionated portions of the three LMWHs, obtained by affinity chromatography [6,7] (no-affinity, NA, and high-affinity, HA fractions), were also considered.

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On the thermodynamics of folding of an i-motif DNA structure

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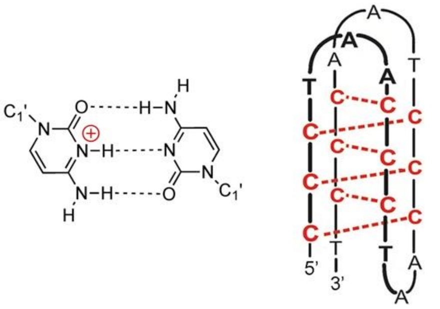
DNA can exist in single-stranded form or fold into secondary structures, which include the canonical double helix as well as non-canonical secondary structures [1]. Cytosine-rich DNA sequences can form non-canonical structures called i-motifs, which occur as four stretches of cytosine repeats form hemi-protonated C·C^{+} base pairs [2]. The growing interest in the i-motif structures as actors in the transcriptional regulation of oncogene expression and thus as potential targets of anticancer drugs [2], increases the need for a deep understanding of the energetics of their structural transitions. Here, differential scanning calorimetry and circular dichroism spectroscopy were used as complementary physicochemical methodologies to characterize the energetics of a DNA i-motif formation [3]. A full thermodynamic characterization of i-motif formation in vitro under favorable conditions was provided, including the evaluation of the energetic contribution of cytosine protonation, thus broadening our understanding about the formation and thermodynamic stability of i-motif DNA structures.



Hemi-protonated cytosine–cytosine (C·C^{+}) base pair and schematic representation of an i-motif DNA structure.

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Effects of seed germination on cowpea β-vignin native structure: a calorimetric and thermodynamic investigation

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β-vignin is the most represented storage protein in cowpea seeds (*Vigna unguiculata*, L. Walp) and belongs to the 7S globulin or vicilin-like family [1]. It is synthesized during seed development and, like other storage proteins, it is traditionally considered the nitrogen reserve that supports seedling growth during the first steps of germination [2]. Literature reports that several biological activities are exhibited upon a regulated and selective proteolytic breakdown by which some transient intermediate peptides are formed and have been shown to possess specific bioactivities [3].

β-vignin consists of two main differently glycosylated isoforms. Moreover, it exists as monomeric and trimeric forms with an equilibrium mechanism that depends on the environment pH: the higher the pH value, the greater the trimer-to-monomer ratio [4]. The full understanding of cowpea β-vignin physicochemical properties is crucial to reveal possible biological roles and to approach applicative uses in various fields, including eco-friendly plant defense, nutrition and nutraceutics.

In this frame, purified β-vignin was subjected to a limited proteolysis by using cowpea proteases extracted from germinating seeds [4] to simulate the early germination process, and a calorimetric investigation was performed through high-sensitivity DSC on both the undigested and digested β-vignin in different buffered environments (pH 9.0, 8.5 and 6.5). A thermodynamic analysis was also accomplished on the β-vignin undigested form to assess the protein stability and thermal denaturation mechanism. The results revealed that the storage protein behavior is rather peculiar if compared to proteins with other biological functions.

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Glassy dynamics and crystallization kinetics of molecular pharmaceuticals

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Active pharmaceutical ingredients (API) show a rich scenario of physical phenomena occurring under thermal treatments. To improve their dissolution rate, API are prepared in amorphous state [1]. Unfortunately, the metastable state can spontaneously reverse to crystalline one, hampering a practical application. Three classes of API are usually identified, according to their crystallization tendency [2]. Differential scanning calorimetry (DSC) can be used as a tool to study the behavior of these compounds [3]. In particular, fast DSC (FDSC) is a novel technique opening new opportunities: thanks to the available high cooling rates a very fast dynamics (down to milliseconds) can be probed [4].

This study uses FDSC to characterize glass-forming ability, physical stability, and crystallization tendency of 3 poorly soluble compounds: indoprofen, bifonazole, and indomethacin (class I, II and III respectively). Indoprofen has a high crystallization tendency, and it is impossible to reach the glassy state through conventional DSC [5]: FDSC gives the possibility to reach the glassy state and study the stability of the glass. We have monitored its isothermal crystallization kinetics both from the supercooled melt and from the glass (see Fig.1), highlighting the differences of these two cases. Bifonazole is a good glass-former [6] and can be studied over a wide interval of scan rates: we unveiled its peculiarities about crystallization tendency and physical stability. Indomethacin is a good glass-former too, but shows a complex crystallization kinetics. In all three cases, a new method, employing FDSC, has been developed to study the dynamics of the amorphous liquid and glassy state in a wider time/temperature range, otherwise not accessible.

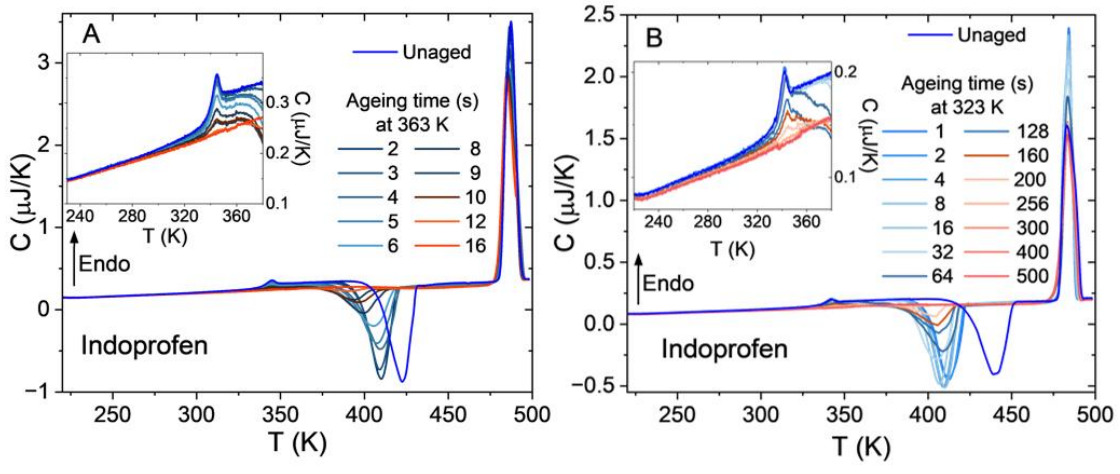

Fig. 1. Isothermal crystallization of indoprofen after cooling at 300 K/s from the liquid state to thecrystallization temperature, probed by reheating at 300 K/s from the glassy state. Panel A: crystallization at 363 K (~Tg+30 K) at different times. Panel B: crystallization at 323 K (~Tg-10 K) at different times. Insets: detail in the glass transition region.

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A comparative study of recycled HDPE and PESu composites enhanced with hemp fibers used as alternative WPCs

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The need for sustainable and environmentally friendly products is becoming increasingly important in modern society, prompting industries and scientific communities to find greener solutions. One promising area for addressing the triple planetary crises of climate change, biodiversity loss, and pollution is the shift towards a circular economy, recycling, and reusing resources. This research focuses on exploring alternative and sustainable materials for constructing Wood Plastic Composites (WPCs). This study investigates the use of recycled or bio-based products to address the plastic waste problem and substitute materials for natural wood, such as the bark of the hemp plant. Hemp offers a lightweight, mechanically stable, and low-carbon footprint option that is renewable and requires low amounts of water, pesticides, and fertilizers to grow.

In this work the chemical, structural, thermal, and mechanical properties of recycled high-density polyethylene (r-HDPE) and Polyethylene succinate (PESu)-hemp fiber composites were evaluated. Since the polymers are hydrophobic, and hemp fibers are hydrophilic, a compatibilizer was used to improve the adhesion of the fibers to the polymeric matrix. The chemical and structural properties of the composites were determined using X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). The thermal properties of the composites were measured by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). More specifically the thermal stability and the thermal degradation of the samples were studied, as well as the thermal phenomena that take place upon heating and cooling of the samples. The mechanical properties were examined using tensile and impact strength experiments. Finally, the degradation of the two different polymer based composites was examined in soil environment. Overall, this study provides promising results for the future of sustainable and environmentally friendly materials in the construction industry.

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Thermo-mechanical analysis of fully-recyclable bio-based epoxy latent systems for green composites manufacturing and their recycling

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Epoxy resins are among the most used and commercialized thermosets due to their outstanding peculiarities, such as their easy processing, cost-effective processability, chemical resistance, high durability, insulating property, adhesive property, low thermal expansion, in addition to good thermal and mechanical properties [1,2]. The latter mentioned performances derive from their covalent intermolecular cross-link bonds, which in turn result in a low recyclability. Currently most of these materials end up in landfills, which is the least preferred approach, according to Environmental Protection Agency's (EPA) guidelines, since it causes severe impacts to the environment. Being the global epoxy composites market size expected to expand at a Compound Annual Growth Rate (CAGR) of 6.2% from 2020 to 2028, the concern about their not recyclability is growing [3]. Moreover, to find properly re-use strategies for the recycled materials obtained it is of major importance within the field of circular economy.

In this context, the present study is focused on a twofold study. A first phase identifies the most performing, in terms of thermo-mechanical properties (i.e., glass transition temperature and flexural properties), fully-recyclable and bio-based epoxy latent resin to manufacture green composites. While, a second phase demonstrates their recyclability using a mild chemical recycling process (schematized in Fig.1) by finding useful re-use strategies for the obtained recycled materials. Several interesting re-use strategies have been identified for the obtained recycled products, thus fulfilling a circular economy approach.

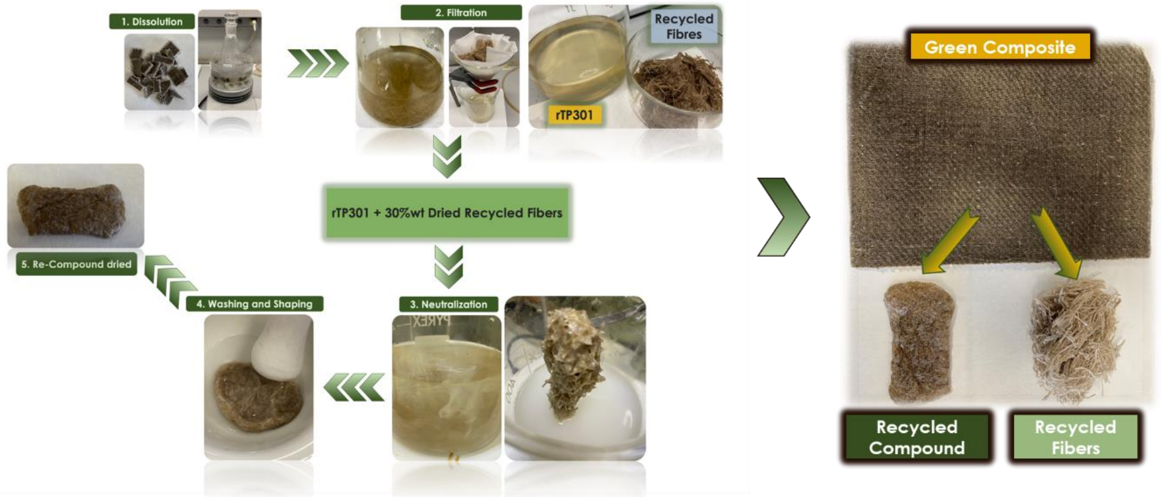

Figure 1: Green composite chemical recycling procedure.

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Thermal stability of an aromatic disulfide containing epoxy vitrimer

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Thermosets are covalently cross-linked networks, thereby forming hard and resistant products. As resins, they are especially suited for structural composite materials due to their high stiffness and good adhesion to the fiber. They play substantial roles in aircrafts, vehicles, buildings, electronics, and so on, as they are chemical-resistant and extremely durable. However, unlike thermoplastics, thermosets cannot be reprocessed due to their insoluble and infusible nature [1].

Vitrimers are a new class of resins that combine the excellent mechanical properties of thermosets with the capability of being thermoformed upon heating [2]. Of all the vitrimers, epoxy-based ones excel in the availability of monomers and ease of synthesis, facilitating their scalability in an industrial setup. In particular, epoxy resin systems incorporating reversible crosslinks based on aromatic disulfides are expected to cause an important impact as fiber-reinforced polymer composites because they show remarkably rapid relaxation times without the need of incorporating catalysts [3]. One of the drawbacks of using disulfide hardeners is their thermal stability which is slightly lower than that of other commercial hardeners commonly used for curing thermosets [4]. Thus, the temperature range at which the sample can be cured and thermoformed is narrowed. Moreover, uncontrolled curing can result in the occurrence of a thermal runaway. Besides, during reprocessing, stress relaxation competes with thermal degradation. The current lack of fundamental knowledge of these key aspects forces a trial-and-error procedure to find suitable matrices for structural composites and the optimal thermal treatment. A deeper understanding of the kinetics of vitrimers would help speed up its market uptake. Thus, saving time and money.

In this study, we analyze the thermal stability of an epoxy vitrimer based on dynamic disulfide bonds. By describing the effect of key processing variables, such as preform thickness and heating rate, we have developed diagrams that accurately depict the conditions under which the vitrimer can be processed and reprocessed.

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Thermomechanical properties of bio-based epoxy resin and daylight curable blends for 3d printing by Liquid Crystal Display (LCD)

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Bio-based epoxy resins are commonly used in a range of applications, including adhesives, coatings, composites, and electrical components. They offer similar performance properties to traditional epoxy resins, including high strength, durability, and chemical resistance [1].
The use of bio-based materials in 3D printing has been gaining increasing attention as a means of reducing the environmental impact of this technology.
In general, it can be stated that most of the formulations developed for stereolithography (SLA), and digital light processing (DLP) are still predominantly derived from non-renewable resources and are associated with significant costs. Despite a growing interest in incorporating biomass materials into these formulations, there have been only a few notable examples in recent literature where strong efforts have been made to achieve this [2].
In this study, a bio-based epoxy resin was blended with a commercial daylight-curable resin [3] at different weight percentages to investigate the potential of this approach for producing 3D-printed parts with improved thermomechanical properties while maintaining the working principle of the LCD (Liquid Crystal Display) printer.
The different formulations were first investigated in terms of their thermomechanical properties before and after post-treatments such as photo- and thermal-curing. This allowed for a comparison of the different blends in terms of their mechanical strength, glass transition temperature, and other relevant properties.
Once the optimal formulation had been identified, 3D print samples were obtained using LCD printing technology. The printed parts were then further characterized using thermo-calorimetric and morphological tests to assess their thermal stability and microstructure.
Overall, the results of this study suggest that blending bio-based epoxy resins with commercial resins can lead to improved properties in additive manufactured parts. This approach has the potential to make 3D printing more sustainable by reducing the use of non-renewable resources, while still maintaining performance standards required for many applications.

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Using thermal analysis for the development and characterization of novel reversible polymer networks for use in photovoltaic modules

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This work concerns the in-depth characterization by thermal analysis of reversible polymer networks based on thermoreversible Diels-Alder (DA) cycloadditions, designed to be employed in photovoltaic modules as self-healing materials. Networks are composed of irreversible poly(methacrylate) chains and reversible furan-maleimide DA crosslinks, allowing for tuneable thermomechanical and self-healing properties by modifying the way these crosslinks are incorporated. This gives rise to fully homogeneous reversible network materials that rely only on DA for their reversibility, as well as (partially) phase-separated, reversible networks, where the incorporation of urethane bonds introduces in addition hydrogen bonding capacity [1,2].

Differential scanning calorimetry (DSC) and microcalorimetry are used to demonstrate the reversibility of the DA reaction, while dynamic mechanical analysis (DMA) confirms that the reversible polymer networks maintain sufficient mechanical properties over a broad temperature range to be suitable for use in photovoltaic modules. The ambient-temperature self-healing capacity, resulting from the reversible nature of this networks, is demonstrated using the same techniques [1,2]. Having ensured that the developed materials exhibit self-healing and suitable mechanical properties, their behaviour after UV-aging was investigated, important for incorporation into photovoltaic modules. It was seen that after 1000 hours of UV-exposure, these poly(methacrylate) networks based on DA crosslinks remain reversible, indicating that these materials are highly promising [3].

This study clearly highlights the importance of thermal analysis techniques for the development and characterization of novel reversible network materials.

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Poly(alkylene vanillates): A novel series of sustainable polyesters based on vanillic acid

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As global energy and resources have faced enormous challenges over the years, conventional petroleum-based polymers are considered as one of the most important environmental threats. The continuous growth of waste accumulation after their short-term use, along with their contribution to greenhouse gases' emissions, have intensified the public awareness over the quest of alternative routes towards the production of polymeric materials[1]. Thus, different approaches for the transition from a petrochemically-dependent society to a bioeconomy have been proposed, both by academic and industrial communities. One of the most prevalent routes is the exploitation of renewable resources towards the production of sustainable monomers, polymers, and chemicals. Within this frame, one of the most promising monomers derived from lignin biomass is vanillic acid (VA), which comprises an oxidation product of vanillin, the most produced aroma chemical and appears as a great alternative building block for thermoplastic polyesters[2–4]. Herein, the synthesis and the indicative properties of novel VA-based polyesters will be presented. Specifically, their structural features, using multiple techniques, such as Fourier-transformed Infrared spectroscopy (FTIR) and Nuclear Magnetic Resonance spectroscopy (NMR), will be illustrated and their thermal behaviour will be discussed. Finally, their mechanical properties will be presented.

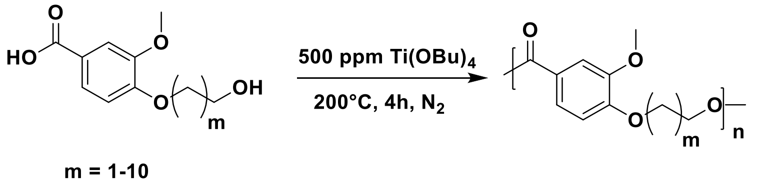

Figure 1. Synthetic route of poly(alkylene vanillates) via two-stage melt polycondensation procedure.

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HNT based geopolymers incorporating wax microparticles as sustainable building materials with coating applications

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This study introduces an innovative protocol for producing halloysite based geopolymers filled with beeswax microparticles derived from Pickering emulsions [1]. The incorporation of microwax into the geopolymers was successfully demonstrated through various techniques, including TGA, DSC spectroscopy, and water contact angle experiments. Based on morphological and structural investigations, it was observed that spherical microwax particles, with a diameter ranging between approximately 3 and 5 μm, were uniformly dispersed within the geopolymeric network, resulting in excellent properties of the hybrid geopolymers in terms of mechanical performance and heat storage capacity, despite their relatively low content in the hybrid material. To make a comparison, hybrid geopolymers were prepared and analyzed by incorporating different quantities of solid beeswax into the geopolymeric matrix. Significant improvements in flexural characteristics and heat absorption capacity were observed only when a substantial amount of solid beeswax was present. In summary, this research presents a straightforward approach for fabricating composite geopolymers with heat storage capacity, facilitated by the presence of phase change materials (microwax particles) confined within the geopolymeric network. The enhanced flexural performance of the hybrid geopolymers makes them suitable for application as building materials. Furthermore, it was demonstrated that the resulting material can be utilized for coating applications as a protective layer on steel substrates. Remarkably, the presence of microwax particles significantly altered the wettability of the steel, enhancing the hydrophobic properties of its surface.

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Characterization of yarns from a Flemish tapestry of the XVIth century and a new Keratin/HNT protocol for the conservation of artwork

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In this study, we proposed a physico-chemical approach for the characterization of yarns from a Flemish tapestry of the sixteenth century and a new conservation protocol for the preservation of the artwork. Thermogravimetric analysis (TGA) allowed us to identify yarn fibers and to estimate their life-time. The dynamic mechanical analysis (DMA) provided direct evidence on the aging effect on the yarns, their conservation state and their performance under different mechanical stresses [1]. Besides, the characterization path of yarns was relevant for proposing a novel conservation protocol based on keratin/HNT dispersions, which were explored for coating protection of wool threads. The aqueous dispersions were investigated by Differential Scanning Calorimetry (DSC) measurements to study the mixing enthalpy that can reflect the interaction between the two components in water. [2] The aesthetical effect of Keratin/HNT coating on wool thread was investigated by colorimetric analysis, optical microscopy and scanning electron microscope (SEM) revealing the HNT distribution in the wool fibers. The consolidation and protection effect of Halloysite/Keratin mixtures in wool thread samples were estimated by DMA before and after UV ray irradiation, as aging process. Moreover, the new procedure was tested on a historical yarn from a Flemish tapestry of the sixteenth century as conservation protocol. In conclusion, the results show that the proposed protocol for wool treatment is a promising material as a reinforcing coating for cultural heritage artwork, also increasing mechanical resistance and UV protection, with a minimal impact on the sample aesthetic aspects [3].

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Kinetic study of the curing process of Perovskite-photocurable polymer based nanocomposite for scintillators

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Resin formulations based on monomers that undergo photopolymerization induced by UV irradiation have extensively attracted the interest of researchers being adopted in stereolithography (SLA), the first additive manufacturing technology patented in 1986–[Jacobs, P. F., Rapid Prototyping and Manufacturing. SME, Dearborn, USA, 1992.]. Selective solidification of such liquid formulations by using UV radiation has been first performed by lasers and then by lamps using DLP (Digital Light Processing) based equipment. The composition of the resin formulation can be customized for specific applications by inclusion of fillers capable to provide functional properties to the 3D-printed object. Among these those sensitive to radiation can be used for customized devices for detecting high-energy radiations with advanced geometries and improved resolution. To achieve this, scintillating materials that can transform high-energy photons into low-energy photons can be implemented into resin formulations [1]. Halide perovskite materials, showing high photon attenuation and fast and efficient emission properties, are a great choice as scintillating materials [2].

This work aims to develop inorganic perovskite polymer-based nanocomposite suitable for SLA fabrication for creating scintillators with high detection power, short time of response while allowing complex geometries. An all-inorganic lead halide perovskite-based powder, $CsPbBr_3$, is used as the scintillating material (filler) due to its large stopping power, high mobility lifetime product, large bulk resistance, and fast response. 'Genesis-Development resin Base' manufactured by Thethon 3D is used as polymeric matrix of the nanocomposite.

The curing process of the nanocomposite was studied by differential scanning calorimetry DSC, to investigate the influence of the perovskite-based powder on the cross-linking of the resin. Photo-DSC was used to study the rate and the enthalpy of crosslinking of the samples. Residual reactivity of these samples was compared with the dynamic DSC study on UV lamp-cured samples with the aim to calculate the ratio of curing to optimize the process for the developed formulations.

By using photo-DSC, the resin material showed a higher normalized photopolymerization enthalpy in the presence of perovskite powder,485 Jg^{-1} compared to 380 Jg^{-1} of the neat resin, despite the presence of the filler responsible for light absorption and scattering. Complete photo-curing of the nanocomposite was achieved in 120 min of UV -irradiation with respect to the pristine resin material that showed residual reactivity after the same time of exposure. The results evidenced that also the rate of photopolymerization was improved in the nano-composite. Photoluminescence measurements gave the characteristic peak of the $CsPbBr_3$ at 520 nm which further confirms the stability of the perovskite in the composite after the deposition and the curing process. These excellent results indicate that the developed perovskite-polymer nanocomposite formulation is a promising candidate as photocurable scintillating material.

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Hybrid organic-inorganic systems via the sol-gel route: Thermal, spectroscopic, and biological properties

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This study aims to characterise organic-inorganic silica-based hybrid biomaterials synthesised via the sol-gel route (Figure 1). In particular, the hybrid systems are made up of 15 and 20 wt% of quercetin (Q), and 6, 12, 24, and 50 wt% of polyethylene glycol (P) as the organic component [1-2]. Fourier-Transform Infrared (FT-IR) and Raman spectroscopy, Thermogravimetry (TG) and Differential Thermal Analysis (DTA) have been used for the characterisation of the hybrids. Furthermore, TG coupled with a Mass Spectrometry device was useful to investigate the thermal behaviour of the hybrids (up to 800 °C) and to analyze the gas mixture evolved upon heating under inert (argon) atmosphere. In addition, antimicrobial activity was also evaluated on the hybrid samples to reveal their inhibiting ability on the assayed Gram-positive and -negative bacterial strains, while a cytotoxic study was performed on NIH-3T3 murine fibroblast cells. FT-IR and Raman's measurements proved the interaction among all the hybrids components. Antibacterial tests revealed a decrease in antibacterial properties with an increment of P percentage. Finally, cytotoxicity assessment highlighted that entrapping quercetin in hybrids at high P content leads to the constitution of materials that enjoy polyethylene glycol biocompatibility, while cytotoxic effects are depleted.

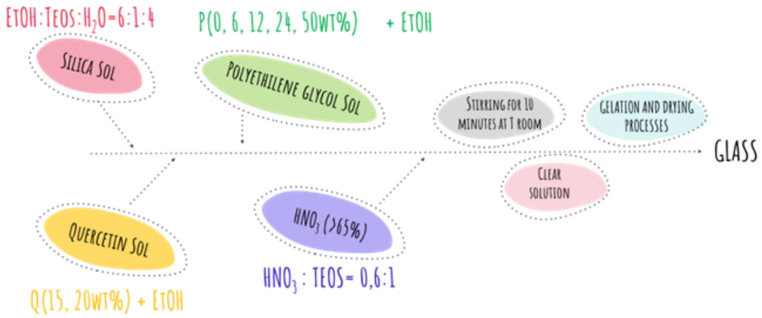

Figure 1: Flow-chart of the used sol-gel route.

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Improvement and implementation of pulse heating technique for the measurement of heat capacity of $MoSe_2$ nanoflakes

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The two-dimensional character of van der Waals layered materials makes them have extraordinary properties compared to bulk materials. Among these properties, the interest in thermal properties in 2D materials has grown in recent years. Having a deep understanding of these properties is crucial for know their behavior and future applications. Heat capacity is a property that determines the amount of energy required to raise the temperature of a substance. Heat transport and thermal conductivity has already been highly studied, but heat capacity has never been measured directly.
In this work we will focus on the improvement and implementation of the pulse heating technique. This technique is a calorimetric method used to measure the heat capacity of a sample by rapidly heating it for a brief period, followed by a period of cooling [1]. With this technique we are able to measure the dependence of heat capacity on the number of $MoSe_2$ layers. The measurements will be made with membrane-based calorimeters, on which Pt is deposited, which acts as a heater/sensor. In this work we will also focus on the development of new microfabricated chips for this technique and the measurement of these materials. The ultimate goal of this project is to be able to determine the heat capacity of a single $MoSe_2$ monolayer.

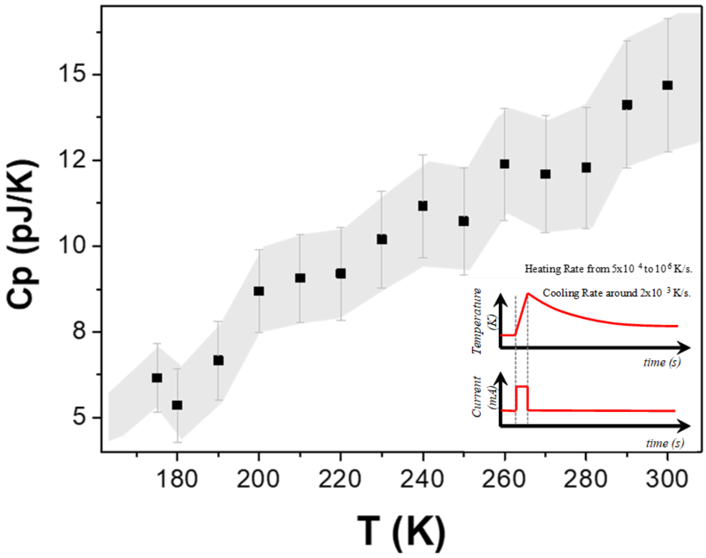

Figure 1: Differential heat capacity of mechanical exfoliated $MoSe_2$ nanoflake. The inset shows the current pulses feeding the calorimeters.

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Thermodynamic study of alkylsilane and alkylsiloxane-based ionic liquids

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The replacement of carbon atoms by silicon atoms in the backbone of ionic liquids has been pointed out as a suitable way to reduce their viscosity and density [1-3]. Here we present the study of the thermophysical properties of ILs bearing alkylsilane and alkylsiloxane chains, as well as some of their analogs with carbon-based chains. With this work, we aim to understand the effect that the use of alkylsilane and alkylsiloxane chains has on the thermophysical properties of ionic liquids.

The phase behavior of these compounds was studied by differential scanning calorimetry (DSC) and their thermal stability was studied by thermogravimetric analysis (TGA). Their heat capacity was measured in the temperature range from $T = 283$ K to $T = 333$ K by means of high-precision differential scanning microcalorimetry (*iSenseDSC*) and, at $T = 298.15$ K, via high-precision drop calorimetry [4]. The volatility of these ILs was studied by means of Knudsen effusion method coupled with a quartz crystal microbalance (KNQ) [5].

For the ILs with carbon-based chains no first-order transitions were detected, however some of the ILs with alkylsilane and alkylsiloxane chains were obtained in the crystalline state. A lower melting temperature was found for the IL with an alkylsiloxane chain when compared with its alkylsilane analog. It was also found that the replacement of carbon with silicon in the cation chain causes an increase in the molar heat capacity. The volatility studies show that the ILs with alkylsilane chains are slightly more volatile, and have similar cohesive energy, to their carbon-based chain analogs. The use of an alkylsiloxane chain produced a more significant effect on volatility, which seems to arise due to a lowering of the cohesive energy.

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Microstructure and high sensitive thermal analysis in $Ni_{55}Fe_{19}Ga_{26}$: influence of martensitic structure in the thermal avalanches

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The crystal structure of martensite phase, as well as martensite start temperature of Heusler alloys, is strongly dependent on both the chemical composition and fabrication process. In particular, in NiFeGa alloys, martensitic transformation occurs on cooling from an austenite, with disordered B2 or ordered $L2_1$ structure, to either a modulated or non-modulated martensite structure, which depends on composition, thermal history and preparation method. In this work, the phase transition of a $Ni_{55}Fe_{19}Ga_{26}$ Heusler alloy prepared by arc-melting has been analyzed. Arc-melted sample exhibits a non-modulated martensite phase at room temperature with gamma phase. This microstructure evolves to a 14M modulated structure with coalescence of gamma phase crystals after 24 h at 1073 K and subsequent quenching. High sensitive differential thermal analysis (DTA) is an adequate technique to ascertain the differences that arise after the thermal treatment. We placed an as-prepared bulk sample (ASB) on a home-made conduction calorimeter [1] and carried out cooling and heating runs at a low rate of temperature change (1 K/h). Afterwards, we repeated the experiment with a thermally treated bulk sample (TTB).

The TTB sample produced a narrower and sharper DTA trace both on cooling and heating that yielded to a larger total enthalpy exchange. Also, the thermal hysteresis (martensite start temperature minus austenite start temperature) was reduced after the thermal treatment. Finally, the thermal treatment enhanced the jerky behavior of the direct transformation. We conducted another experiment at a lower rate of temperature change (40 mK/h or 10 µK/s) which allowed us to identify a series of thermal pulses that revealed the intermittent nature of the direct transformation in TTB samples. The distribution of energy sizes follows a power-law with an exponential cutoff $p(E) = E^{-\varepsilon} \cdot e^{-E/E_c}$. The exponent ($\varepsilon \sim 2$) agrees with previously reported exponents for cubic to monoclinic martensite transformation in single crystals [2].

Acknowledgements: This work was supported by the PAI of the Regional Government of Andalucía (FQM-121), the VI and VII-PPITU from the Universidad de Sevilla (Spain) and the Junta de Andalucía-Consejería de Universidad, Investigación e Innovación (project ProyExcel_00360). A. Vidal-Crespo acknowledges the financial support of the VI-PPITU from the Universidad de Sevilla (Spain).

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Thermophysical analysis of phenanthroline derivatives: A multitechnique approach

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In the context of our interest on the thermodynamic characterization of nitrogen heterocyclic compounds, this communication is concerned with the experimental thermophysical studies that have been recently developed on two phenanthroline derivatives - bathophenanthroline and bathocuproine (figure 1).These compounds exhibit properties that make them relevant ligands in coordination chemistry and potential candidates for their use as charge carrier transporting materials in organic semiconductor devices [1]

The thermal behaviour of the two compounds has been studied using several techniques, namely differential scanning calorimetry, thermogravimetric analysis, and simultaneous thermal analysis. In order to determine the respective enthalpies of sublimation, vapor pressure measurements were carried out using different methods, including Knudsen effusion mass loss/mass spectrometry, isothermal thermogravimetry, and a quartz crystal microbalance technique. Additionally, the enthalpy of sublimation for each compound was measured calorimetrically using high-temperature vacuum drop-microcalorimetry.

The results obtained provide a deeper understanding of the phase transition behavior for these compounds from condensed phases to the gaseous phase, shedding light on molecular decomposition and intermolecular forces inherent to the species. This knowledge contributes to the comprehensive characterization of the thermophysical properties of these nitrogen heterocyclic compounds.

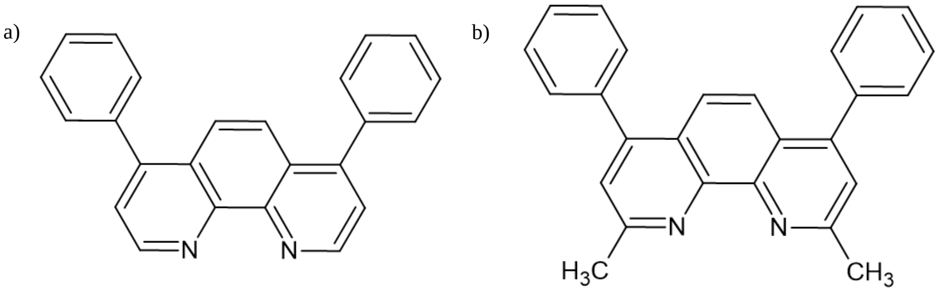

Figure 1: Structural formula of a) bathophenanthroline and b) bathocuproine

Acknowledgements: The authors acknowledge FCT for the financial support through the projects UIDB/QUI/00081/2020 and IMS-(LA/P/0056/2020). JMSF thanks the European Union for funding the Erasmus + project under which some of the work was developed. VLSF thanks FCT and FCUP for the Program Contract established under the transition rule of Decree Law 57/2016, amended by Law 57/2017.

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On the use of TGA for the study of degradation of thermal energy storage materials: analysis of the influence of evaporation and mass sample size

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An important tool for studying the thermal behavior of materials used in energy storage is the thermogravimetric analysis (TGA). One key application of TGA is estimating the thermal degradation of materials by means of accelerated methods. However, two commonly neglected phenomena lead to inaccuracies in TGA measurements and subsequent analysis of the data for this purpose. One of these phenomena is the influence of sample size. The use of a single sample size in TGA measurements is common [1], nonetheless, the employed sample size could significantly condition the degradation temperature of materials, and so, the obtained estimations. On the other hand, TGA measurements are typically performed in an open crucible. This can cause evaporation to be one of the main mass loss mechanisms of certain materials, which is difficult to separate from the degradation mechanisms observed in the experiments. The research herein carried out investigate these events to establish adequate procedures for the evaluation of the degradation of energy storage materials.

In order to analyze the sample mass influence, the onset temperature of three different materials for latent thermal storage were assessed, i.e.: xylitol, erythritol and palmitic acid. The sample sizes ranged from 2.5mg to 2g, for two different heating rates: 5Kmin^{-1} and 20Kmin^{-1}. The results show a clear mass dependence, especially for small masses.

On the other hand, to reduce the contribution of mass loss due to evaporation, the effect of using crucibles with a pierced lid was experimentally studied. The placement of a lid increases the pressure inside the crucible and therefore on the liquid, reducing evaporation. Furthermore, the influence of the evaporation was analyzed by means of simulations from a Computational Fluid Dynamics model, whose results were compared against experimental data to attain conclusions.

Acknowledgements: This work is part of the project TED2021-131061B–C32, funded by the State Research Agency (SRA) MCIN/AEI/10.13039/501100011033 and by the European Union "NextGenerationEU"/PRTR program.

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Study of environmental mobility-related properties of three chlorinated pesticides

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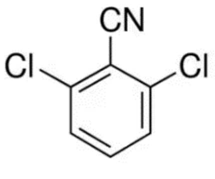
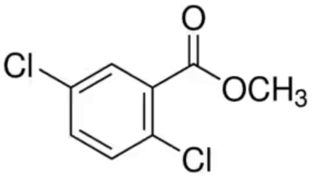
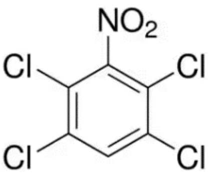
Over the last century, the use of pesticides has emerged as an extremely effective approach to pest management in agriculture. This practice has significantly enhanced crop yields, ensuring a consistent food supply year-round at reasonable prices. A notable advantage of the widespread application of pesticides is their ability to control various disease-carrying vectors, thereby reducing infections, fatalities, and the global spread of these illnesses. However, excessive production and usage of certain pesticides can lead to severe ecological and biological imbalances, posing risks to the environment. Such imbalances manifest in the contamination of water, air, soil, and living organisms, disrupting ecosystems, diminishing biodiversity, and endangering human health. Consequently, this work aims to provide essential information on the experimental determination and subsequent estimation of relevant physical-chemical properties that help assess the environmental fate of three substituted benzenes with pesticide activity. The study includes the volatility (vapor pressures) and phase transitions of dichlobenil (2,6-dichlorobenzonitrile), methyl 2,5-dichlorobenzoate, and tecnazene (1,2,4,5-tetrachloro-3-nitro benzene), as well as the determination of their solubility in water (Sw). The sublimation properties derived through vapor pressure measurements [1,2] were combined with those obtained through solubility experiments [3] yielding other crucial parameters such as solvation (hydration) and Henry's constants. All the experimental properties were incorporated into an existing database previously developed by Monte and Almeida [4] for other pollutants (halogenated benzenes), which enabled the development of simple equations to predict environmental mobility properties at 298.15 K for these compounds.



Dichlobenil



Methyl 2,5-dichlorobenzoate



Tecnazene

Acknowledgements: This work was supported by the Fundacão para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020), IMS-Institute of Molecular Sciences (LA/P/0056/2020)). ARRPA is financed by national funds through the FCT-I.P., in the framework of the execution of the program contract provided in paragraphs 4, 5 and 6 of art. 23 of Law no. 57/2016 of 29 August, as amended by Law no. 57/2017 of 19 July.

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Thermal decomposition of formamidinium tin triiodide perovskite investigated by thermal analysis and effusion techniques

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Since their appearance in the photovoltaics panorama in 2009 [1], perovskite solar cells have triggered attention of researchers, thanks to hybrid perovskites' exceptional optoelectronic properties (especially suitable band gap values) and ease of synthesis, making them currently the fastest-advancing photovoltaic technology [2]. However, the road towards their commercialization is still hampered by poor thermal and chemical stability; moreover, the best performances on a laboratory scale have been obtained with Pb-based perovskites, which have raised some additional concerns due to lead toxicity.

The need to improve tolerance to environmental agents led to multiple modifications of perovskite composition with respect to the first studied example, namely $CH_3NH_3PbI_3$ (methylammonium lead triiodide), primarily with the introduction of formamidinium cation ($CN_2H_5^+$) besides methylammonium; in turn, the search for safer alternatives to lead has driven the development of Sn-based perovskites, which have been receiving in the last years an ever-growing attention.

In order to establish the actual perspectives for commercial diffusion of perovskite solar cells, it is fundamental to clarify their behavior in conditions potentially attainable during operation. In the last few years, the thermal stability of Pb-based hybrid perovskites has been studied by our group with several experimental techniques [3,4]. However, thermal degradation of tin halide perovskites has not been elucidated yet, so a detailed investigation is still necessary.

Therefore, we examined formamidinium tin triiodide thermal decomposition in different conditions by a multi-technique approach, based on the combination of TG-DTA and effusion techniques (Knudsen effusion mass spectrometry and mass loss). TG-DTA experiments performed at different heating rates allowed to derive an overall value for the activation energy of the decomposition processes, by applying the isoconversional method. The composition of the vapor phase produced upon heating was investigated by Knudsen effusion mass spectrometry and the partial pressures of the various gaseous species were measured in the temperature range 366-462 K, allowing an elucidation of the main degradative paths:

$$CN_2H_5SnI_{3(s)} \rightleftharpoons SnI_{2(s)} + CN_2H_{4(g)} + HI_{(g)}$$
$$CN_2H_5SnI_{3(s)} \rightleftharpoons SnI_{2(s)} + NH_{3(g)} + 1/3\ H_3C_3N_{3(g)} + HI_{(g)}$$
$$CN_2H_5SnI_{3(s)} \rightleftharpoons SnI_{2(s)} + NH_{3(g)} + HCN_{(g)} + HI_{(g)}$$

Interestingly, besides the above reported decomposition channels, an abundant release of $SnI_{4(g)}$ was also observed, so confirming the role of oxidation of Sn(II), normally present in tin halide perovskites, to Sn(IV) [5]. In order to support the interpretation of mass spectra, the sublimation of SnI_2 and SnI_4 was also investigated.

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Influence of nanoconfinement on phase transitions of ionic liquids for smart energy storage devices

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The fast depletion of fossil fuels creates the necessity of researching alternative energy sources as renewable energy production. The investment and use of renewable energy resources help in reducing the future consequences of climate change, making possible a transition to a new decarbonized economy. However, to harness the potential of these renewable resources, it is essential to develop new energy storage devices [1] such as rechargeable batteries, supercapacitors or fuel cells.

One of the most interesting applications of ionic liquids (ILs) is as electrolytes in electrochemical energy storage applications due to their amazing characteristics such as low flammability, low vapour pressure, high ionic conductivities, wide electrochemical stability [2] and the practically unlimited combinations that can be formed; the large number of cations and anions make it possible to obtain the most suitable compound for each application.

A smart procedure to improve industrial safety is to immobilize these ILs, or their mixtures, in a matrix, nano scaffolds, for its use in smart electrochemical devices. The resulting material is named ionogel, and it brings similar electrical properties as the liquid state being mechanically stables. Ionogel synthesis also provides an intelligent way to achieve the mechanical stiffness to block the growth of lithium dendrites improving their lifespan [3].

The thermal analysis of these possible new electrolytes is essential to determine the optimum operating temperature range as well as determine the phase transitions which have direct consequences on ionic conductivity, which is a fundamental magnitude in electrolytes characterization. So, the main aim of this work is to fully characterise and compare the thermal behaviour by differential scanning calorimetry (DSC) of pure and binary mixtures (IL + lithium salt) of IL both liquid and ionogel samples.

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Evolved gas analysis. What about quantification? Focus on the couplings between thermogravimetry and gas chromatography mass spectrometry

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Coupling TGA to MS, FTIR, GC-MS, or µGC-MS instruments clearly enhances the basic information given by TGA alone.

The composition of emitted gases obtained by evolved gas analysis (EGA) provides an in-depth look at the mechanisms of decomposition/degradation of materials as well as information on the toxicity of the material during heating. EGA also allows de-formulating a material to understand its physico-chemical behavior under heating.

The couplings mentioned above are powerful techniques that yield both quantitative (mass loss) and qualitative (identification) information about the gaseous products released during a TGA measurement. Each coupling has its own specificity. Interpretation of infrared spectra or mass spectra becomes more complicated when many unknown gases are simultaneously released. In this case, a separation step becomes necessary.

An interesting coupling such as ***TGA-Storage interface-GC-MS*** can be used for the analysis of complex gaseous mixtures coming from plastics, bitumen, resins, silicones, waxes, etc. Another coupling allowing separation of small molecules such as permanent gases, light solvents, light and medium VOC could be the ***TGA-µGC-MS***. With these two couplings, the emitted gases will not only be separated and identified, but also quantified by using different methods of quantification and this will be shown through several examples of applications.

Dielectric relaxation spectroscopy study of the evolving glass transition during cure of a reversible network based on Diels-Alder cycloaddition

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In the past decades, polymer networks have been extensively investigated through numerous techniques, including Dielectric Relaxation Spectroscopy (DRS). DRS allows the study of thermophysical properties such as molecular dynamics of polymers and other soft matter, giving complementary information to other thermal analysis techniques. Using DRS, the cure of irreversible networks has been thoroughly investigated in literature [1] while studies on reversible covalent network formation are notably scarce [2], and particularly absent for systems based on Diels-Alder (DA) cycloadditions. Such dynamic networks based on thermoreversible DA reactions are commonly developed as promising intrinsic self-healing materials, thanks to the fact that DA bonds preferentially break in case of damage and reversibly reform, which leads to a repeatable healing cycle and an increased lifetime for numerous applications, such as sustainable coatings [3].

In this work, the molecular dynamics of a reversible network, based on the furan-maleimide DA reaction of a 4-functional furan-functionalized Jeffamine coupled with a 2-functional maleimide, are studied systematically by DRS using isothermal as well as non-isothermal measurements at frequencies between 10^{-1} - 10^{7} Hz. The focus is on the α-relaxation, representative of the cooperative segmental dynamics linked to the glass transition temperature (T_g) of the material.

The characteristic relaxation times of this relaxation process, τ_α, are derived via conventional Havriliak-Negami fits from dielectric spectra [4] measured in non-isothermal DRS experiments, which were performed after isothermally curing the networks at 55 °C for different reaction times. The temperature dependent $\tau_\alpha(T)$ are then modelled using a Vogel-Fulcher-Tammann (VFT) law for each individual experiment. Subsequently, a more global approach is attempted, where one unique set of VFT parameters is used to describe all experimental relaxation traces, with and without including effects of the reaction by introducing a kinetic model to predict the cure conversion [5]. Based on this description, a new technique for continuous cure monitoring is proposed and tested through the simulation of a system curing isothermally at 55 °C. This technique allows to compute in real-time, at any stage of the isothermal or non-isothermal cure process, the dynamic T_g from the relaxation time τ_α, using only the sample temperature and three VFT parameters and from the global fit procedure. This promising approach might stimulate new applications of DRS-based cure monitoring.

The authors thank the Research Foundation - Flanders (FWO-Vlaanderen) for financial support (PhD fellowship of Jessica Mangialetto (1128520N)).

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The new concept of DSC 300 Caliris® - Ideal for phase transitions and purity

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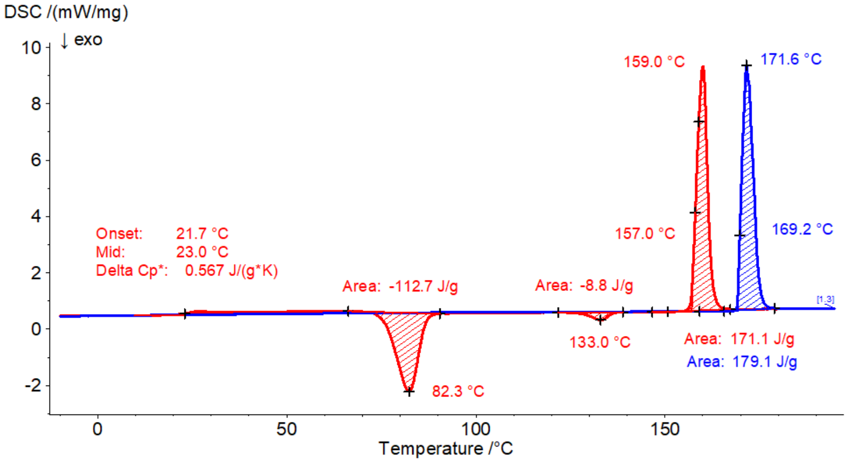

Fig. 1. Polymorphism of Paracetamol.

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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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POSTER COMMUNICATIONS

Thermochemistry of 1-*H*-1,2,4-triazole amino derivatives

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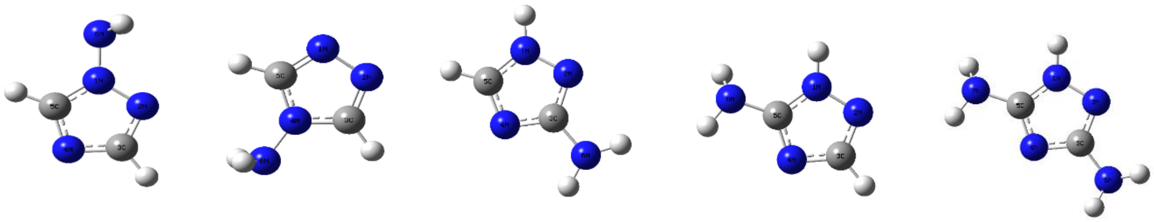
Amino-triazoles have gained attention in the field of energetic materials due to their high energy content and stability. Enthalpies of formation are essential properties in evaluating the energy output and performance characteristics of these compounds. They provide insights into the heat release, combustion behavior, and overall energy storage capabilities of amino-triazoles, which are relevant for applications such as propellants, explosives, and pyrotechnics. This information is valuable also for pharmaceutical companies, as amino-triazoles have shown potential in drug discovery and development. Enthalpies of formation are also crucial in designing and optimizing synthetic routes for amino-triazole compounds. In fact, by knowing the enthalpy of formation, chemists can predict the energy changes involved in the synthesis process and determine the most efficient conditions to obtain the desired compounds.

This work is focused on the thermochemical study to determine the enthalpy of formation of amino-1-*H*-1,2,4-triazoles. Experimentally, the enthalpies of formation in the crystalline phase and the enthalpies of sublimation were determined for 3-amino- and 3,5-diamino-1-*H*-1,2,4-triazole. For 4-amino-1-*H*-1,2,4-triazole only the enthalpy of sublimation was measured.

Gas-phase standard molar enthalpies of formation were also estimated using theoretical calculations performed with the G3(MP2) composite approach. The excellent agreement of these estimates with experimental results, support the extension of this study to the estimate of this property for the remaining compounds not studied experimentally. The results obtained are interpreted in terms of structural contributions.



(a) (b) (c) (d) (e)

Figure 1. (a) 1-Amino-1H-1,2,4-triazole; (b) 4-Amino-1*H*-1,2,4-triazole; (c) 3-Amino-1*H*-1,2,4-triazole; (d) 5-Amino-1*H*-1,2,4-triazole ; (e) 3,5-Diamino-1*H*-1,2,4-triazole

Acknowledgements: This work was supported by the Fundacão para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Sciences, University of Porto (PEst-C/QUI/UI0081/2013). L.M.P.F. Amaral thanks FCT/MCTES funding through the Individual Call to Scientific Employment Stimulus 2018 (CEECIND/03202/2018).

Electron correlation in aromatic molecules: Analysis of conjugation in naphthalene and fluorene derivatives

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Electron correlation has been extensively studied in the last decades due to its central role in physical and quantum chemistry. The nature of this energy still eludes the chemists, being frequently distinguished in various forms, such as dynamic and static correlation [1].

In this work, some naphthalene and fluorene derivatives were studied with the aim to comprehend how the correlation energy in relatively large aromatic systems behaves when certain changes to the molecule structure are made. To achieve this, the compounds were firstly synthesized and characterized using UV-Vis and NMR spectroscopy. The standard molar entropies, enthalpies and Gibbs energies of sublimation were measured using the Knudsen Quartz Crystal Effusion technique, by measuring the vapor pressures as a function of temperature. The standard molar enthalpies of formation in the crystalline phase were determined by mini-bomb Combustion Calorimetry. Using these results, the standard molar enthalpies of formation in the gas phase were derived. With the use of the homodesmotic reaction scheme shown in Fig. 1, the π conjugation energy in the molecules studied was experimentally quantified, and its dependence on molecular structure (type of spacer and position of phenyl rings) analyzed. Molecular energetics was tentatively described by computational calculations using various levels of theory: DFT, HF, MP2, Coupled Cluster, and Configuration Interaction. Most of the molecules studied exhibited noteworthy energetic stabilization as a consequence of π conjugation, which was also manifested in their optical properties and more planar molecular structures (lower phenyl-spacer dihedral angles). However, the HF, MP2, and DFT results were unable to describe the experimental findings, suggesting the importance of static correlation in these systems.

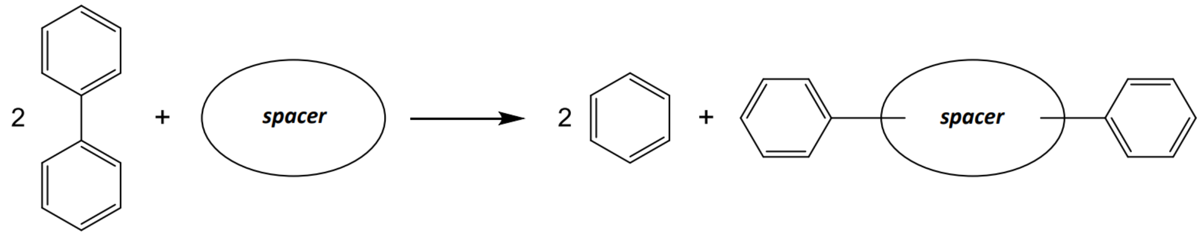

Figure 1: Homodesmotic reaction in the gaseous phase used to quantify π-electron conjugation in the molecules studied.

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Study of the association of aza crown ethers with some metal ions and ligands

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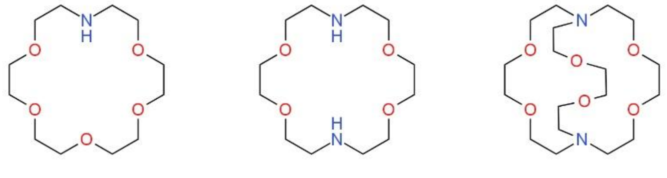
The aza crown ethers are molecules with a structure similar to those of the crown ethers [1] but with some oxygen atoms substituted by nitrogen atoms [2]. These changes in the structure cause that the ability to interact with other molecules is different between crown ethers and aza crown ethers. The aza crown ethers have the capability to associate with not only alcaline and alcaline earth metal ions, such as crown ethers, but also with transition metal ions. On the other hand, cryptands are macrocycles similar to crown ethers and aza crown ethers but with a bicyclic structure [3] that makes these cage molecules more capable to associate with small molecules or metal ions trapping them into their cavity [4]. Despite these capabilities of association in aza crown ethers and cryptands, there are very few studies [5] that report the thermodynamic parameters of association and most of them are focused on the role of the proton of the amino group in the association. In this work we report the results of the parameters of association of the 1-aza-18-crown-6 (1A18C6); 1,10-diaza-18-crown-6 (1,10DA18C6) and cryptand [2.2.2] (CR222), whose molecular structures are shown in Figure 1, with barium and calcium ions as well as 4-aminoazobenzene bromide, using Nano Isothermal Titration Calorimetry (Nano ITC). In this methodology the enthalpy, the stechiometry and the equilibrium constant are obtained from the heat measured in a series of titrations between the macrocycle (titrant) and the ion or ligand (titrant). The integration and normalization of the heat measured from each titration results in a series of points fitted to an ideal sigmoidal curve from which the above mentioned thermodynamic parameters are derived. The results obtained to date suggest that, for some of the metal ions there is an intense association while for the 4-aminobenzene bromide exists a moderate association, when these chemical species in solution interact with the aza derivatives and the cryptand.



1-aza-18-crown-6 1,10-diaza-18-crown-6 cryptand [2.2.2]

Figure1. Macrocycles structures in study

Acknowledgements: The authors thank the Consejo Nacional de Ciencia y Tecnología (Conacyt-Mexico) the financial support (grants 104299 CB-2008 and 286452 CB-2016) and the scholarship awarded to D.E.

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Thermal evolution of NiAl-citrate LDH in air and inert atmosphere: a comparison

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Layered doubled hydroxides (LDHs) belong to a class of 2D materials, also known as anionic clays, with general formula: $[M^{2+}_{1-x}N^{3+}_{x}(OH)_2]^{x+}(A^{n-}_{x/n})^{x-} \cdot mH_2O$.
Where M and N are respectively a divalent and a trivalent cation, A is an anion with *n* charge, *x* is the molar ratio N/(M+N) and *m* is a value between 1 and 4. The structure is multi-layered, made of positively charged sheets of octahedral metal hydroxides hosting anions at the interlayer.
The flexibility of the structure and the possibility to have different combination of N, M and A make this class of compounds very interesting in a lot of different fields, from catalysis to energy storage applications.[1], [2].
In this work is investigated the thermal evolution of NiAl-citrate LDH both in air and inert atmosphere. In fact, the decomposition of citrate leads to completely different results depending on the environment of the heating procedure: in pyrolytic condition it evolves, through a complex mechanism, in CO able to reduce the cations forming a NiAl based intermetallic compound, not losing the initial layered structure.

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Thermochemical study of two long hydrocarbon-chain lactones

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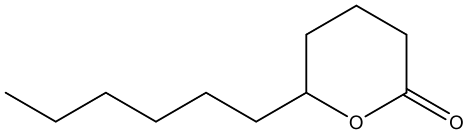
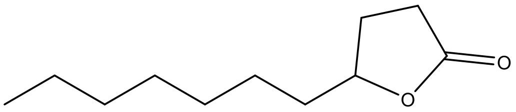
Several lactone derivatives have acquired significant interest in the synthesis and biosynthesis research, and also in the valorization of biomass-derived intermediates [1-3]. The availability of data related with energetic properties of these compounds has primordial relevance for the characterization of their role in the processes in which are involved. Despite this, most of those properties are scarce in the literature, leading us to develop an experimental and computational thermochemical study of some biomass-derived cyclopentenones and lactones [4, 5].

This work presents a calorimetric study of two long hydrocarbon-chain lactones, undecanoic δ-lactone and undecanoic γ-lactone (Fig.1). The standard molar enthalpy of combustion in the liquid-phase and the standard molar enthalpy of vaporization of each compound were determined calorimetrically: the combustion experiments were performed by static-bomb combustion calorimetry and the vaporization study was done using a high-temperature Calvet microcalorimeter. Therefore, the standard molar enthalpy of formation in the gas-phase, at 298.15 K, was calculated based on the experimental data obtained on the study of the compounds. In addition, it is intended to study the correlation energy vs. structure for the lactones studied and other alkylated δ-and γ-lactones already available in the literature.



Undecanoic δ-lactone



Undecanoic γ-lactone

Figure 1. Molecular structures of lactones.

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Thermal stability investigation and curing kinetic analysis of a bio-derived epoxy adhesive

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Environmental crisis along with restrictions on harmful emissions have turned global market towards greener solutions. Construction industries mainly incorporate petrochemical adhesives, resulting in undesirable formaldehyde and volatile organic compounds release [1]. The present study investigates the thermal properties of a bio-based, low-temperature curing epoxy, aiming in the development of a more sustainable future in the manufacturing field. Initially, thermal stability of both the stoichiometric and the mixture with excess diamine was evaluated by means of Thermogravimetric Analysis (TGA), while the crosslinked network presenting higher resistance to thermal cracking was kinetically studied through Differential Scanning Calorimetry (DSC). Constant heating rate and isothermal experiments were performed, revealing both the initialization of curing and the glass transition temperature T_g at temperatures near 0^0 C. According to the advanced isoconversional method proposed by Vyazovkin, the activation energy appeared constant throughout the curing process, most probably indicating a single step reaction mechanism [2]. Several reaction models were examined, mainly describing the polymerization process as nth order reaction with autocatalysis. Isothermal predictions, derived from constant heating rate DSC coefficients, found to describe isothermal crosslinking in a very satisfying way, resulting in advanced curing conditions.

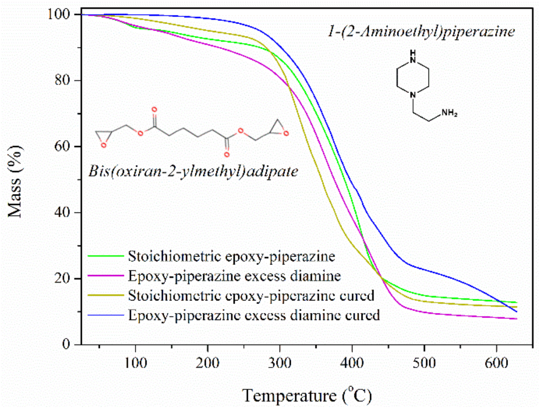

Figure 1. Thermal decomposition profile of epoxy-diamine before and after curing (N_2, 10°C/min).

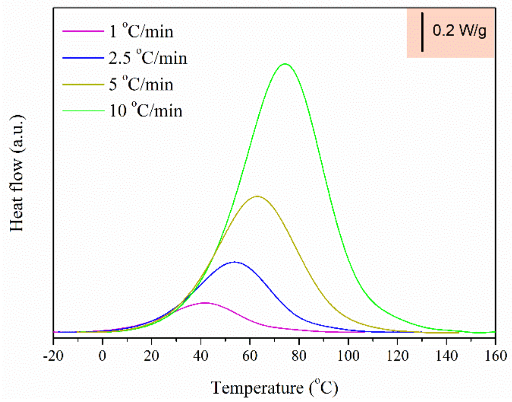

Figure 2. Exothermal curing curves under different heating rates by means of DSC experiments.

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Influence of irradiation on the non-isothermal decomposition and kinetics of the polymeric backsheets of photovoltaic (PV) modules

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The weathering stability of polymeric backsheets is one of the basic properties for the reliability of photovoltaic (PV) modules. Polyolefin (PO) backsheets represent alternative to the most used poly(ethylene terephthalate) (PET) backsheets. In order to investigate the influence of the irradiation on the thermal properties of PO backsheets, samples were subjected to damp heat test (T = 85 °C; 85% RH) according to IEC 61215 37 and sun simulation test (T = 60 °C; 40% RH; irradiation of 1000 W/m^2 in the wavelength range of λ = 300–2500 nm) for an exposure time of up to 2000 h. During the aging, samples were irradiated from the inner side, as it would be under real service conditions. Thermal decomposition of samples prior (0 h), after 1000 h and 2000 h of aging was performed using non-isothermal thermogravimetry at four heating rates (2.5, 5, 10 and 20 °C/min). The data obtained by non-isothermal decomposition were used to perform the kinetic analysis. Kinetic analysis was performed using the Netzsch Thermokinetics Professional program. In the first step, the Friedman isoconversion method included in the Netzsch Thermokinetics Professional program was applied, the goal of which is to determine whether it is a kinetically simple or kinetically complex degradation process. It was found that the thermal decomposition of these polymers is a complex process from a kinetic point of view. Using non-linear regression analysis, kinetic models were calculated that best describe the complex process of isothermal decomposition of the examined polymer materials. It was concluded that accelerated aging affects the kinetics of the non-isothermal decomposition of the investigated polymer materials.

Kinetic investigation of oxidative thermal decomposition of levonorgestrel

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Kinetic studies are, nowadays, of great importance in the characterization of pharmaceuticals, including active pharmaceutical ingredients (APIs), excipients and even coating and packaging materials [1,2]. Since there are numerous flaws in reporting kinetic results in the characterization of materials, several protocols and good laboratory practices were reported by highly-reputed scientists in order to obtain realistic and credible data [1].

In this study, we have focused into obtaining realistic kinetic parameters regarding the decomposition of levonorgestrel (abbreviated LNG, namely 17alpha-ethynyl-18-methylestr-4-en-17beta-ol-3-one), which is a second-generation synthetic progestogen that is the active component of the racemic mixture of norgestrel, primary used as an emergency contraceptive [3,4]. The necessity of this study resides in the lack of reported kinetic data for this compound, which is currently used at large scale in the medical domain in solid formulations and as well in intrauterine systems (LNG-IUS) [5].

The thermolysis mechanism of LNG in dynamic oxidative atmosphere was investigated using TG/DTG/HF data. Five thermoanalytical curves were recorded for LNG in 30–800 °C temperature range, at different heating rates (β = 2, 4, 6, 8 and 10 °C·min^{-1}), and the DTG data were preliminary processed using the ASTM E689 method, followed by the use of Kissinger–Akahira–Sunose, Flynn-Wall-Ozawa and Friedman isoconversional methods.

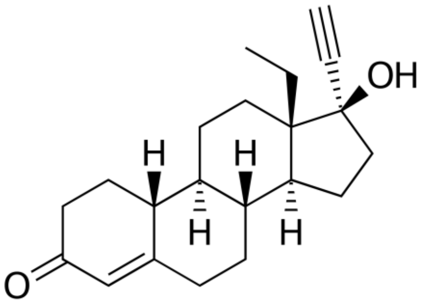

Figure 1. Structural formula of LNG

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Thermal stability and decomposition of olmesartan medoxomil

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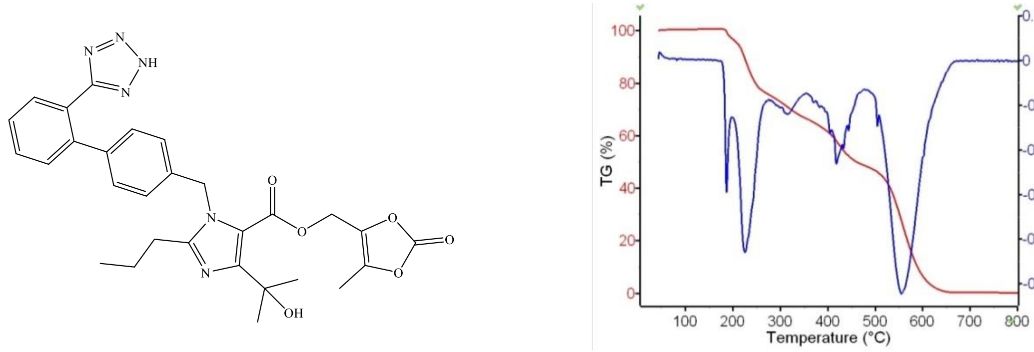
Olmesartan medoxomil (OLM) is an angiotensin receptor blocker [1], used in solid dosage forms for *per os* administration in the treatment of hypertension [2]. Versions are available as the combination olmesartan/hydrochlorothiazide and olmesartan/amlodipine, but as well as a single-pill combination containing three antihypertensive agents [3].

To our knowledge, there are no reported data regarding the kinetic of decomposition of OLM in solid state. Kinetic studies were carried out according to protocols suggested in literature [4] using five different TG/DTG curves recorded at heating rates below 10 °C·min^{-1} and employed three methods: one preliminary simplistic kinetic method (Kissinger), followed by two isoconversional methods – the integral method of Flynn-Wall-Ozawa and the differential method of Friedman.



(a) (b)

Figure 1. (a) Structural formula of OLM and (b) TG/DTG data recorded in air atmosphere at a heating rate β = 6 °C·min^{-1}

Acknowledgments: This paper was financially supported by the Project "Network of excellence in applied research and innovation for doctoral and postdoctoral programs / InoHubDoc", project co-funded by the European Social Fund financing agreement no. POCU/993/6/13/153437.

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Kinetic analysis of non-isothermal decomposition of gestrinone

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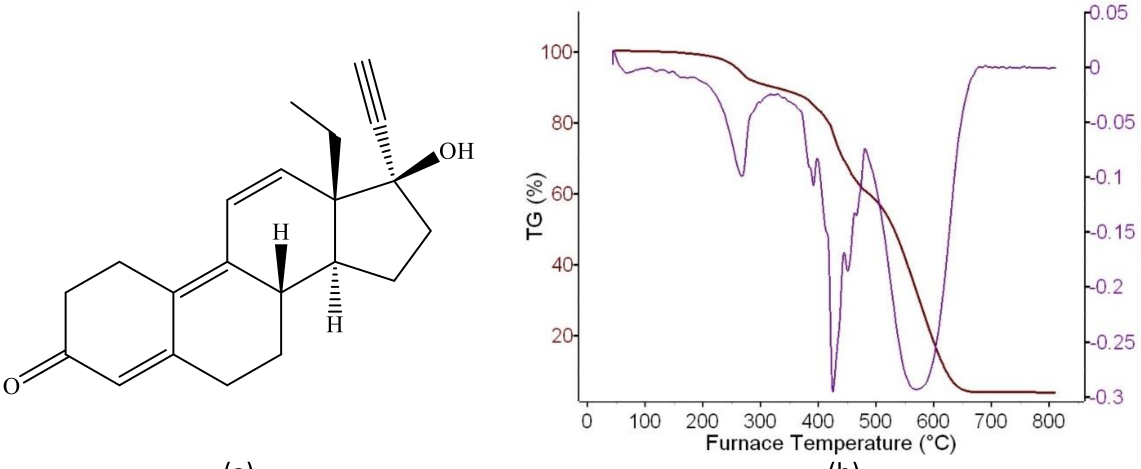
Gestrinone (GST), also known as ethylnorgestrienone (Figure 1a), is a synthetic derivative of 19-nortestosterone and possesses an androgenic, weak estrogen-like, anti-estrogen, weak-progestin and strong anti-progesterone properties. GST is currently used in the treatment of endometriosis mainly in the form of capsules and evaluated for vaginal administration [1], and lately studied for its potential antitumoral effects [2]. Because of its therapeutic effects [3], both those demonstrated and those under study, its low oral absorption and lack of various pharmaceutical formulations it is necessary to evaluate the stability profile of this drug in different conditions, so the integrity of the molecule during processing is maintained.



(a) (b)

Figure 1. (a) Chemical structure of GST and (b) Thermal analysis data (TG/DTG) obtained at a heating rate of 10 °C·min^{-1}.

Thus, the solid-state stability of GST was evaluated using spectroscopic (FTIR) and thermoanalytical (TA) methods. The obtained TA data were collected using five different heating rates $\beta = 2, 4, 6, 8$ and 10 °C·min^{-1} (example in Figure 1b) in dynamic air flow, and were processed using three isoconversional methods, namely Kissinger–Akahira–Sunose, Flynn-Wall-Ozawa and Friedman. A discussion regarding the decomposing of GST under thermal stress was also carried out.

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DSC and EPR investigations on the effects of bis-(3-hydroxy-4-pyridinonato) zinc (II) complexes on DMPC liposomes

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Since the 1980s, researchers have been studying the potential antidiabetic effects of zinc ions in mouse models. Some studies have shown that oral administration of inorganic zinc (II) can significantly reduce blood glucose levels. However, the therapeutic dose required for this effect was found to be too high due to poor bioavailability and absorption, leading to concerns about its safety profile.

The use of chelators to improve the therapeutic potential of Zn (II) in diabetes has shown some promising results [1,2]. Studies have demonstrated that zinc chelation can enhance the action of insulin and improve glucose metabolism in *in vivo* experiments. Among the different classes of chelators, pyrone and their hydroxylated analogues, have been of particular interest due to their chelating properties towards transition metal ions, including zinc. In particular, 3-hydroxy-4-pyridinone derivatives, has been investigated for its potential antidiabetic properties [3]. These chelators can be easily functionalized, which provides the option for tuning physicochemical and biological properties, such as bioavailability after oral administration, lipophilicity, and chelating ability.

In the present work, seven 3-hydroxy-4-pyridinones-Zn (II) complexes with diverse lipophilicity were prepared and characterized. The aim was to explore the molecular interactions between these complexes and DMPC liposomes, which serve as a representative model of cell membranes.

To investigate these interactions, differential scanning calorimetry (DSC) and electron paramagnetic resonance spectroscopy (EPR) techniques were used, which provide valuable biophysical information. Understanding these molecular interactions can guide the development of more effective and safer zinc-based therapies for diabetes.

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Funding: This work was financial supported with funding from FCT/MCTES (UIDP/50006/2020) through national funds.

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Physicochemical characterization of polymeric membranes with Riluzole for amyotrophic lateral sclerosis treatment

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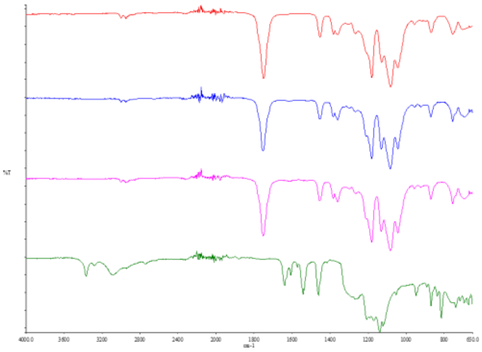
Riluzole (Rilu) is a neuroprotective drug that acts as a sodium channel blocker against the pathological influx of sodium to inhibit abnormal glutamatergic neurotransmission in the central nervous system (CNS). This drug is safe and well-tolerated treatment for patients with amyotrophic lateral sclerosis (ALS) [1, 2]. Rilu ($C_8H_5F_3N_2OS$) is a drug that falls into the category of benzothiazoles. The average absolute oral bioavailability of Rilu is 60%, while the drug is approximately 90% absorbed. It shows a linear pharmacokinetics over a dose range of 25-100 mg administered every 12 hours [3].

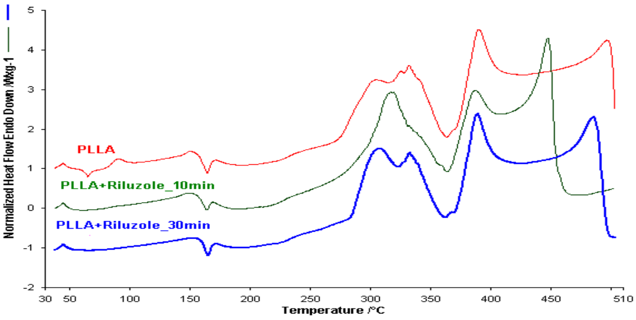
The topical formulation of Rilu was obtained by immersing the Rilu in the Polylactic acid (PLLA) membrane in the following order: Rilu was dissolved in DMSO or methanol. The PLA membranes were introduced in the Rilu solution, one membrane was kept for 10 minutes in the drug solution and the other membrane for 30 minutes.

TG, DSC 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 FT-IR spectrums were recorded with a Perkin Elmer Spectrometer 100 with U-ATR technique. This technique allows to record IR spectra of all solid or liquid samples without any preparation beforehand. TG/DTA measurements were performed on a Perkin-Elmer DIAMOND thermo-balance for obtaining simultaneously the TG, DTG and HF curves. The thermal behavior for all of the samples was recorded in air (Lindegas, 5.0) atmosphere with a flow rate of 100 ml·min^{-1}. Samples with mass between 5,0 and 15,0 mg were added to aluminum crucibles.



FTIR spectra for: PLA, Rilu 10, Rilu 30, Riluzole



Normalized Heat Flow for PLLA, Rilu 10, Rilu 30

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Thermal behavior of polymer-based systems containing antibiotic and anesthetic with medical use

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Drug delivery systems are methods designed to ensure that drugs enter the body and arrive where they are needed [1]. The unquestionable feasibility of transdermal and transmucosal drug therapy has been recognized over the past decade, and this therapeutic system has become established as an effective alternative to oral and other parenteral forms of drug delivery [2].

The ideal drug delivery system should be biocompatible, inert, easy to administer and remove, comfortable for the patient, safe from accidental release, and finally, inexpensive to manufacture and sterilize [3].

The aim of this study is to prepare and characterize alginate-based membranes in which amoxiklav and local anesthetics from the class of amides (articaine, mepivacaine, bupivacaine, ropivacaine) were incorporated as active ingredients. In the present study, the results of several complementary physicochemical techniques (TG, FTIR, SEM- scanning electron microscopy, UV-Vis ultraviolet-visible), allow to determine the best membrane variant to be used.

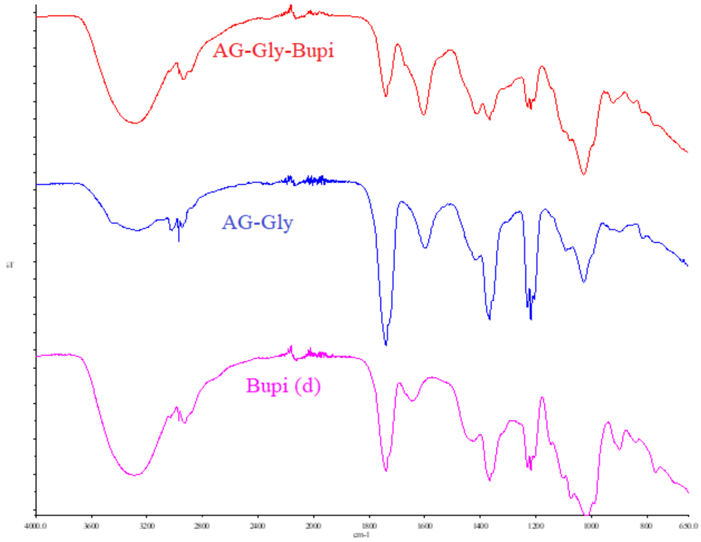

Figure 1. FTIR of AG-Gly-Bupi membrane, AG-Gly membrane and Bupi dissolved

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Preformulation studies for membranes with acetaminophen, propyphenazone and caffeine

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Formulations containing acetaminophen, also called paracetamol (Paracet), propyphenazone (Perf) and caffeine (Caff) are often prescribed as a combination for pain relief. Acetaminophen is a widely used over-the-counter analgesic and antipyretic. Propyphenazone is a nonsteroidal anti-inflammatory drug derived from pyrazolone incorporated into many over-the-counter analgesic combinations. Caffeine is a xanthine alkaloid used as a psychotropic stimulant and is found in coffee, tea and cocoa. This combination of active pharmaceutical ingredients causes reduction in the amount of prostaglandin, while caffeine is also known to enhance the analgesic effects of acetaminophen and propyphenazone [1, 2].

Preformulation studies play an important role in the development of new pharmaceutical formulations [3]. In obtaining and developing new pharmaceutical formulations, it is very important to know the physicochemical properties of drugs and pharmaceutical components [4].

The present study aims to obtain the best pharmaceutical formulation with alginate-based membrane containing acetaminophen, propyphenazone and caffeine, for possible transdermal application to eliminate the side effects associated with oral administration.

The new pharmaceutical formulations obtained were characterized by electron microscopy SEM coupled with EDX, FTIR, thermogravimetric analysis and UV-Vis.

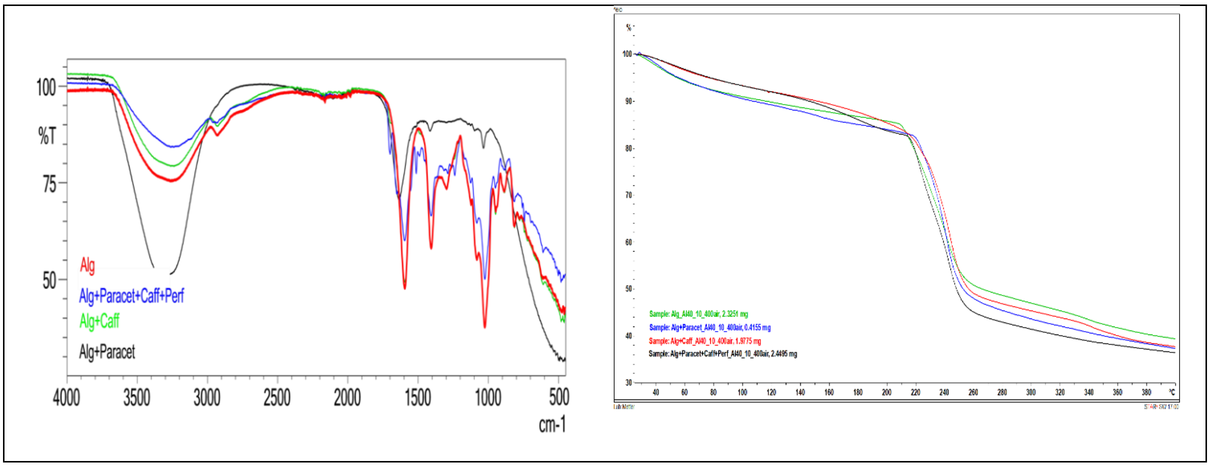

Figure 1. FTIR and TG analysis of membranes with alginate, acetaminophen, caffeine and propyphenazone

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Discovery of a NOR-PABA salt through the coamorphous thermal conversion

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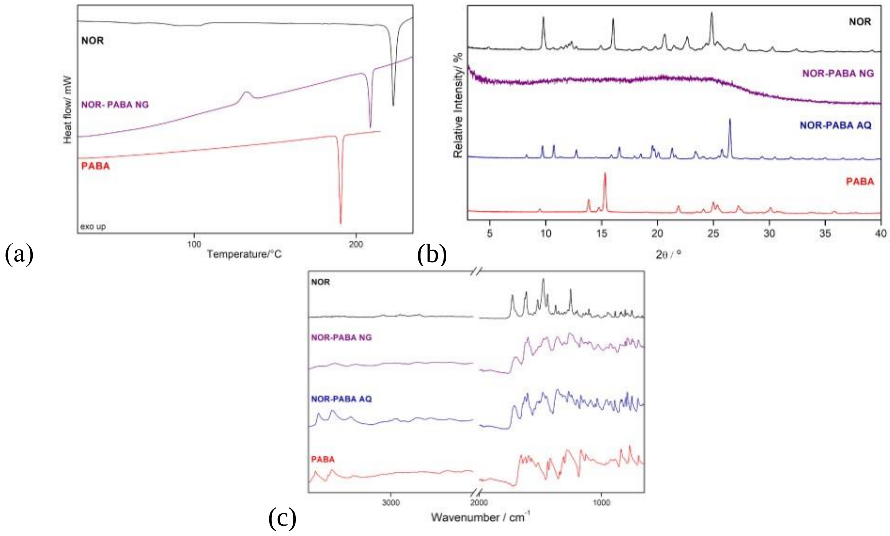
The development of multicomponent solid forms is a strategy widely used by scientific researchers and by the pharmaceutical industry to overcome some issues related to physicochemical properties of drugs [1,2]. In this regard, the investigation of the interaction between the antibiotic Norfloxacin (NOR) and p-aminobenzoic acid (PABA) resulted in the identification of two different multicomponent solid forms, a coamorphous and a salt.

Samples were prepared through the mechanochemical method (neat grinding), which favors the rearrangement of molecules in the solid state and promotes the formation of the multicomponent material [3]. In addition, the thermal treatment and the characterization of the system was conducted through Differential Scanning Calorimetry (DSC). The samples were also investigated using X-ray powder diffraction (XRPD) and infrared spectroscopy (IR).

The DSC curve of the NOR-PABA system (Figure 1a) showed different thermal behavior compared to the precursors, evidenced by an intermediate melting point (204ºC). Initially, the binary mixture exhibits an amorphous structure, as confirmed by XRPD analysis (Figure 1b). After the thermal treatment (NORPABA AQ; Figure 1c), the diffractogram showed crystalline behavior, indicating that the exothermic event presented in the DSC (131ºC) refers to the crystallization of the sample. Furthermore, the IR analysis helped to elucidate that this coamorphous system is thermally converted into a NOR-PABA salt.



(a) (b)

(c)

Figure 1 – (a) DSC curve NOR-PABA system, (b) XRPD and (c) FTIR of NOR-PABA system before and after thermal treatment.

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Binary diagrams of therapeutic deep eutectic solvents based on ketoprofen and terpenoids

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Therapeutic deep eutectic solvents (THEDES) are multicomponent liquids, usually formed by an active pharmaceutical ingredient (API) and a coformer, which are held together by non-covalent intermolecular networking, mainly hydrogen bonds, resulting in a profound depression in the melting point of the system. THEDES are studied aiming at improving the solubility and permeability of APIs [1,2], and the solid-liquid equilibrium (SLE) diagrams are constructed to determine the liquid phase region and the stoichiometry of the eutectic mixture [1].

Samples were prepared from the mixture of ketoprofen with menthol (MENT) or thymol (THYM) in different molar ratios, under constant stirring and heating for 1 hour. The samples were investigated using infrared spectroscopy (IR), and the SLE diagrams were constructed to define a binary eutectic system.

FTIR spectra of ketoprofen, and studied systems are shown in **Figure 1 (A)**. The C=O stretches of Ketoprofen are observed at 1694 cm^{-1} and 1654 cm^{-1}, while in KET:MENT, the C=O stretches are observed to be shifted to 1709 cm^{-1} and 1662 cm^{-1}, and in KET:TYMO system, the C=O stretches are observed at 1708 cm^{-1} and 1647 cm^{-1}. Therefore, these systems interact through hydrogen bonds between the C=O and O-H groups.

SLE diagram, shown in **Figure 1 (B)**, exhibits an expected behavior of the proportion 0.90 to 0.40, correspond to the ideality of the solid-liquid equilibrium, which is not seen below 0.40, with a deep deviation from ideality between 0.1 and 0.35. Proportions between 0.1 and 0.2 present melting below the theoretical temperature, being liquid at room temperature, while proportions between 0.25 and 0.35 present only glass transition events. A similar behavior is observed in **Figure 1 (C)**, where the system presents deviation from ideality from the proportion 0.1, therefore only the proportion 0.1 presents crystallization, while the proportions between 0.12 and 0.40 present only events of glass transitions, all these data confirm the deviation from ideality in the studied systems.

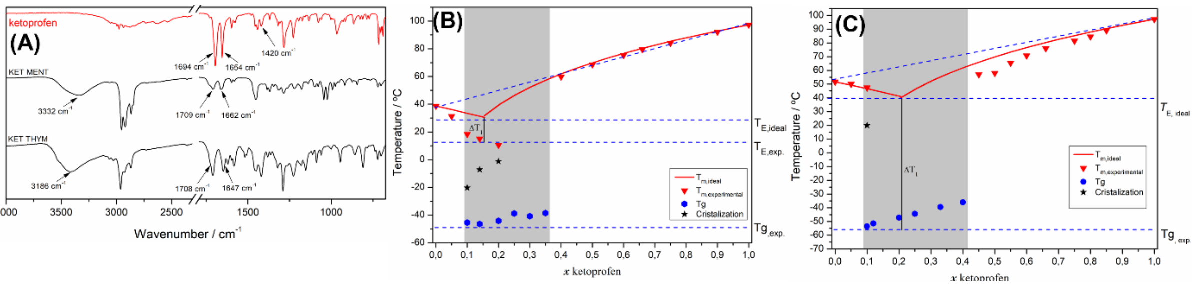

Figure 1: (A) FTIR spectra of Ketoprofen, KET:MENT, and KET:MENT systems; (B) Binary diagram of KET:THYM system; (C) Binary diagram of KET:THYM system.

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Evaluation and control of pharmaceutical blood products by TGA and Chemometrics

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A careful control of pharmaceutical blood products is performed prior to market distribution in order to ensure medicines quality and more safety for recipients. Several analytical tests based on complex and laborious method are involved in the routine practice for the regulation and batch release. Novel analytical strategies able to highlight the real composition of the biological product are required more and more by the National Authority involved in pharmaceuticals control, since novel and different manufacturing approach are emerging. TG/Chemometrics is well known in pharmaceuticals and complex biological matrices characterization. [1,2]

In this study, the coupling of Thermogravimetry and Chemometrics was tested to analyze blood-derived products, available on the pharmaceutical market and distributed by different manufacturers. A characteristic thermal profile was identified through analysis of 30 microliter of the sample which did not require any pre-treatment. TG and DTG curves were imported in the chemometric package and investigated in order to develop accurate and precise models of prediction. The aim of the work was to provide a rapid and cost-effective analytical tool for quantifying the active compound and highlight difference in manufacturing process. Therefore, the Partial Least Squares (PLS) algorithm was selected to discriminate pharmaceuticals according to these variables. Results and analysis of unknown products confirmed effectiveness of the Thermogravimetry associated with Chemometrics for the evaluation and control of pharmaceutical blood products in order to ensure the identity and the quality of the blood derivatives for human use.

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Compatibility study of mirtazapine with several excipients used in pharmaceutical dosage forms employing thermal and non-thermal methods

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Mirtazapine (MRT) is an atypical tetracyclic compound used in the treatment of depression, anxiety and obsessive-compulsive disorder [1], being usually formulated as a hemihydrate (MRTHH). Considering the increasing use of antidepressants worldwide and the numerous types of pharmaceutical solid dosage forms, studies regarding drug-excipient compatibility are highly important in order to evaluate possible interactions. The selection of adequate excipients influences not only the dosage form, but also the metabolism of the active substance, the stability of the formulation and its shelf-life [2].

The aim of the present study was to evaluate the compatibility between MRTHH and ten different pharmaceutically excipients. Binary mixtures (1:1 w/w) were prepared by trituration in the presence of ethanol, followed by drying at 40 °C for 12 h as to ensure the complete vaporization of the solvent. The samples were placed in sealed vials and kept at room temperature. The pure compounds (MRTHH and each excipient) and the prepared mixtures were subjected to thermal analysis (TG/DTG and DSC). A single-step decomposition was revealed during thermal analysis for pure MRTHH after dehydration (Figure 1) and was used to evaluate possible thermal-induced interactions with each evaluated excipient. In addition, Fourier transform infrared spectroscopy (FTIR) and Powder X-ray diffractometry (PXRD) were also employed as to confirm the results obtained during thermal analysis.

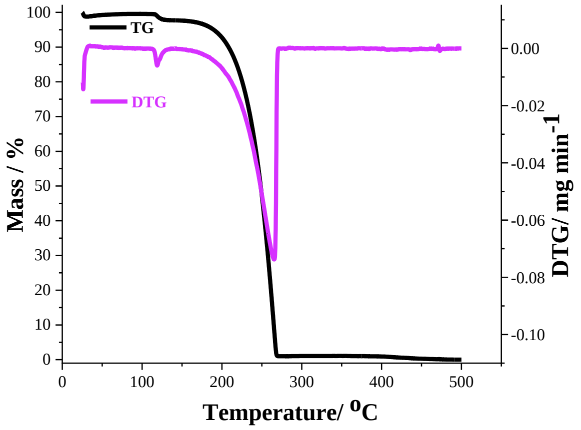

Figure 1. Thermoanalytical profile of pure MRTHH obtained in air atmosphere at β = 10 °C·min^{-1}

Acknowledgements: This work was funded and supported by the infrastructure of West University of Timisoara, postdoctoral grant 3869/0-1/26.01.2022.

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Preparation and instrumental screening of binary adducts containing moxonidine

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Monoxidine (MOX, Figure 1a) is an active pharmaceutical ingredient that acts as an agonists of α2-adrenergic receptors, lowering blood pressure (BP) through a reduction of brain sympathetic outflow [1]. According to reported data [2], MOX shows a moderate lipophilicity (reported computed logP data are 0.77, 1.60 and 1.31) and low water solubility (0.8 mg/mL), revealing that the biopharmaceutical profile can be improved by increasing the water solubility of this drug. Different strategies can be used in increasing the water solubility of drugs, including formation of cocrystal and salts. Having a pK_a value of 7.45 [2], MOX can form either salts or cocrystals with different coformers, depending of their pK_a values: if the difference in pK_a of the base and acid (ΔpK_a) is larger than 3, the formation of a salt is expected, while for $\Delta pKa < 3$, a co-crystal is expected [3]. Hydrated MOX saccharinate was reported in 2019 by Allada et al. [3], being the only literature reference that was found in this field.

In this study, we prepared five binary adducts containing MOX as active pharmaceutical ingredient and as coformers we used five dicarboxylic acids, generally recognized as safe (Figure 1b-f), namely malonic, DL-malic, succinic, glutaric and L-aspartic acids. Binary adducts were prepared in 1:1 molar ratio, using the slow solvent evaporation technique. For the characterization of obtained solids, FTIR and TG/DTG/DSC investigational tools were employed.

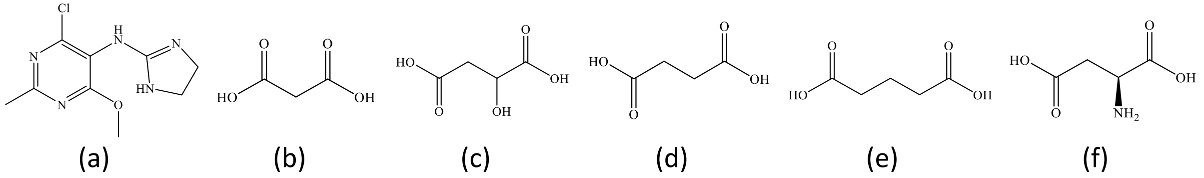

Figure 1. Structural formulas of active ingredient MOX (a) and coformers: (b) malonic acid; (c) DL-malic acid; (d) succinic acid; (e) glutaric acid and (f) aspartic acid.

Acknowledgments: This paper was financially supported by the Project "Network of excellence in applied research and innovation for doctoral and postdoctoral programs / InoHubDoc", project co-funded by the European Social Fund financing agreement no. POCU/993/6/13/153437.

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Microcalorimetric assessment of *Pseudomonas aeruginosa* growth under the effect of copper sulfate solutions

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With the rising use of metallic implants worldwide, bacterial infection has become a major concern due to its significant impact on patient health and national healthcare budgets. This study aimed to evaluate the sensitivity of *Pseudomonas aeruginosa*, a common bacterium responsible for implant surgery infections, to different concentrations of copper sulfate solutions.

Microcalorimetry is a highly sensitive experimental discipline that focuses on the study of the thermal effects of reactions or physical changes, in which the energy bring into play by any process or transformation occurs on a scale involving very small amounts of heat [1]. It arouses interest in biological sciences because heat flow is strongly related to the kinetics and thermodynamics of biological processes [2]. As all living things exchange heat as a result of their metabolism, the heat rate is an adequate measure of the metabolic activity of organisms and their constituent parts, cells and subcellular levels [3].

The bacteria strains utilized were *Pseudomonas aeruginosa*, ATCC 27853 and were acquired from the Spanish Type Culture Collection (CECT) and American Type Culture Collection (ATCC). The metallic solutions used were provided by the Laboratory of Chemistry and Applied Physics of the University of Vigo. Suspensions of 10^6 CFU/ml of *Pseudomonas aeruginosa* were mixed with different dissolutions of copper sulfate with concentrations of 0.75, 1.5, 3.0 mM and saturated. pH and temperature of the samples were measured using a basic 20+pHmeter before and after each experiment to determine the modification of the medium pH.

To determine the heat flow resulting from bacterial metabolism, at constant pressure, a Calvet microcalorimeter [4] has been used. The inner chamber of the microcalorimeter was set to the physiological temperature of the human body (309.65 K), and the heat output produced by bacteria metabolism was collected at intervals of 22.2 seconds for 48 hours using a data acquisition and processing system.

Equation 1 was used to calculate the amount of heat emitted (Q) throughout the culture time using the obtained data from the microcalorimeter.

$$Q = K \cdot A \qquad (1)$$

where A is the area under the curve (AUC), calculated by the trapezoidal method, and K is a constant whose value of 23.8 $J \cdot \mu V^{-1} \cdot h^{-1}$ was determined from the electrical calibration of the equipment.

Acknowledgements: We appreciate the financial support provided by project ED431C 2020/06 V055 of the Xunta de Galicia of Spain.

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Preliminary studies on local hemostatic desorption of carbazochrome loaded on chitosan/HA biocomposite

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Research suggests that nano- structured composites using biodegradable polymers and bioactive ceramics, such as biphasic calcium phosphates (BCP), possess the ability to simulate the surface and chemical properties of bone [1], [2]. By developing chitosan/BCP composite scaffolds with controlled morphology and rigidity we can increase mechanical properties of the scaffolds due to the fact that chitosan scaffolds alone cannot meet the requirements for hard tissue engineering applications. Also, by incorporation of a local hemostatic drug into the scaffolds we can cease the bleeding that occurs during most of the medical procedures [3].

This study consists in an initial adsorption of carbazochrome on chitosan scaffolds that contain dispersed hydroxyapatite particles. After the adsorption of the drug, the desorption of it was observed at different pH values depending on the possible applications of the drug-loaded scaffold. The scaffolds used were obtained by lyophilization. Chitosan solutions, with HA particles dispersed in, were froze beforehand lyophilization at -20˚C. At the end of lyophilization, some of the obtained scaffolds were treated with NaOH in order to stabilize the macrostructure.

Characterisation of the scaffolds and HA were done by means of SEM, FT-IR, TGA, EDX and DLS. UV-VIS spectroscopy was used for monitoring the adsorption and desorption of charbazocrome.

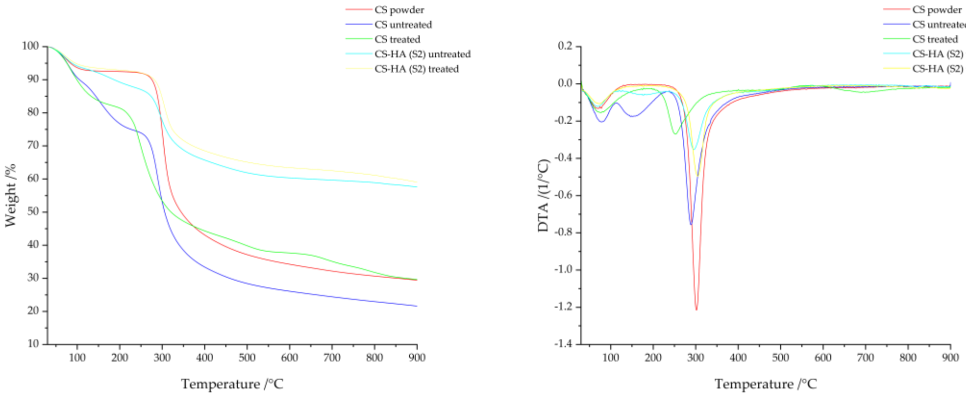

Fig. 1. TGA and DTA curves of chitosan scaffolds

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Preformulation studies of levonorgestrel

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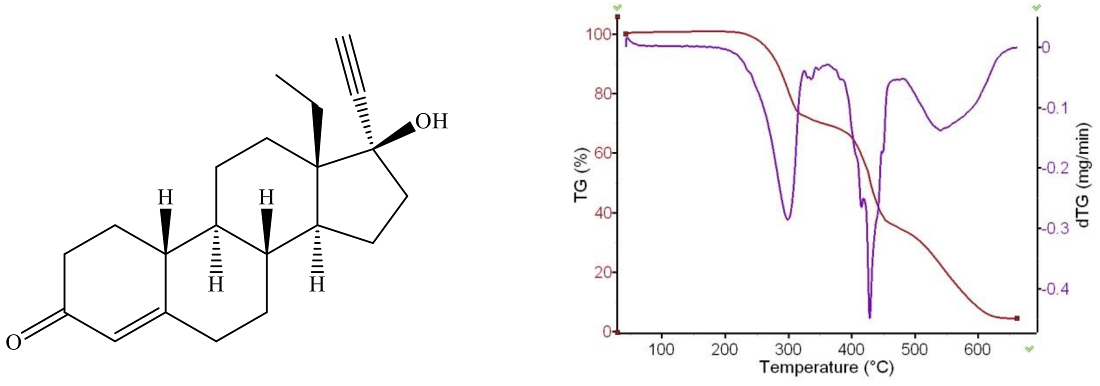
Levonorgestrel, also called the morning-after pill (LNG, chemical structure presented in figure 1a), is a synthetic progestogen presenting structural similarities with progesterone. It is mostly used for its contraceptive effect in the form of intrauterine devices, subcutaneous implants, patches, dragées, tablets, coated tablets and orodispersible tablets being the first contraceptive that was used containing only a derivative of progestogen [1,2]. Because of its wide use and various pharmaceutical formulations, it is necessary to evaluate the presence of any potential interactions between the active pharmaceutical ingredient and pharmaceutical excipients in the development of new formulation which possess increased stability and shelf-life, and an optimized biopharmaceutical profile.



(a) (b)

Figure 1. (a) Chemical structure of LNG (b) and thermal analysis (TG/DTG) data obtained at a heating rate $\beta = 10$ °C·min^{-1}

The purpose of this study was to assess if there are any interactions between LNG and several excipients used in the pharmaceutical field, having different roles in the development of solid formulations. The studies were carried out on binary mixtures containing LNG+excipient.

For the formation of the binary mixture, each excipient was used in a 1:1 mass ratio with the substance of pharmaceutical interest, LNG, and the instrumental investigation results were compared to the ones of pure LNG and excipients. Alongside thermal analysis (TG/DTG/HF) (figure 1b presents the TG and DTG curves recorded for LNG a heating rate of 10 °C·min^{-1} in dynamic air atmosphere), FTIR spectroscopy was also used to evaluate the occurrence of possible interactions.

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Study of thermophysical properties of marine peloids for applications in thalassotherapy

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Marine peloids [1] are ~~those~~ mixtures that include elements or substances from the sea among their components. One of the fundamental substances is seawater, which can vary in salinity depending on its origin. They may also contain microalgae [2] of marine origin that provide the peloid with biocompounds and facilitate its maturation over time.

The main use of marine peloids is thalassotherapy in its different forms of application: wraps, poultices or baths depending on the characteristics of its fluidity.

The thermophysical properties are of great importance in the field of thermotherapy [3] within thalassotherapy and this work will study the specific heat, density, thermal conductivity and thermal diffusivity.

The studied mixtures contain marine water with a salinity of 35 g/kg, microalgae (*Nannochlorosis sp* and *Tetraselmis sp*) and clays (bentonite and kaolin).

Specific heat has been determined using a CALVET microcalorimeter [4]. The density of the mixtures was carried out by a pycnometric method [5]. A Decagon KD2 Pro conductivity meter was used to measure thermal conductivity [6]. And finally, thermal diffusivity was calculated from the data obtained on thermal conductivity, density, and specific heat [7].

The data analysis of the thermophysical properties of the mixtures studied indicates that they are suitable for applications in Thalassotherapy.

Acknowledgements: We appreciate the financial support provided by the project ED431C 2020/06 V055 of the Xunta de Galicia of Spain.

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Helleborus purpurascens - Untargeted low-molecular metabolomic approach to antitumoral phytocarrier system based on silver nanoparticles

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Helleborus is a medicinal plant used in traditional medicine since ancient times.
Chemical screening and recent studies on pharmacological activity have demonstrated the main therapeutic properties for which the plant is recommended as a herbal remedy.
Silver nanoparticles (AgNPs) show remarkable biological activities and are used in numerous biological applications, although there are controversies regarding their toxicity.
This study reports for the first time the development of a easy, simple, target phyto-engineered system that cumulate the beneficial effects of *Helleborus purpurascens*, silver nanoparticles coated with chitosan.
The complete metabolites profile of Romanian wild-grown *Helleborus purpurascens* was carried out based on gas chromatography-mass spectrometry and mass spectrometry.
The morfo-structural properties of newly phyto-engineered system were investigated through FT-IR, XRD, UV-Vis, SEM-EDX, DLS techniques. The thermogravimetry analysis was performed to consider the thermic stability.
Antioxidant activity was evaluated using a combination of in vitro methods (total phenolic assay, 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging assay and total antioxidant capacity (TAC).
The results of the antioxidants assays showed that the phyto-engineered system shows higher antioxidant properties than its components: hellebore and AgNPs.

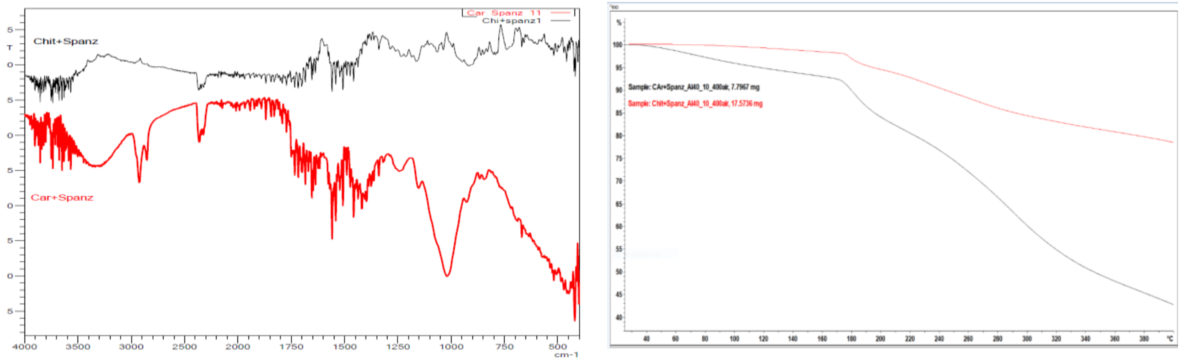

Figure 1. TG and FTIR analysis of Samples with *Helleborus purpurascens*

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Compatibility study between active substances from the sartans class with various excipients using multiple technics

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Medicines from the sartan class (Irbesartan, Losartan, azilsartan and valsartan) are used to treat patients with hypertension (high blood pressure) and those with certain heart or kidney diseases. The drugs work by blocking the action of angiotensin II, a hormone that constricts blood vessels and causes blood pressure to rise.

In order to successfully design a new pharmaceutical form, one of the main considerations in the beginning stages of the process is represented by the compatibility anhydrous lactose, talc, magnesium stearat, colloidal silica, polyvinylpyrrolidone K30, starch, Manitol. The binary mixtures were prepared by trituration of equal masses of Sartans and each excipient in agate mortars for 5 min. The solid samples were then sieved and transferred in sealed vials and kept under ambient conditions until analyses were carried out. Thermal induces interaction for binary mixture between Sartans and excipients was studied using a TG/DTG/HF (see Fig. 1) and FTIR study.

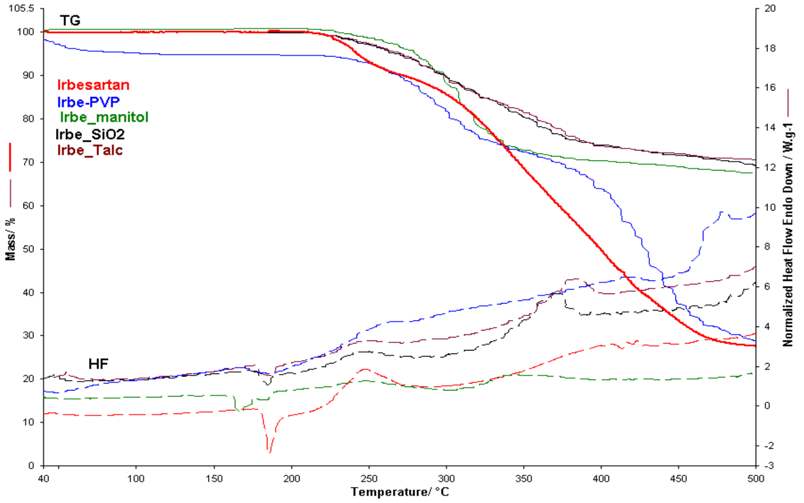

Fig.1: Comparative curves TG/HF for Irbesartan and binary mixture with PVP, Manitol, Talc, SiO_2

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Thin polysaccharide films as carriers for local anesthetic and anti-inflammatory drugs

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Researchers in the biomedical field, especially those involved in drug delivery, have been attracted to polysaccharides due to their outstanding properties [1]. The most prevalent naturally occurring macromolecular polymers are polysaccharides since they can be obtained from diverse renewable sources which include algae, plants, and microorganisms (fungi and bacteria). The most common method of administering local anesthetics, with the aim of relieving local pain, involves injection at or near the painful site. That is why this study aimed to obtain polysaccharide membranes as carriers for local anesthetics, and anti-inflammatory substances for a possible transdermal delivery of these active principles, which could improve compliance and reduce patients' general discomfort. The study will use TG, DSC (Figure 1), UV-Vis, SEM-EDS and FTIR analyses, wanting to highlight the ease of obtaining polysaccharide membranes with local anesthetics and anti-inflammatory agents and provide relevant information that can contribute to the selection of "good membrane candidate" for potential use in transdermal delivery.

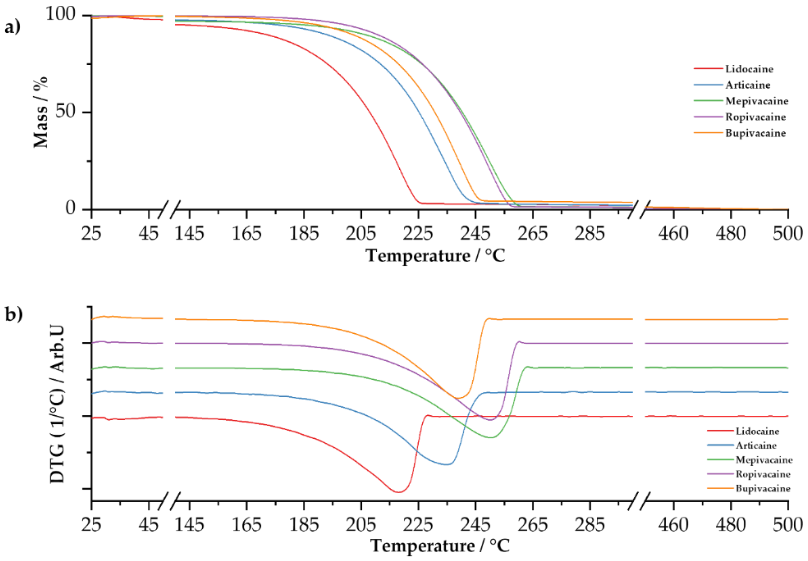

Figure 1. *TG (a) and DTG (b) curves for local anesthetic drugs.*

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Application of thermal analysis techniques in the thermo-chemical recycling of multilayered food packaging

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Multilayered packages -though one of the most common packaging waste - is quite difficult to recycle. This is because their multi-layered nature makes it difficult to process them conventionally with a single method. It is therefore necessary to find effective separation and degradation techniques for the recycling of packaging including different materials, such as polymers, aluminum and/or paper.

In this context, the aim of this research was to find effective methods for the recycling of multilayer packaging used in foods, such as in milk or fresh juice bottles. Introductory clues are provided on the necessity of waste utilization, composition and recycling methods of such packaging in the literature as well as on the analysis of the principles of the analytical and specifically thermal techniques used to record the properties of the material layers. On the other hand, the research part focused on finding the most suitable conditions for the separation of the layers of the packages and their subsequent thermal degradation. The separation of the layers occurred by water treatment in an alkaline environment and then identification and analysis of the separation products took place via FT-IR, TGA and DSC. Using the procedure the paper and aluminum layers were successfully separated from the main polymer part. In order to identify the type of the polymer, TGA and DSC techniques were used. It was thus revealed that the polymer layered consisted of low density polyethylene (LDPE). In order to study the thermo-chemical recycling of the plastic part recovered, thermal pyrolysis was applied to the isolated polymer layers (LDPE) and analysis of the polymer layer fragments was carried out via GC / MS in line with the pyrolizer. A typical pyrogram is shown in Figure 1 were it was clear that a mixture of hydrocarbons was produced from C_3 to C_{25}.

Based on the previous it was concluded that the temperature applied in the water treatment processes does not affect the properties of the degraded PE. LDPE exhibits T_c and T_m slightly larger than virgin commercial LDPE – possibly due to the addition of additives, which make it more resistant to thermal processes. On the other hand, the cracking process results in useful hydrocarbons as well as substituted compounds that can be used as secondary bio-fuels.

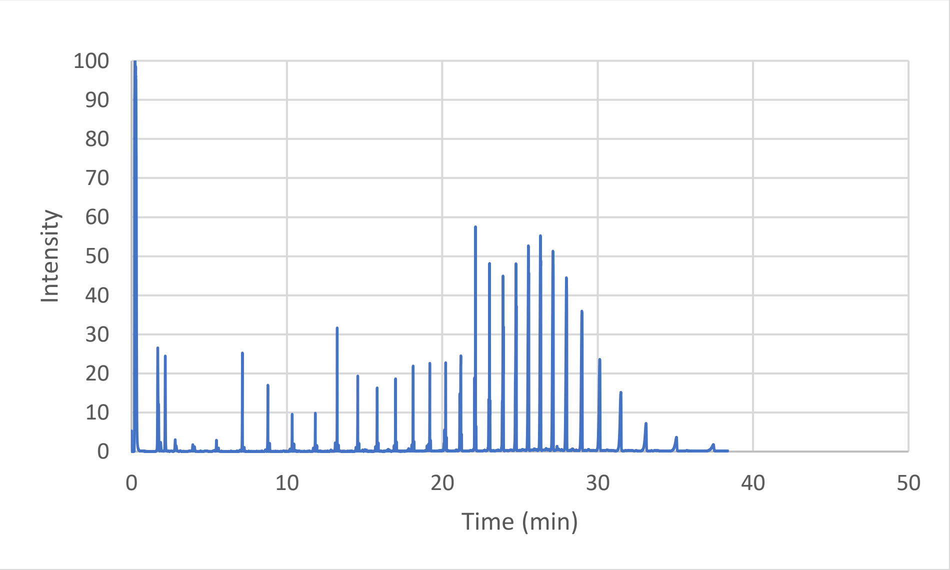

Figure 1: GC/MS chromatogram obtained after pyrolysis of the plastic part of the multilayer packaging showing the production of a mixture of hydrocarbons.

Thermal behavior of polyhydroxyurethanes vitrimers from Brazilian biomass

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Although carbon dioxide (CO_2) occurs naturally, its emissions have been increasing due to anthropogenic activities, and its increasing atmospheric concentration levels are causing a greenhouse effect. In efforts to develop new carbon dioxide utilization (CDU) methodologies, the catalyzed reaction of CO_2 with epoxidized vegetable oil, obtained from Brazilian Macaw oil and Baru oil, to form carbonated oils (CMWO and CBO) for novel and sustainable monomers was explored [1]. For the polymerization reaction, three diamines were selected as cross-linkers: 1,6-diaminohexane (HDA), lysine (LYS), and 4,4’-methylenebis(cyclohexylamine) (MBCA). CBO or CMWO were cured with amine cross-linker in equimolar quantity, considering the number of carbonate and amine groups. The mixture was cured at 140 °C for 72 hours. All weldable and renewable polymers underwent thermal characterizations (TGA, DSC and DMA). All the polymers presented thermal stability (T_s), withstanding temperatures above 200 °C. DSC analyses indicated events related to the glass transition (T_g) and the topology-freezing transition (T_v), permitting an exchange of bonds and hence a welding process by using red light (660 nm). Each property regarding mechanical and thermal analyses can be seen in Table 3. DSC and DMA curves are presented in Figure 1.

Table 1. Thermal, mechanical and cross-linking properties of the polymers

	CMWO			CBO		
	HDA	LYS	MBCA	HDA	LYS	MBCA
T_s – *TG (°C)*	231.0	204.0	249.1	231.0	204.0	249.0
T_g – DSC (°C)	-11.5	9.4	-0.8	0.3	12.2	-0.8
T_v – DSC (°C)	46.6	46.9	50.8	60.4	52.5	62.7
tan-δ (°C)	1.7	-3.5	-	0.8	10.2	-
Stress (MPa)	1.6	1.5	1.6	1.5	1.6	1.6
Strain (%)	61.3	5.0	24.3	44.6	20.3	36.4
Cross-linking Density (mol m^{-3})	91.8	159.1	-	24.3	148.7	-

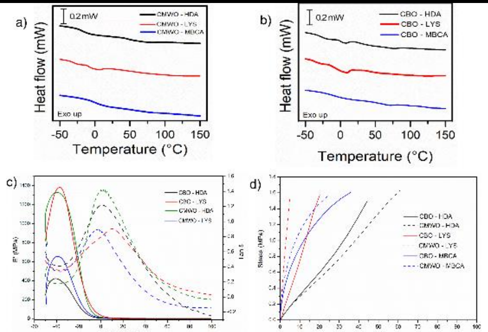

Figure 1. a) DSC curves for CMWO polymers; b) DSC curves for CBO polymers; c) DMA results for the CMWO and CBO polymers showing storage modulus – E’ (dashed line) and *tan-*δ (solid line); and d) stress-strain experiment results for each polymer.

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[1] Alarcon, R.T.; Lamb, K.J; Cavalheiro, E.T.G; North, M.; Bannach, G. *Journal Applied Polymer Science* **2023,** e53962.

Thermal behaviour of renewable copolymers from maleinized and carbonated vegetable oil

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Renewable polymers from maleinized or carbonated oils are well known in the literature [1]. However, for the first time a copolymer was synthesized using both oil derivatives and five different amines as cross-linkers (Hexanediamide-HDA, Lysine-LYS, 4,4'-Diaminodiphenylmethane-DAM, Melamine-MEL, and Tris(2-aminoethyl)amine-TAA. The macaw palm oil (*Acrocomia aculeata*) is part of Brazilian biomass and was selected due to its higher production when compared to soybean oil. Macaw palm produces 4,000 L of oil per hectare of crop; this is much higher than the soybean, which produces only 500 L per hectare [2]. Carbonated macaw oil was reacted with an amine cross-linker, thereafter, the maleinized macaw oil was added in the reaction system. These mixtures were cured in a silicon tray at 110 °C for 12 hours. All renewable polymers underwent thermal characterization (TGA, DSC and DMA). The thermal stability varied from 138.43 °C to 173.66 °C depending on the cross-linker. The glass transition temperature (T_g) obtained from DSC curve were similar to *tan-δ* obtained by DMA-relaxation measurement. The DMA-relaxation curve for DAM polymer was not obtained, because of its higher vitreous character. These materials are rubber-like polymers, and do not support higher stresses; however, they showed good strains. Each property regarding mechanical and thermal analyses can be seen in Table 3. DSC, relaxation measurement, stress x strain curves, and cross-linking density are found in Figure 1.

Table 1. Thermal, mechanical and cross-linking properties of the polymers

	P-HDA	P-LYS	P-DAM	P-MEL	P-TAA
T_s – TG (°C)	173.66	138.43	162.06	162.71	170.35
T_g – DSC (°C)	3.63	4.47	-5.18	-15.05	5.07
Tan-δ (°C)	4.22	14.69	-	-9.99	6.94
Stress (MPa)	0.07	0.06	0.13	0.04	0.09
Strain (%)	34.73	73.75	43.38	74.75	66.37
Cross-linking Density (mol m^{-3})	32.4	73.8	-	50.3	30.6

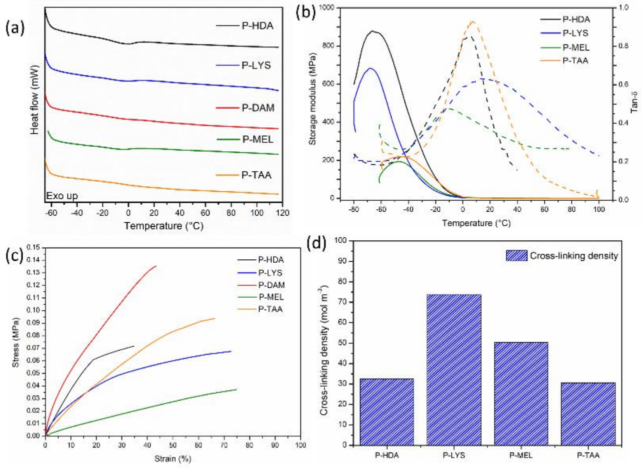

Figure 1. a) DSC curves b) DMA relaxation results showing storage modulus – E' (solid line) and *tan-δ* (dashed line); c) stress-strain results; and d) cross-link density results

Acknowledgements: The authors wish to thank São Paulo Research Foundation - FAPESP (grant 2019/22217-8, 2021/14879-0, and 2021/02152-9).

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A new biobased polymer with potential vitrimers properties

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Polymeric materials are an important material class for almost all society fields, as a result, its global consumption and therefore production have increased year by year. However, most of them are derived from non-renewable sources, thus, renewable polymers, also called biopolymers, have been emerging as alternative materials. However, to expand their application, their thermal and mechanical properties must be improved in comparison with those from non-renewable sources. Based on this, and in the present work demonstrate the synthesis of a new polymer derived from maleinized grape seed oil (MGSO), which was synthetized as described in a previous paper [1] and 2-Hydroxyethyl disulfide (2HD, Sigma-Aldrich, <=100%). Both monomers were mixed in equimolar proportions and then cured in an oven at 150 ºC and the reaction progress was monitored by gel content (GC%). The simultaneous thermogravimetric-differential thermal analysis (TG-DTA) and dynamic mechanical analysis (DMA) were performed following the same conditions described in the literature [2]. Based on CG% evolution over time (Figure 1-a) it is observed that until 8 h of reaction the CG% increased, after this, no significant change is observed. Aiming to investigate the effect of CG% in the thermal properties of polymer three samples were analyzed by TG-DTA, and their results curves can be seen in Figure 1-b. The thermal profile is very similar among samples; however, the sample cured for 5 h presented thermal stability equal to 190 ºC, while the other cured at 8 and 12 h were thermal stability up to 210 and 212 ºC. Then, 8 h was choose as the ideal time of polymerization. The final polymer exhibited a glass transition at -5.0 ºC, as can be seen in they tanδ curve (Figure 1-c). The final polymer will be teste as a vitrimers material.

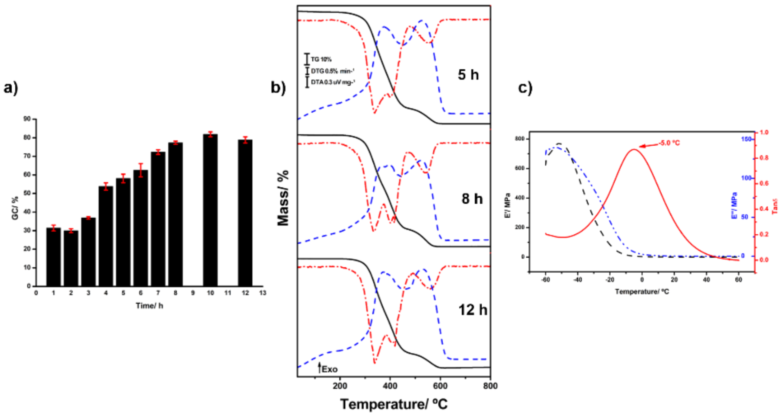

Figure 1- *a)* Gel content evaluation caption of polymerization, *b)* TG/DTG-DTA curves and *c)* Storage (E'), loss (E'') modules and tanδ curves.

Acknowledgements: The authors thank FAPESP (grants: 2021/02152–9; 2021/14879–0; 2022/03489-0), CNPq (grants 150233/2022-1 and 303247/2021-5), for financial support.

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Thermal characterization of a new rosin acids derivative

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Rosin acids (AR) are biomasses from Pinus and can be extracted by distillation from resin (obtained from Resin Industry) or from black liquor (obtained from Pulp and Paper Industry). AR can be considered as a cheap and renewable source in synthesis of polymeric materials [1]; however, one of problems in its use, is the necessity of purification to obtain the abietic or dehydroabietic acids, which are the most rosin acids used in material synthesis [2]. In the present work, we have used AR without any purification, by reacting it with melamine (MEL). By their TG/DTG-DTA curves (Figure 1-a), it is observed that the thermal profile of product is different from the precursors. MEL and AR are thermal stable until 250 ºC and 201 ºC, respectively. In the other hand, the product is thermal stable until 150 ºC, presenting a small mass loss of 15.48% until 267 ºC, which is the main difference of product. The product also exhibited a different color under ambient light, and emits in a different wavelength, as can be seen in Figure 1-b. Comparing the DSC curves of AR and product (Figure 1-c), it is seemed that the product presents a glass transition (T_g) in higher temperature (T_g = 40.6 ºC, using heating ratio equal to 20 ºC min^{-1}) than the AR (T_g = 59.6 ºC, using heating ratio equal to 20 ºC min^{-1}). These results suggest that the new product was successfully obtained, which was corroborated by NMR.

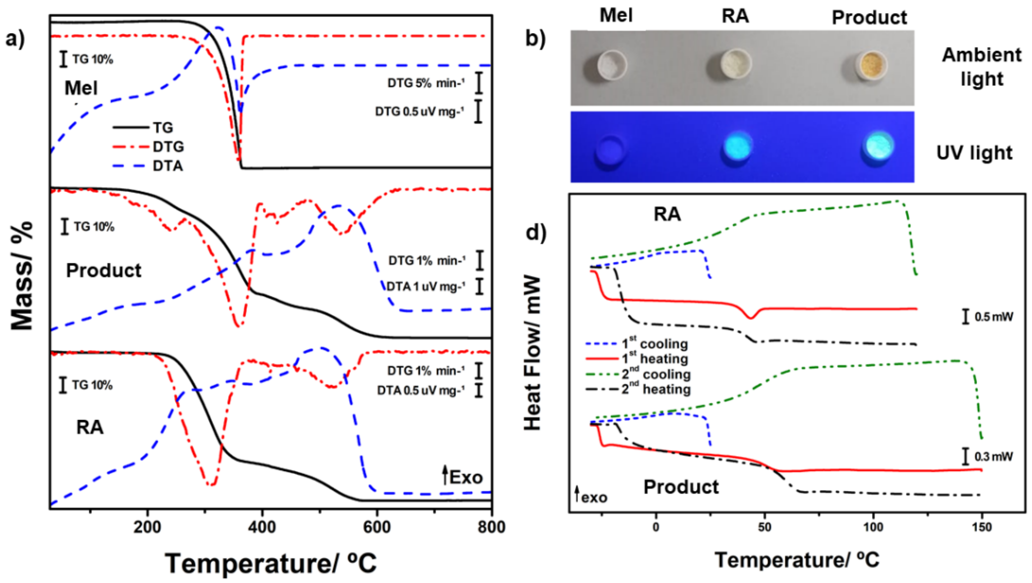

Figure 1- *a)* TG/DTG-DTA curves of melamine (MEL), rosin acids (RA), and product obtained after their reaction, *b)* reactants and product under ambient and UV lights, and *c)* DSC curves of RA and product, and

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In-situ monitoring the curing of pMDI with soybean protein

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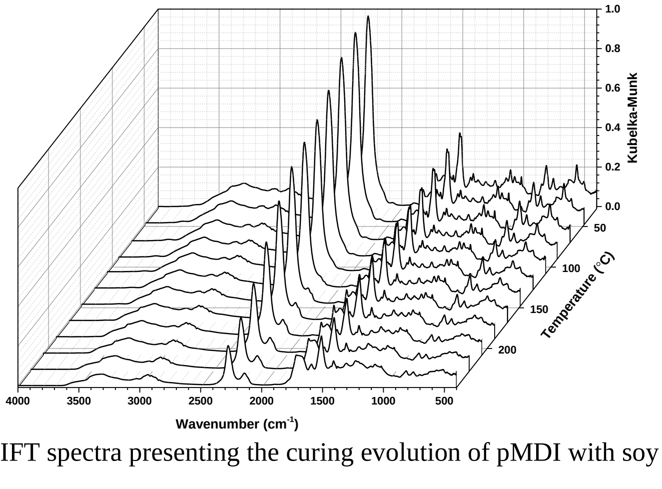
Polymeric diphenylmethane diisocyanate (pMDI) is a resin that shows great promise as an adhesive for wood and wood-composite applications. This formaldehyde-free resin offers several advantages, including fast curing time and the ability to withstand moisture. In this study, we explore how pMDI cures when it interacts with soybean protein. Soybean protein, which is a commonly extracted by-product during the production of soybean oil, is chosen to act as the filler in order to align with circular economy principles and to reduce cost expenses. By investigating the interaction between pMDI and soybean protein, we aim to gain insights into the potential of this composite material for use in wood and wood-composite applications.

To investigate the curing behavior of pMDI and soybean protein composites, various weight ratios of soybean protein (5, 10, 20, 30, 40, and 50%) were mechanically mixed with neat pMDI. The curing process was analyzed using differential scanning calorimetry (DSC) and conventional attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. In addition, the curing process was also observed *in-situ* using diffuse reflectance FTIR (DRIFT) mode with a gas-purged high-temperature environmental chamber. These analytical techniques provided insights into the evolution of the curing process of pMDI and soybean protein composites, allowing for a better understanding of the potential of this material for use in wood and wood-composite applications.

This study explores the ability of diffuse reflectance FTIR (DRIFT) spectroscopy to follow the in-situ curing of resins. To address measurement issues stemming from contamination of the environmental chamber's sealing window, various sample crucibles and gas flows were employed. The analysis of the resulting data revealed a decrease in isocyanate and hydroxyl groups at 2274 and 3300 cm^{-1}, respectively, indicating the successful curing of pMDI with soybean protein. Furthermore, a new band at 2140 cm^{-1} emerged, suggesting the formation of a carbodiimide group. It is worth noting that, even after the curing process, the FTIR band at 2274 cm^{-1} did not disappear entirely for every pMDI to soybean protein ratio. This finding implies that isocyanate groups remain available for reaction with wood, a crucial factor in the production of wood composites.



In-situ DRIFT spectra presenting the curing evolution of pMDI with soy protein.

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Rheological and thermal characterization of Funori gel

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The thermal properties and rheology of funori, the polysaccharide derived from red algae genus *Gloiopeltis,* were investigated in this study (Figure 1). It is well known that the presence of counter ions can remarkably influence the rheology of several anionic polysaccharides [1]. For this reason, the aim of this work is to study the effects of the addition of $BaCl_2$ solutions at different molarities (0.05 M, 0.1 M, 0.2 M, 0.3 M, 0.5 M) on 1% w/w Funori solutions. The samples were characterized by differential scanning calorimetry (DSC) and dynamic rheometry at different temperatures. Funori gel formation is a slow process that is highly dependent both from the amount of cations contained and cooling processes [2]. $BaCl_2$ solutions exhibited a strong effect on Funori gelling formation: with enhancing salt concentration, G' and G'' values increased in the selected concentration range (up to 0.2 M) but then gradually decreased with new additions in the salt content. Apllication for surface cleaning in Cultural Heritage are foreseen.

Figure 1. Funori gel − made with Funori 1% w/w and $BaCl_2$ 0.2 M – Tube inversion test

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Polymer/surfactant hydrogels for drug delivery: thermal and rheological characterization

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Hydrogel systems are highly versatile colloidal platforms widely used for drug delivery, especially in, but not limited to, dermal and transdermal therapies. Some of these hydrogels are aptly named "*smart*" delivery systems, as they are responsive to certain stimuli such as pH, light or temperature, only releasing their cargo when specific conditions are met and the stimulus (stimuli) triggered [1]. Thermoresponsive hydrogels undergo physicochemical changes, such as phase transitions, with changes in temperature [2]. In this work, we developed a hybrid polymer/surfactant hydrogel system based on the poloxamer F127 and lysine-derived surfactants developed by our research group, 14Lys10 and 10Lys14 [3, 4]. Both components of this system are thermosensitive and suffer phase transitions with temperature increase, which, in some instances, result in significant microstructural and rheological changes of the hybrid gel. To study these transitions, we utilized a combination of differential scanning microcalorimetry (microDSC), light microscopy and rheometry to fully characterize the hydrogels and understand how they might be utilized for drug delivery applications.

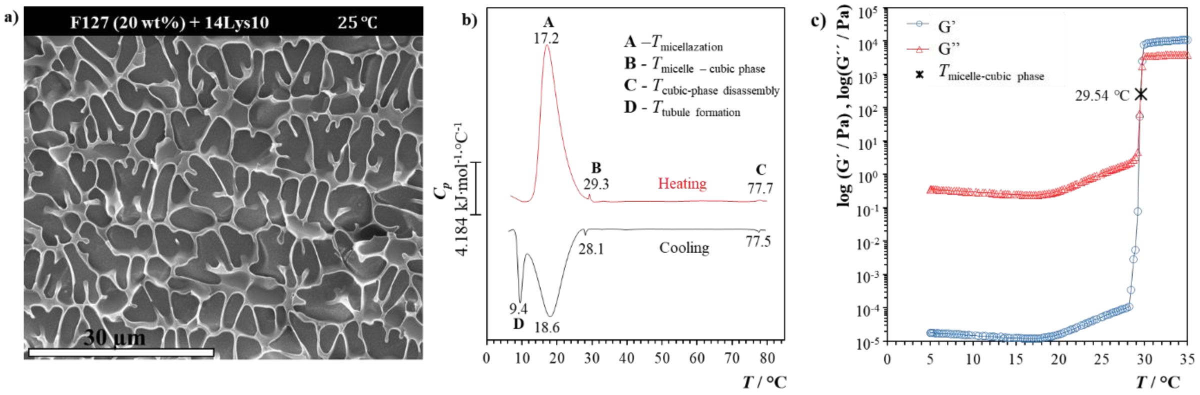

Figure 1: Structural, thermal and rheological characterization of the F127/14Lys10 hydrogel: a) cryo-SEM imaging of the hydrogel microstructure, b) DSC thermogram showing the various phase transition peaks; c) changes in rheological properties (loss and storage moduli) with increasing temperature.

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UV aging effects on PLA-based composite materials with wastes from olive-oil production

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Every year more than 2.000.000 tons of olive-oil is produced in Europe, which is 2/3 of world's production. The wastes generated from these procedures are aimed to be valorized by incorporating them in polymer matrix. Poly(lactic acid) (PLA) is a biobased polyester with multiple applications, especially in the fields of packaging and medicine. However, its drawbacks, such as brittleness, sensitivity to temperature, and slow degradation limit its massive production. To tune the properties of PLA, olive stones were incorporated in its polymer matrix using melt-mixing. In addition, a chain-extender (Joncryl 4400) was added in order to increase the surface adhesion between the polymer and the filler. The prepared composite materials were further examined during aging under artificial weathering environment for different durations. For this purpose, ultraviolet (UV) chamber was used as accelerated aging technique. The artificial photodegradation mechanism was explored by a combination of FTIR, DSC, SEM and mechanical properties evaluation, providing a better understanding of UV impact on commercially polymers. The results of this work are very promising towards their use in plywoods.

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Ceramifiable door seals with reduced fire hazard and reduced emission of gaseous organic compounds from PAHS and PCDDS/FS group

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Development ceramifiable composites has grown significantly since beginning of the 21st century due to increasing demands originating from fire protection regulations for public property and high-rise buildings.

Ceramisation is the process of producing a rigid, durable ceramic coating on the surface of a polymer composite when its exposed to elevated temperature or fire. The ceramic layer produced on the surface of the material effectively limits the spread of flame and diffusion oxygen into the inner layers of composite.

Ceramifiable composites are key materials for the manufacturing of cables sustaining electrical circuit integrity in case of fire and in the last years to the production non-flammable door seal dedicated to the fire protection doors.

Present work demonstrated that the silicone rubber composites containing zinc borate, glass frits, magnesium hydroxide as well as melamine cyanurate not only indicate low flammability in comparison to classical composites made from silicone rubber, but also these materials, in the fire conditions, emits little amount of toxic compounds from the group of PCDDs/Fs and PAHs.

Dioxin, PCDDs/Fs, have a hormone-like effect due to their chemical structure, which is similar to steroid hormones. In addition, the negative effect of dioxin on the human immune system was proven. Dioxin, depressing immune resistance, may lead to an increase in susceptibility to various types of infections, thyroid disease and increase risk of cancer. The carcinogenic effect of PAHs, especially benzo(a)pyrene, has been proven and is currently beyond doubt.

It should be also emphasis that ceramifiable composites have satisfactory mechanical properties, what's allows using them to production seals dedicated to the fire protection doors.

Keywords: door seal, ceramifiable, toxicity, PCDDs/Fs, PAH.

Bacterial adhesion on a synthetic polymer matrix of poly(vinyl alcohol)

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Poly(vinyl alcohol) (PVA) is a polymer whose mechanical properties depend on its molecular weight and degree of hydrolysis. This polymer, due to its physicochemical properties and significantly porous structure, is a potentially optimal matrix for the immoblilization of bacterial cells on its surface. This is important due to the potential use of PVA as a carrier of bacteria for biocementation and bioremediation of soil or water. One such bacteria is *Viridibacillus arvi* U1, which is characterized by efficiency of its action in bio-cementation processes. In addition, this material can be easily modified or mixed with other polymers to create a composite with the interesting properties.

Properties of the PVA matrix has been determine with the use thermogravimetric (TG), Fourier transform infrared spectroscopy (FTIR) as well as coupled TG-gas analyzer method (toxicometric indexes).

The degree of bacterial adhesion to the material was estimated with the UV spectroscopy method.

Keywords: Poly(vinyl alcohol), PVA, TG, thermogravimetry, FTIR, bacteria adhesion, biofilm

Sputter deposition of metal nanoparticles in ionic liquid films obtained via thermal evaporation

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The aim of this study was to investigate the sputter deposition of metal nanoparticles (silver and gold) onto thin films of various imidazolium-based ionic liquids (ILs). A diverse range of ILs with different anions, including acetate, trifluoroacetate, triflate, and bis(trifluoromethylsulfonyl)imide, was explored. Additionally, the study examined the impact of modifying the alkyl chain length and symmetry of the cationic moieties. The specific combinations of ILs studied included $[C_2C_1im][Ac]$, $[C_2C_1im][TFA]$, $[C_2C_1im][OTF]$, $[C_2C_1im][NTf_2]$, $[C_4C_1im][NTf_2]$, $[C_8C_1im][NTf_2]$, $[C_2C_2im][NTf_2]$, and $[C_5C_5im][NTf_2]$. The ILs serve not only as media to capture the metal atoms but also as stabilizers during the formation of nanoparticles, as they tend to form aggregates of small and uniform sizes [1-3].

Ionic liquid (IL) films of different thicknesses were obtained in the form of microdroplets through vacuum thermal evaporation. The IL films were deposited onto glass substrates coated with indium tin oxide. The process of thermal evaporation was conducted by carefully controlling the effusion temperature, deposition rate, and deposition time. The use of Knudsen cells as evaporation sources provided a means to achieve precise and reproducible control over the mass flow rate [4,5]. The sputtering process of the metals onto ILs when conducted simultaneously with argon plasma promoted the coalescence of microdroplets of ILs and the incorporation and stabilization of silver (AgNPs) and gold nanoparticles (AuNPs) in the coalesced IL films. The formation/stabilization of metal nanoparticles into the ionic liquid (IL) films was confirmed through high-resolution scanning electron microscopy (SEM) and UV-Vis spectroscopy [1].

Based on the experimental findings, the investigated IL films exhibited higher suitability as capture media for the formation and stabilization of AgNPs. On the other hand, controlling the conditions to favor the formation of AuNPs proved to be more challenging. The gold particles tended to aggregate and form a thin film on the surface of the IL film. Considering the formation of AgNPs it was observed that IL films with greater thicknesses provided a more favorable environment for the formation of small metal particles. Among the ILs investigated, those containing longer alkyl chains in the cation and the anion NTf_2 demonstrated better results in terms of AgNPs formation. Additionally, ILs containing the acetate anion were found to be particularly conducive to the formation of large silver aggregates. Of all the ILs studied, $[C_5C_5im][NTf_2]$ showed particular promise for the stabilization of AgNPs. When exposed to argon plasma and Ag bombardment, larger IL droplets acted as confining agents, preventing the aggregation of AgNPs and facilitating their stabilization within the IL films [1].

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Spectroscopic and thermoanalytical studies of agents for chemo-mechanical caries removal

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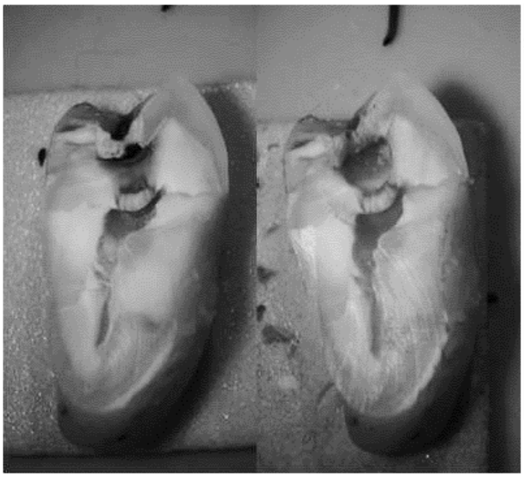
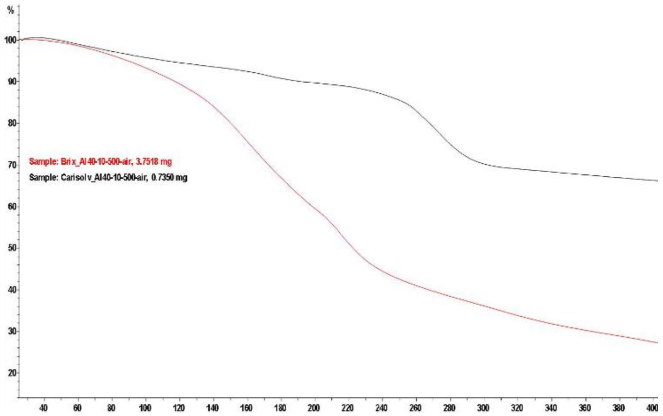
The chemical-mechanical removal of dental caries has attracted the interest of the scientific world in recent years in connection with the increasing demand for minimally invasive methods in dentistry, including the atraumatic restorative technique (ART), which is used mainly in children [1].
Carisolv (RLS Global AB, Sweden) is a caries removal product first launched in Sweden in 1998. The system consists of two solutions mixed together to form a gel containing sodium hypochlorite, sodium chloride, carboxymethylcellulose, and three amino acids [2].
BRIX3000 (Brix SRL, Argentina), a sodium hypochlorite-free agent, was first produced in Argentina and launched in 2016. It is an enzymatic gel that initiates proteolysis of collagen from affected dentin. Its active ingredient, papain, is an endoprotein from green papaya (*Carica papaya*) that resembles human pepsin and has bactericidal, bacteriostatic and anti-inflammatory effects [3].
The study proposes to analyze by combined techniques (FTIR, DSC, TG, SEM, RAMAN) the physicochemical properties of the two chemical agents, by treating caries on extracted teeth and evaluating how they act (evaluation by microscopy, VistaCam) to achive a comparison between the two substances. The correlation of the physicochemical properties with their comparative efficacy would allow to formulate some conclusions regarding the ideal choice of the chemical-mechanical agent for caries treatment.



Untreated tooth (left) and tooth treated with BRIX 3000 (right)



TG of caries removal product BRIX3000 and Carisolv

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Impact of deposition rate on the morphology of pure and mixed ionic liquids via thermal evaporation

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The wetting behavior of ionic liquids (ILs) on the mesoscopic scale significantly impacts a wide range of scientific fields and technologies [1-4]. Particularly under vacuum conditions, these materials exhibit unique characteristics [4]. This study explores the effect of deposition rate on the nucleation, droplet formation, and droplet spreading of IL films obtained through thermal evaporation [5]. Four ILs were examined, consisting of an alkylimidazolium cation (C_nC_1im) paired with either bis(trifluoromethylsulfonyl)imide (NTf_2) or triflate (OTf) as the anion. Each IL sample was simultaneously deposited on indium tin oxide (ITO) and silver (Ag) surfaces. Additionally, the co-evaporation of [C_2C_1im][OTf] and [C_8C_1im][OTF] was investigated, varying the film composition and thickness. The formation of an ionic liquid mixture film was achieved by simultaneously depositing the pure ILs using a customized physical vapor deposition (PVD) technique [6,7]. The mass flow rate was reproducibly controlled using Knudsen cells as evaporation sources. The film morphology was evaluated using scanning electron microscopy (SEM).

The wettability of the substrates by the pure ILs was significantly affected by changes in the mass flow rate. Specifically, the results indicated that an increase in the deposition rate intensified the droplet coalescence mechanisms on the ITO surface, which is characteristic of higher surface diffusion. Conversely, a smaller impact was observed on the Ag surface due to the strong adhesion between the ILs and the metallic film. Droplets from long-chain ILs deposited on ITO surfaces showed intensified coalescence, irrespective of the deposition rate [5]. Regarding the ionic liquid mixtures, we examined the adsorption, nucleation, and growth of mixture films containing C_2C_1im and C_8C_1im at different proportions. Our findings revealed that the enrichment of C_8C_1im in the mixture enhanced droplet coalescence mechanisms on ITO surfaces. These systems offer greater potential for targeted applications of ionic liquid films and present a whole new set of fundamental scientific inquiries.

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Recycling volcanic fly ashes through geopolymers: synthesis and characterization

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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.

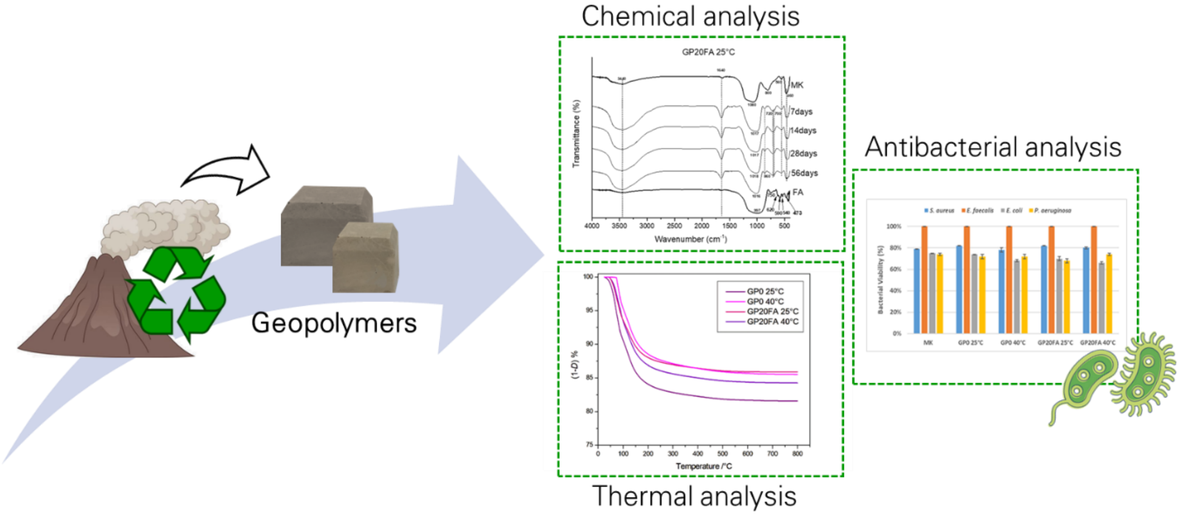

Figure 1: graphical representation of the study performed.

Acknowledgements: This work was partly supported by "SCAVENGE" financed by Università degli Studi della Campania Luigi Vanvitelli in the framework of "Piano Strategico di Ateneo 2021-2023 - Azione strate-gica R1.S2". The authors would also like to thank Prochin Italia Prodotti Chimici Industriali Srl (Italy) for donating the sodium silicate used in this work.

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Thermal stability of thermoelectric Cr-substituted and Fe-substituted Higher Manganese Silicides

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Higher manganese silicides ($MnSi_{\sim 1.75}$, HMS) are considered among the most promising alternative p-type materials for mid- to high-temperature thermoelectric applications. HMS are economic and eco-friendly, being composed of high-abundant and non-toxic elements, and they exhibit good mechanical and chemical stability. Their thermoelectric performance is enhanced through doping, reaching the maximum figure of merit ZT=1.05 [1]. High oxidation resistance and good thermal stability are highly desired properties for thermoelectric materials, especially in the temperature region where their figure of merit peaks, in order to maintain their performance at its highest potential.

The current study focuses on the oxidation behavior and thermal stability of HMS-based materials synthesized by pack cementation. More specifically, Cr-substituted and Fe-substituted HMS powders were subjected to non-isothermal heating in air from room temperature up to 1200 °C. Isothermal tests of 12 h were also performed in air at 540 °C or 560 °C for selected Cr-substituted or Fe-substituted HMS samples, respectively. Finally, the selected HMS-based powders were subjected to thermal cycles in the range of RT-550 °C and RT-560 °C for Cr and Fe addition, respectively, aiming to examine the possible degradation that the materials would undergo operating in a thermoelectric application. The tests were carried out using a thermogravimetric (TG) setup. All the powders were characterized regarding their structure and phase composition before and after oxidation by X-Ray diffraction analysis (XRD), while the morphology and chemical composition were investigated using a scanning electron microscope (SEM) equipped with an EDS analyzer. The HMS-based materials exhibit remarkable oxidation resistance in the temperature region of maximum thermoelectric performance, as well as sufficient thermal stability during the cyclic procedure.

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Thermo-kinetic behavior of Ce-doped 45S5 bioactive glass

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Thermo-kinetic behavior of Ce-doped 45S5 bioactive glass [1, 2] (addition of CeO_2 up to 1.5 mol.%) [3] was explored by means of calorimetry and thermomechanical analysis. The apparent activation energy of structural relaxation was estimated to vary in the 540 – 670 $kJ\cdot mol^{-1}$ range. The relaxation process exhibited broad distribution of relaxation times and the relaxation motions were found to only weakly depend on the material's structure. The activation energy of viscous flow was found to vary in the 585 – 615 $kJ\cdot mol^{-1}$ range; the viscosity itself showed Arrhenian behavior within 10^7 – 10^{11} Pa·s. Thermal stability of the glasses was found to be non-monotonous and generally very low, with the most stable glass composition being 45S5 + 0.5 mol.% CeO_2. The cold crystallization [4] was found to behave autocatalytically, with the activation energy decreasing from 360 to 310 $kJ\cdot mol^{-1}$ with the gradual addition of CeO_2. While the bulk glasses were crystallization-resistant up to 620 °C, the powdered material with CeO_2 content $\geq$ 1 mol.% was predicted to crystallize even at temperatures slightly above the glass transition temperature.

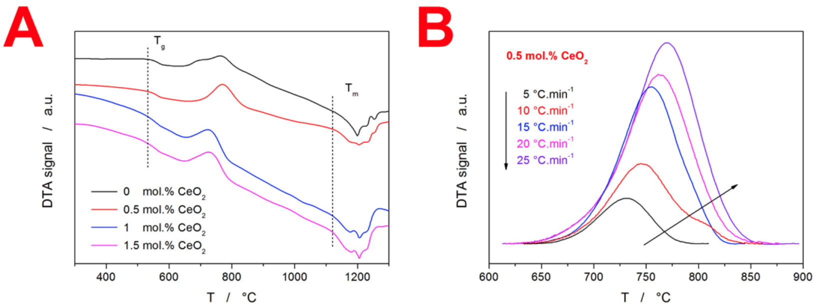

Figure 1.: A) Example DTA curves obtained for the present Ce-doped bioactive glasses at 25 $°C\cdot min^{-1}$.
B) Set of DTA crystallization signals obtained at different q+ for the bioactive glass containing 0.5 mol.% CeO_2.
(Exothermic effects evolve in the upwards direction.)

Acknowledgements: This work was supported by The Slovak Grant Agency for Science under Grant No. VEGA 2/0091/20, APVV-21-0016, and thanks to The Ministry of Education, Youth and Sports (grant no. LM2018103).

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Structural interpretation of the glass transition behavior in the Al_2O_3-doped lead-borate glasses

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Two series of aluminum lead borate glasses, $(Al_2O_3)_y(PbO)_{35-y}(B_2O_3)_{65}$ and $(Al_2O_3)_y(PbO)_{70-y}(B_2O_3)_{30}$ [1, 2], were prepared and effect of PbO → Al_2O_3 substitution on their structure and thermal properties was studied. The semi-quantitative analysis of the Raman spectroscopy [3] data was used to structural interpretation of glass transition behavior in the Al_2O_3-doped lead borate glasses. The mechanisms of structural reorganization of glassy network under PbO → Al_2O_3 substitution were found to differ for the studied series although Al^{3+} ions are incorporated in the glass network in form of AlO_4 units in the both cases. The formation of AlO_4 tetrahedra is accompanied by transformation of various isolated borate anions into finite-sized metaborate chains as well as the conversation of four-fold coordinated $[BØ_3O^-]^-$ species with one non-bridging oxygen atom into fully polymerized $[BØ_4]^-$ tetrahedra in the $(Al_2O_3)_y(PbO)_{70-y}(B_2O_3)_{30}$ glasses. In the series of glasses with high concentration of B_2O_3, $B^{[4]} \rightarrow B^{[3]}$ transformation including the shift of $[BØ_4]^- \leftrightarrow BØ_2O^-$ equilibrium toward the right side is the main process of structural reorganization caused by PbO → Al_2O_3 substitution. In this case, the change in the network connectivity is determined by competition between increasing the amount of Al-O-B bonds against the background of decreasing the amount of B-O-B bonds between borate structural species. The structural relaxation behavior in the glass transition rage was described in terms of the Tool-Narayanaswamy-Moynihan model [4]. The activation energy for the relaxation movements was found to be non-monotonous in case of both compositional series.

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Kinetics, and structural relaxation of the Al_2O_3-PbO-B_2O_3 glasses

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In this work, the kinetics of the structural relaxation and cold crystallization of the given glass systems were described. Thermokinetic behavior was investigated using X-ray diffraction analysis, differential scanning calorimetry, and Raman spectroscopy. The–Narayanaswamy–Moynihan model [1] was used for describing glass transition kinetics. Furthermore, Raman spectroscopy was used for the structural changes and movements of the characteristic structural units to explain the compositional evolution of the relaxation parameters [2]. Finally, the empirical autocatalytic model of Šesták and Berggren and the nucleation-growth Johnson-Mehl-Avrami model were used to describe the complex crystallization kinetics. The temperature-dependent activation energy was successfully applied and compared to real-life experimental data by using the Avramov-Šesták concept [3]. The corresponding methodology was critically reviewed.

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Thermotropic ionic liquid crystals tunable by the spacer length in 14-s-14 gemini surfactants

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Thermotropic liquid crystals (TLCs) are structures that possess an intermediate degree of order between the crystalline solid and the isotropic liquid phases. Often they can respond to external stimuli such as mechanical stress or electrical fields, thus changing their optical properties (e.g. birefringence and color) [1]. In this work, we investigate the influence of the number of methylene groups in the covalent spacer (s) on the formation of thermotropic ionic liquid crystals by 14-s-14 gemini. Previouly, the thermal behavior of 12-s-12 gemini surfactants was seen to show non-monotonic features with increasing spacer length [2]. Here, we analyse the 14-s-14 family and the range of the spacer length was greatly extended, s = 2 to 20. The thermal stability of the compounds was assessed by thermogravimetric analysis (TGA) and the phase transition thermodynamic parameters determined by differential scanning calorimetry (DSC), while the mesophases were assigned by polarized light microscopy (PLM). X-ray diffraction (XRD) was also carried out to extract structural information. In general, non-monotonic trends are also observed with increasing spacer length. Compounds with s < 8 melt and decompose nearly concomitantly. Isotropization to the liquid phase is observed only for spacers ≥ 8 and a U shape trend is observed with a minimum isotropization temperature found for 14-12-14 (Figure 1). The overall results show how the spacer length can be used to tune the formation of ionic liquid crystals pointing to a balance between the chain length and spacer length in order to optimize the molecular interactions/packing parameters in the ionic lattice.

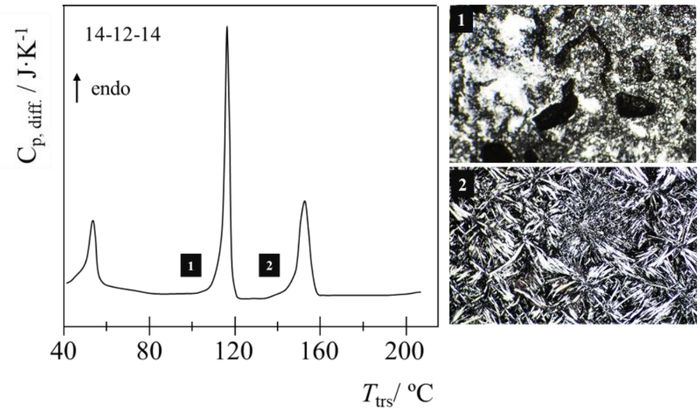

Figure 1: DSC thermogram and illustrative PLM images of the phases formed by the 14-14-14 surfactant: 1, 100 °C, granite-like texture, M1 phase and 2, 150 °C, fine lancets, SmA phase.

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Evolution of hydroxyapatite particle size by thermal treatment and polymer matrix diffusion

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A popular method for the synthesis of hydroxyapatite (HA) particles is using the wet chemical precipitation method due to the low cost of reagents and the applied steps [1]. By using organic macromolecules containing polar functional groups during synthesis, such as COOH and OH, can influence the synthesized HA particles properties. The functional groups provide a greater affinity to positive Ca^{2+} ions and the nucleation of HA crystals in the solution [2] [3].

In this study, solutions at different concentrations of chitosan and sodium alginate were used as nucleation medium for the HA particles. The calcium and phosphate presursor solutions were firstly adjusted at a pH of 12 and added to the polymer solution with a concentration varying from 5 to 10 % w/v, reported to the stoichiometric mass of HA according to the synthesis reaction. After synthesis, the resulted powder was calcinated at 1000˚C.

The effects that the polymers have on the properties of HA particles were monitored by means of SEM, FT-IR, EDX, DLS and TGA, before and after the thermal treatment in order to see how the system evolves till crystallisation of HA occurs.

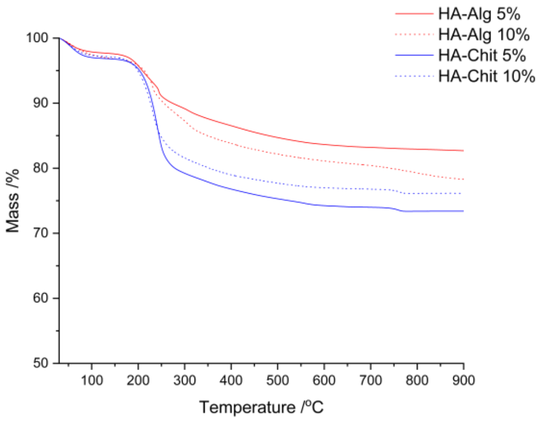

Fig. 1. TG curves of the samples

Table 1. Particle size of the sample by DLS

Sample	Dried at 60˚ C (nm)	Treated at 1000˚C (nm)
HA-Alg 5%	589	728
HA-Alg 10 %	703	2381
HA-Chit 5%	2340	1022
HA-Chit 10%	2181	1722

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Thermal and structural analysis of a $Fe_{65}Co_{35}$ soft magnetic alloy for different manufacturing conditions

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The demand for spring magnets is rapidly increasing due to their wide range of applicability. The use of these magnets is present in fields such as microwave absorption, magnetic recording media and in many biomedical applications [1]. It must be noted that microwave absorption can also be achieved with amorphous soft magnetic composites [2]. A spring magnet is a composite material where a soft magnetic alloy, in low weight percentage, is added to a hard magnetic alloy to enhance the hard magnetic alloy. The applicability of spring magnets depends mainly on selecting the most suitable soft and/or hard magnetic alloys. This study focuses on the structural and thermal analysis of a soft magnetic alloy with a nominal composition of $Fe_{65}Co_{35}$. Six samples were prepared with this nominal composition by mechanical alloying in a Fritsch Pulverisette P7 planetary ball mill spinning at 400 rpm with a ball-to-powder ratio of 5:1. Three milling times were selected to produce two samples per milling time. Samples were milled for either 10, 25 or 50 hours. For each milling time, one sample had 1 mL of cyclohexane added to it acting as a process controlling agent (PCA). Structural analysis was carried out by X-Ray Diffraction (XRD) by applying the Rietveld method alongside a thermal analysys carried out by Differential Scanning Calorimetry (DSC). The principal aim of the study was to analyse how structural and thermal behaviour varied for different milling times and the use of a PCA.

The use of a PCA alongside the different milling times have had a clear effect on the structural and thermal behaviour of the alloy. Structural analysis by XRD confirmed the nanocrystalline structure of all samples with varying crystal sizes. More specifically, longer milling times achieved smaller crystal sizes than shorter milling times. Also, the use of a PCA made the crystal size for all the alloys even smaller than without it. The sample milled for 10 hours presented a smaller crystal size than that of the sample milled for 50 hours without using a PCA. Thermal analysis, carried out by DSC, showed that there were clear differences between samples manufactured without PCA and those with it. Milling time affected thermal behaviour also, however, its effects were not as significant as the use of a PCA. All six samples presented a reversible structural transformation at 680ºC which was associated to the ordering of the A2 phase of Fe-Co alloys to the more stable B2 phase [3]. Another peak at 519ºC was detected only for the samples manufactured with the PCA. This process was associated with the non-reversible transformation of a metastable pattern of anti-phase domains of a tetragonal $FeCo_3$ structure [4]. It is believed that the use of a PCA which contains carbon favoured the formation of this tetragonal structure (similar to steels).

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Effect of the boron addition on the thermal behaviour and microstructure of Fe based powdered alloys

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The thermal study of nanostructured iron-based alloys by differential scanning calorimetry (DSC) is a powerful way that summarizes the structural changes during heating, after mechanical alloying, in a temperature range [1,2]. Complementary structural information is obtained by X-Ray diffraction (XRD).

In the present work, we have investigated the structural and thermic properties of nanocrystalline $Fe_{50}Co_{25}Ni_{15}B_{10}$ (B Amorphous or Crystalline) alloy powders (prepared by the mechanical alloying process) at the range of temperature between 50 and 700°C. The addition of boron element in Fe-based alloys provokes the deformation of the lattice, which facilitate the process of amorphization and/or nano-crystallization exhibited during milling [3]. After 100 h of milling, the DSC curve shows two exotherms approximately in the intervals (400-500ºC) and (500-600ºC) with respect to the boron-free alloy (as shown in the figure). Indeed, the formation of intermediate intermetallic phases based on supersaturated solid solutions produced by high-energy mechanical milling could present these transformations which are accompanied by structural changes favourable to the introduction of defects [4].

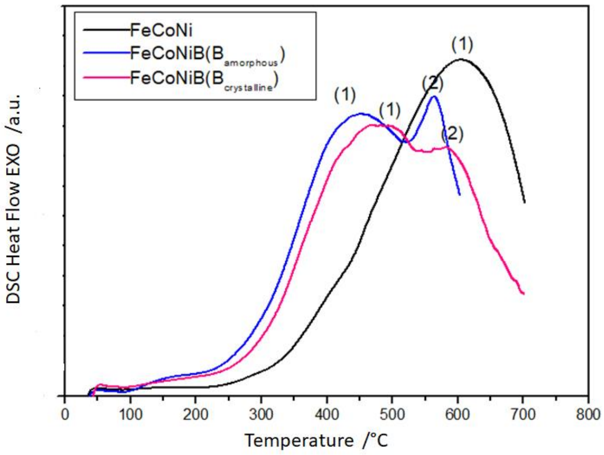

Figure: DSC scans of several DSC

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Physical chemical and thermal properties of geopolymers for Cultural Heritage

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Geopolymers are inorganic materials produced activating aluminosilicates with solutions of alkali hydroxide or alkali silicate in a green process, at room temperature, or in any case at much lower temperatures than those necessary to produce traditional cements or ceramics [1,2]; they have a marked chemical-mineralogical similarity with ceramic bodies and show mechanical, chemical, and thermal properties that seem well suited to their use in the field of Cultural Heritage interventions. The structure and performance of these materials strictly depend on the characteristics of their precursors. In this study different types of raw materials, selected as potential precursors, were studied as they are and calcined at 700 °C. Geopolymers based on *basalt mud*, *Pliopleistocene clay*, *Numidian clay*, and *ash* were also studied. All the samples were characterized with a multi-analytical approach using thermogravimetric analysis (TGA), thermogravimetry coupled with evolved gas analysis (EGA) using Fourier transform infrared spectrometry (TGA–FTIR), differential scanning calorimetry (DSC) and X-ray computed microtomography (μ-CT) for the evaluation of the three-dimensional structure and porosity of the sample. Thermogravimetric analyses were also performed on a representative series of samples subjected to artificially accelerated aging by exposure to UV rays or acetic acid vapours under controlled conditions. Some artificially aged samples were also studied by DSC and micro-CT analyses. The wide set of materials required a statistical analysis approach of the data by Principal Component Analysis (PCA) and Hierarchical Clustering analysis (HCA).

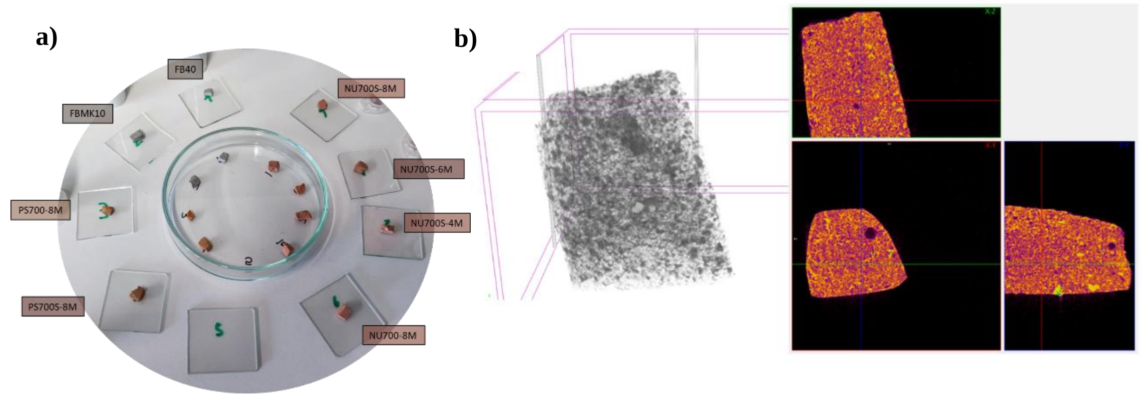

Figure 1: a) Overview of the raw materials studied b) 3D view of the sample FBMK10 obtained by μ-CT analysis.

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Thermo-magnetic analysis of MnCo(Fe)Ge(Si) mechanically alloyed systems

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Mechanical alloying produces thermodynamically disfavored reactions and destabilizes equilibrium systems, which allows us to obtain amorphous precursor systems whose homogeneity at very small scale can reduce both time and temperature of treatment for a finer control of the microstructure. This strategy has been successfully applied to the development of MnCo(Fe)Ge-type magnetocaloric materials [1]. In this work, different amorphous precursors, $MnCo_{0.8}Fe_{0.2}Ge_{1-x}Si_x$ (where $0 < x < 0.6$) with partial substitution of Si for Ge have been obtained by mechanical alloying, which, after annealing, developed different phases according to composition. The microstructure is studied by X-ray diffraction. The stability of mechanically alloyed precursors was analyzed through DSC experiences. Thermomagnetic measurements allow us to analyze the magnetocaloric effect through the magnetic entropy change, ΔS_m, and the adiabatic temperature change was indirectly estimated from heat capacity, $c_{p,0}$, measurements. For $x \leq 0.4$ an intermetallic austenite phase ($P6_3/mmc$ space group) is developed, and for $x = 0.6$ a mixture of phases between austenite and martensite (Pnma space group) is formed. Despite the absence of expected martensitic transformation, the magnetocaloric response is significant in these alloys and increases as the amorphization of the precursors system is enhanced.

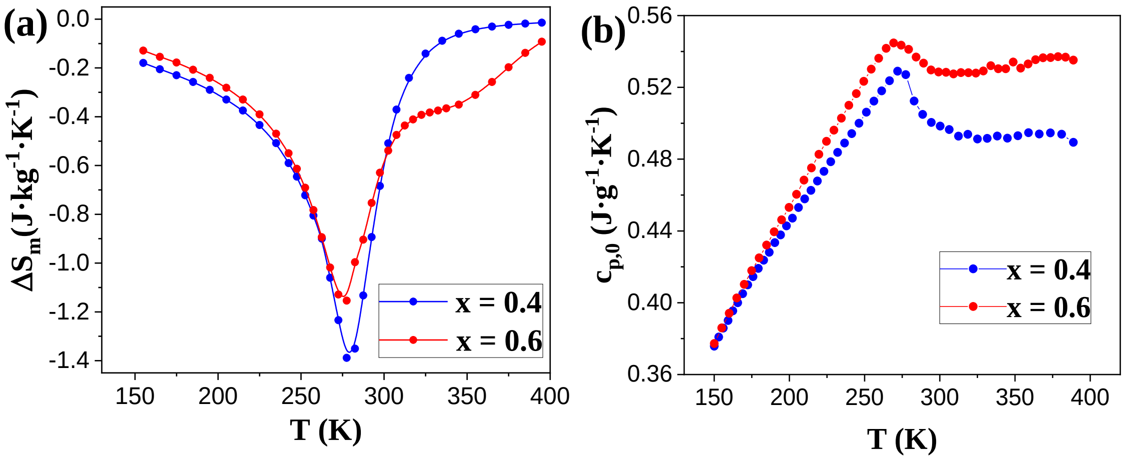

Figure 1: Temperature dependence of $\Delta S_m(\mu_0 H = 1.5\ T)$ (a) and specific heat $c_{p,0}(\mu_0 H = 0\ T)$ (b) for $x = 0.4$ and 0.6 samples milled for 100 h.

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Exploring dual-source thermal evaporation to create perovskite thin films for photovoltaic applications

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The utilization of dual-source vapor deposition by thermal evaporation is explored for the fabrication of perovskite thin films for solar cell applications. The vapor deposition technique employed in this study utilizes a thermal evaporation apparatus based on multiple Knudsen cells, each with independent temperature control [1,2]. This enables the sublimation of the two precursors of the perovskite (methylammonium iodide and lead iodide), which require different temperatures due to their distinct vapor pressures. Upon sublimation, both precursors deposit on the substrate under a perovskite structure (methylammonium lead iodide). This method allows for exceptional purity, crystallinity and homogeneity in the resulting perovskite films [3-6]. The morphological, structural, and optical properties of the perovskite films were obtained by high-resolution scanning electron microscopy, X-ray powder diffraction, and UV-vis spectroscopy, respectively.

Additional experimental investigations involving the integration of a hole transport layer are presented. A pentacene thin film, deposited using the same thermal vapor deposition equipment, improved the performance of the perovskite solar cell. Comparative analysis of the current-voltage (I-V) curves is presented, highlighting the performance disparities between the perovskite solar cell based solely on the perovskite film and the perovskite solar cell enhanced by the hole transport layer (pentacene). The vapor-deposited organic layer was also found to enhance the crystallinity and stability of the perovskite film.

Overall, this work demonstrates the potential of dual-source thermal vapor deposition as a versatile and efficient technique for fabricating perovskite solar cells, with the ability to enhance their performance through the incorporation of compatible functional layers such as pentacene.

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Evaluation of the effect of biodiesel content in diesel / biodiesel fuel blends on gums and sediments formation using thermogravimetry

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Diesel is worldwide the most consumed petroleum-based fuel. The thermodynamic efficiency of diesel internal combustion engines is greater when compared to gasoline engines [1]. Diesel sold in Brazil is a diesel/biodiesel blend containing 10% by volume of biodiesel (B10), which increases fuel degradation during storage time. Fuel degradation results in lower molecular weight products than biodiesel and heavier products such as gums/sediments (GS) [2]. The aim of this work was to evaluate the effect of the biodiesel in diesel/biodiesel fuel blends on the GS content formed after the storage period, using thermogravimetric techniques (TG / DTG).

Samples were prepared using commercial soybean biodiesel (B100) and S10 diesel with different volumetric biodiesel percentage, from 10% (B10) to 50% (B50). They were stored at room temperature in amber glass bottles (similar to ASTM D4625) [3]. Every 30 days, a bottle of each blend was opened and a sample collected for analysis. Opened bottles, after sampling, were discarded. This procedure was repeated for 180 days. Blends oxidized and not oxidized (immediate age) were analyzed using thermogravimetry (TG) and derivative thermogravimetry (DTG).

Thermogravimetry shows that, as the B100 content increases regarding diesel, the interactions between the two fuels are distinct, which result in changes of the TG/DTG curve profile. It is also observed that the increase of B100 promotes the retardation of the mass loss steps of the blends to higher temperatures. The final (T_{endset}) and the maximum (T_{onset}) degradation temperatures are affected as well. For example, the *onset* temperature value of pure diesel at immediate age is 134 °C, while for the B25 and B50 blends, the values are 140 °C and 164 °C, respectively.

The TG/DTG curves of the sample showed that increasing biodiesel content in the blend, the percentage of GS formed for the same aging age increases. GS content values for B10, B20 and B50 samples, after the first 30 days of storage, were 0.47, 0.77 and 1.80 by mass %, respectively, and after 180 days, these percentages values had grown to 1.06, 1.70 and 3.19.

Moreover, the formation of GS is correlated with the proportion of the blend constituents. The profiles of TG/DTG curves for each blend are a function of the added percentages of biodiesel in the mixture**.** The experimental results obtained showed that the degradation products formed during the storage of fuels, gums/sediments (GS), can be quantified using thermogravimetric techniques.

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Thermodynamic study of the effect of functional groups on anthraquinones: Leucoquinizarin, chrysazin and 2-methylanthraquinone

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The fundamental structure of anthraquinones (AQs) consists of three fused hexagonal rings with two ketone functional groups at positions 9 and 10 (figure 1a). In addition to their extensive usage in various fields such as pharmacology, chemistry, biochemistry, and industry [1], AQs have attracted attention due to their potential as anolytes in fully organic redox flow batteries, which have significance implications for large-scale energy storage [2].

The goal of this work is to study the thermodynamic properties of AQs with different functional groups, namely –OH (figure 1b and 1c) and $-CH_3$ (figure 1d), positioned at various location within the ring structure, using a combination of experimental and computational methods.

Experimental studies employing calorimetric and effusion techniques were conducted to explore the thermophysical and thermochemical properties of AQs. These studies enabled the determination of enthalpies of formation in the crystal and gas phases, as well as enthalpies of sublimation. Complementary computational studies were also undertaken, using the G3(MP2)//B3LYP composite method.

The acquisition of this knowledge regarding the properties of AQs serves multiple purposes. Firstly, it enables the establishment of an energy-structural relationship, providing insights into how the energy content of these compounds relates to their structural characteristics. Furthermore, these findings contribute to the advancement of tautomeric studies concerning these derivatives, as they have the ability to form keto-enol tautomers.

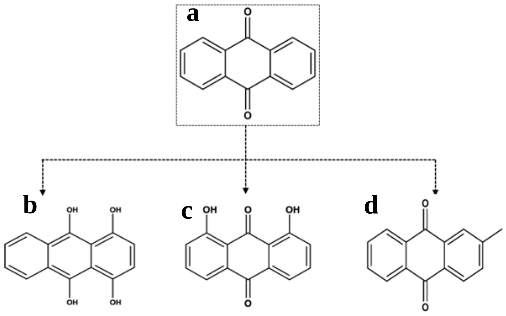

Figure 1: Structural formulae of anthraquinone (**a**); leucoquinizarin (**b**); chrysazin (**c**) and 2-methylanthraquinone (**d**).

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Long-term thermal stability of different ionic liquids and their mixtures with salt. Comparison with its nanoconfinement

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Thermal stability is an essential property to select the most suitable compound for energy related applications such as high-temperature lubricants, thermal fluids and solvents for high-temperature organic reactions and electrolytes for electrochemical devices [1].

This work presents firstly a study of the thermal stability of 5 ionic liquids (ILs) with different ion nature. The experiments were performed simultaneous Mettler Toledo TGA/DTA from 75ºC to 800ºC, using a scanning rate of 10ºC/min, with an air flow of 20 cm^3/min. [2].

To use these ILs in electrochemical devices is essential to dope them with electrochemical relevant salts, essentially lithium salts, although the formation of lithium dendrite can reduce the durability of these devices. To reduce the dendrite growth in the electrolyte, a gelation process could be performed achieving a mechanical stiffness that prevents spillage and improves industrial safety [3]. However, both, salt addition and gelation, could modify the thermal behaviour of the ILs.

This work also analyzes the effect of salt addition and confinement on the thermal stability of the above liquids using the onset temperature and the maximum operation temperature, widely described in previous papers of our research group [1].

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A study of Posidonia oceanica leaves thermal profile and their potential use as fillers for decorative laminate manufacturing

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Posidonia Oceanica (PO), which is a seagrass species found in the Mediterranean Sea, has gained great interest over the last few years in panel manufacturing for various applications, including construction and furniture [1]. The utmost benefit of the panels produced lies in their environmentally friendly nature, since seagrass is a renewable resource. The current work focuses on PO leaves and PO panels thermal decomposition via Thermogravimetric Analysis (TGA), a critical study concerning the properties of the final product. Raw PO leaves degradation occurred in 4 stages under inert conditions, in contrast to air atmosphere, where they decomposed in 5 stages. Initially, up to about 200^o C, water molecules escape, both in the form of moisture and those bonded in the structure. Later on, devolatilization takes place, along with char formation, a stage that is extended up to about 600^o C and 450^o C, under N_2 and air environments, respectively, the last being followed by char oxidation [2]. Degradation occurring at elevated temperatures is mostly associated with inorganics, like carbonates and alkali chlorides, while the aforementioned suggestions are further confirmed through the heat flow signal variation, which is simultaneously detected with the weight loss curve. The main difference between raw PO leaves and PO leaves after water treatment's thermal profile lies in the significantly reduced mass residue of the last due to the great amount of NaCl removal. Finally, the thermal cracking of a PO panel binded with a commercial epoxy adhesive was investigated. Results showed that PO panel presents a rather satisfying thermal stability when compared to raw PO leaves, most likely indicating a successful penetration of the epoxy resin inside the organic structure, an assumption clearly observed through Scanning Electron Microscopy (SEM) illustrations. Overall, the use of PO leaves in thermoset composite manufacturing can lead to a promising development in sustainable design and construction.

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Thermal and toxicological characterization of n-alkyl-ammonium nitrate ionic liquids (n=2, 3, 4, 5, 6, 8) for energy applications

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The most used ionic liquids (ILs) are protic IL from ammonium nitrate family, whose physical properties and toxic environmental effect are still largely unknown. In this work, the liquid range, thermal stability and toxicity levels of this family of ILs, were determined. Therefore, these compounds and its mixtures with other substances (salts, solvents, etc.), can be used as electrolytes for next generation electrochemical smart devices [1, 2] and as candidates to replace conventional Heat Transfer Fluids (HTFs) among others energy applications [3,4-6].

In order to select the best candidate for each application, it is essential to know the liquid range of these compounds. The liquid range, which is the temperature interval between melting (or glass transition) and the thermal degradation temperatures.

In this work a comparison of the liquid range of six n-alkyl-ammonium nitrate ILs with increasing alkyl chain length (n=2,3,4,5,6,8) was performed. The lower limit of this liquid range was obtained from the thermal behavior study using a differential scanning calorimeter and the highest limit was determined by the thermal stability analysis trough thermogravimetry analysis. Additionally, the toxicity was evaluated through the inhibition of bioluminescence of *Alivibrio fischeri* marine bacteria using the Microtox® technique [7].

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Laboratory effectiveness of Firefighting Foam based on eco-friendly soap compounds on two different Galician soils. Thermal characterization

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The use of firefighting foams and other natural, or synthetic, additives for improving the extinguishing effect of water in forest fires has been increasing in the last decades and nowadays became a widespread practice. However, due to the negative and sometimes long-lasting environmental impact of several of the most used firefighting agents there is a growing interest on the development of alternative "eco-friendly" formulations [1,2].

Kawahara et al. [2] developed a novel firefighting foam, with significantly lower environmental risk and suitable for its application in forest fires, consisting of natural soaps, methylglycinediacetic acid (MGDA) as chelating agent, propylene glycol, hexylene glycol and water.

The present work studies the effect of this flame retardant on two Galician soils with different organic matter content. These soils were exposed to different thermal shocks and exposure times, to simulate different intensity fires. Thermal analysis of heated and unheated soils was performed through differential scanning calorimetry and thermogravimetric analysis, for characterizing the influence of the organic matter content on the thermal shocks impact on soils.

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Performent engineered adsorbent for hexavent chromium from water solutions

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Water and waste management are essential pillars of a sustainable economy. The increased level of pollution and climate change affect water resources.

Heavy metals are a category of pollutants that affect health and biodiversity.

Among the various methods used to remove pollutants from water, adsorption is one of the most efficient and ecological. The latest research addressed the low-cost, performance and recyclable materials development for water remediation.

This study report a new engineered adsorbent based on egg shell waste and other recyclable materials for hexavent chromium removal. A batch adsorption study was performed to investigate the *kinetic parameters* influence on adsorption efficiency. The newly adsorbent prepared was characterized through electron microscopy SEM coupled with EDX, BET, FTIR and thermogravimetric analysis. The maximum efficency was over 99%.

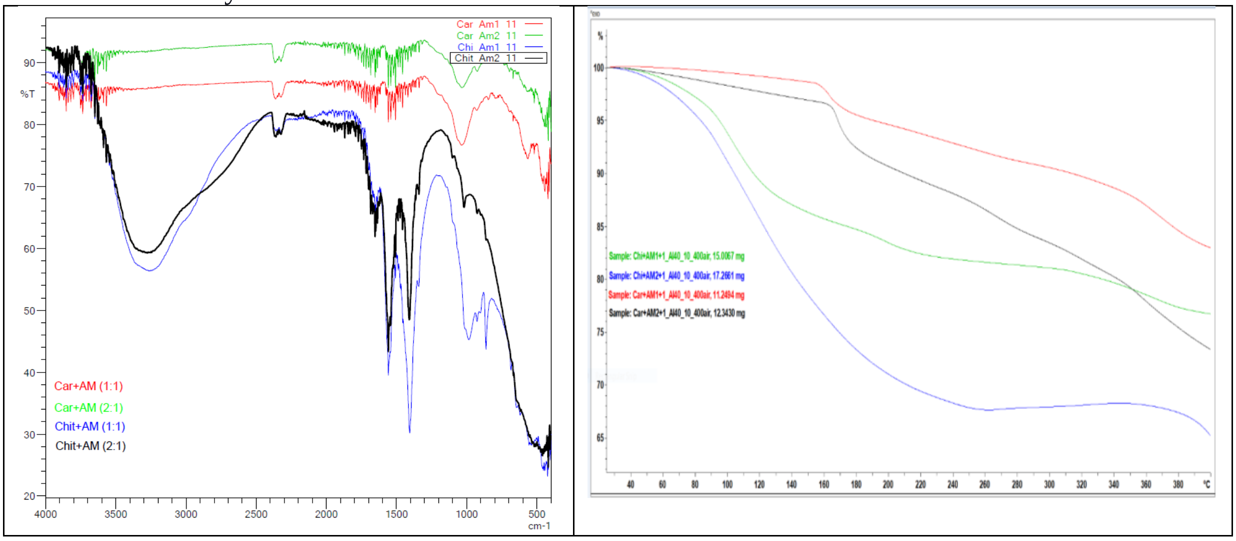

Figure 1. FTIR and TG analysis of samples with recyclable materials and biopolymers

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Upgrading and testing a high precision microcalorimeter for the determination of heat capacity

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This work presents the refurbishment, upgrading and testing of a differential scanning microcalorimeter - *iSenseDSC*. In order to improve the performance of the original apparatus (SETARAM micro DSC III) several changes were made. In regard to temperature stability, the original heat pumping and exchanging system was replaced by a more modern and efficient system (produced by Laird Thermal Systems), the location of the temperature control point was changed, and a temperature control module was built. Furthermore, the overall insulation of the calorimeter was reinforced. To enhance the calorimetric signal's quality, a new pre-amplification system (originally developed in the former Thermochemistry Laboratory of the University of Lund) was installed.

The evaluated parameters include the temperature stability, calorimetric noise level, time constant, calorimetric signal linearity, and temperature dependence of the calorimetric sensitivity. The temperature was calibrated by means of a reference probe. The changes allowed the achievement of a temperature stability better than ± 0.5 mK, a calorimetric signal noise level around ± 50 nV and a calorimetric sensitivity ranging from 100 (at T = 283 K) to 110 mV/W (at T = 333 K).

The incremental temperature step method was adopted for the high precision heat capacity measurements. The blank area was determined, and sapphire (NBS SRM 720) was used as calibrant. The overall performance of the system was tested by measuring the heat capacity of some recommended substances, namely benzoic acid, anthracene and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonylimide) ($[C_6C_1im][NTf_2]$). The result obtained with the test substances revealed low dispersion (0.5 %) and an uncertainty better than 1 % (in the temperature range from 283 to 333 K).

Upon comparison of the data obtained with the new *i*Sense*DSC* microcalorimeter system (refurbished and upgraded version of the SETARAM microDSC III) and data reported in the literature obtained with high precision techniques (namely adiabatic calorimetry and drop microcalorimetry), small deviations were found (> ±0.5 %).

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Fast differential scanning calorimetry: new solutions in data treatment to investigate organic molecular glass-formers

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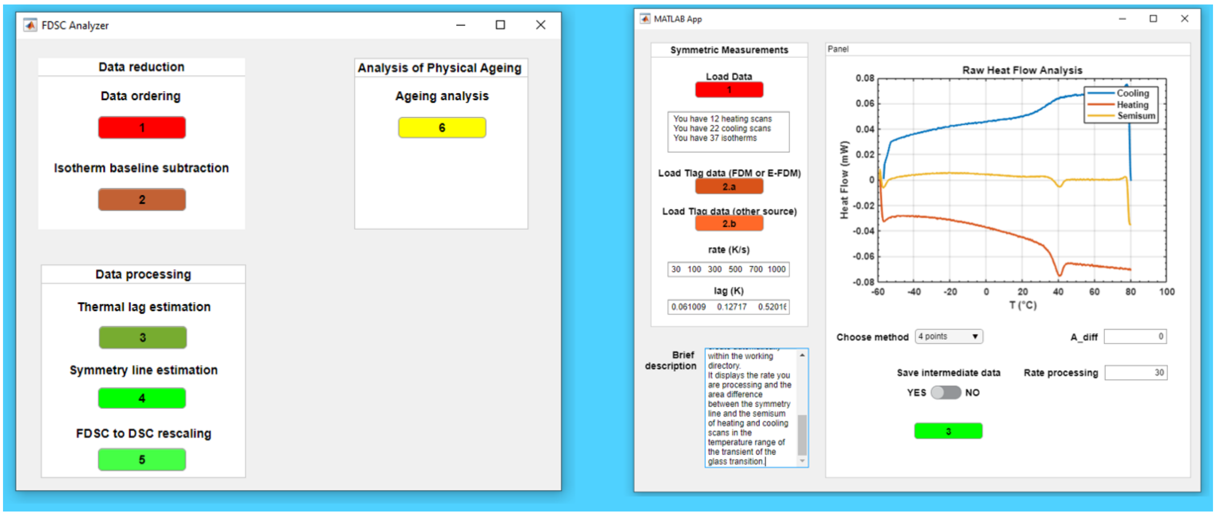
Differential scanning calorimetry (DSC) is a well appreciated technique for its ability to characterize materials in a quick manner. Further improvements in this direction come from fast DSC (FDSC) which gives access to scanning rates up to 10^5 K/s [1,2]. FDSC can allow the study of a system, limiting reorganization or degradation processes, a feature extremely useful when studying organic materials [2]. Nevertheless, new solutions are still needed for some critical problems, among which we mention: 1) the assessment of thermal lag under scan, occurring at non optimal conditions (like for organic molecular materials); 2) a feasible way to probe static thermal gradients across the sample, causing smearing effects in the measured scan; 3) a robust physical model to rescale the FDSC specific heat capacity to the one measured by DSC which is considered as a standard.

In a recent paper [3] we have tried to answer to all this points, providing: i) an alternative way to estimate the dynamical thermal lag by using the temperatures of maximum slope of the heating and cooling scans through the glass transition region; ii) a new interpretation of the heat flow losses influenced by the sample and depending on the sign of the scanning rate; iii) the use of the glass to liquid transition on heating to probe and quantify static thermal gradients across the sample. These novel approaches have been tested on three prototypical molecular glass-forming materials, i.e. glycerol, orto-terphenyl and poly(propyleneglycol), and recently implemented on a software developed in house (see Fig. 1) for fast and automatic data analysis.



You have 12 heating scans
You have 22 cooling scans
You have 37 isotherms

rate (K/s): 30 100 300 500 700 1000
lag (K): 0.061009 0.12717 0.52016

Brief description: within the working directory.
It displays the rate you are processing and the area difference between the symmetry line and the semisum of heating and cooling scans in the temperature range of the transient of the glass transition.

Choose method: 4 points
A_diff: 0
Rate processing: 30

Fig. 1: Screenshot of several windows of the software. Left panel: overview of the main window with all possible functions. Right panel: window of "Symmetry line estimation" button, which evaluates the heat flow losses.

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