

XLII National Conference on Calorimetry, Thermal Analysis and Applied Thermodynamics

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BOOK OF ABSTRACTS



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GICAT

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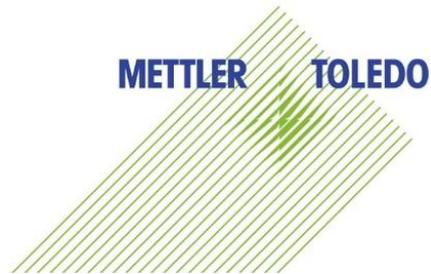
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FOREWORD

The XLII National Conference on Calorimetry, Thermal Analysis and Applied Thermodynamics, AICAT2020 takes place in Udine as online event in January 27-28, 2021. Jointly organized by AICAT (Italian Association of Calorimetry and Thermal Analysis) and GICAT (Interdivisional Group of Calorimetry and Thermal Analysis of the Italian Chemical society) gathers experts in Calorimetry, Thermal Analysis from Italy and across Europe since late 1970s.

The aim of the conference is to provide an opportunity to disseminate the most recent results of research works where calorimetry and thermal analysis techniques, combined with other experimental methods, have a central importance. Moreover, critical exchange of scientific information, discussion on fundamental and applied research aspects as well as on latest instrumental innovations are part of this congress.

After the 1992 edition hosted by our University, the AICAT executive board assigned to Udine the organization of the 2020 conference. The spreading of the COVID19 global pandemic forced the cancellation of the in-person event initially planned in June 2020 at the Palazzo Garzolini di Toppo Wassermann, location of the “Scuola Superiore” of the University of Udine. Thanks to the support of AICAT-GICAT executive boards, University staff and sponsors, the organizing committee has been able to transform the original congress into an online one preserving the entire scientific program.

Scientific sessions are grouped according to topics which include applications of calorimetry and thermal analysis in the fields of cultural heritage, polymers, biomaterials, chemical thermodynamics, food science, inorganic materials, kinetics and catalysis, instruments and methods and life science. This Book of Abstracts has been organized accordingly. The cultural heritage session is dedicated to Prof. Giuseppe Della Gatta, founder and first AICAT President, who passed away during 2020.

Every two years, during the AICAT-GICAT Conferences, two prestigious prizes are given to a recognized scientist and to a young researcher, in recognition of their research activity. In this edition, Prof. Giuseppe Arena (University of Catania) will be awarded the AICAT-TA prize for his outstanding contribution in the use of calorimetry for the study of intermolecular interactions and binding equilibria in solution (“Calorimetry: a priceless tool for characterizing intermolecular interactions and binding equilibria in solution. Retrospective and perspectives”). The “Alberto Lucci” prize, reserved to young emerging scientists, will be awarded to Dr. Maria Paciulli (University of Parma) for her significant contributions in applications of calorimetry in food science (“Differential scanning calorimetry of encapsulated food ingredients”). Once again, we want to congratulate them. In addition, AICAT made available eight participation grants to promote the involvement of brilliant young researchers. This year two international peer-reviewed journals will dedicate special issues to our conference: Journal of Thermal Analysis and Calorimetry (Springer) and Entropy (MDPI).

The Organizing Committee acknowledges the University of Udine and the Polytechnic Department of Engineering and Architecture for supporting the organization, both for the initial in-person congress and the on-line edition later, AICAT-GICAT boards for their continuous support, and Lucci Family and TA Instruments for sponsoring the awards.

We gratefully acknowledge all the companies supporting AICAT2020: Mettler Toledo, NETZSCH Geraetebau GmbH, Alfatest Srl, MP Strumenti, EDISES. AICIng (Italian Association of Chemistry for Engineering) is also acknowledged for the patronage.

Finally, we thank all participants of the conference and all young members of the organizing committee that helped us in these special times, with the hope that will keep a satisfying memory of this challenging AICAT 2020 event.

Andrea Melchior
Chair of the Conference

Marilena Tolazzi
Co-Chair of the Conference

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AICAT-TA AWARD

Calorimetry: a priceless tool for characterizing intermolecular interactions and binding equilibria in solution.

Retrospective and perspectives

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Keywords: Solution calorimetry, equilibria, coordination chemistry, speciation

Solution calorimetry has proven to be a versatile and useful technique. Calorimetry measures a universal signal (heat) and hence does not require any labelling or modifications of the molecule being investigated as other techniques do. Noteworthy, calorimetry may provide direct access to the stability constant, the stoichiometry, and the enthalpy of binding of an equilibrium reaction in a single experiment. The principles of such a method were described more than half a century ago [1,2] and received new impetus thanks to the introduction of titration calorimeters [3]. The introduction of titration calorimeters with increased detection limits and equipped with small volume cells have significantly increased the accessible range of formation constants and determined the surge in popularity for the study of chemical binding phenomena and the widespread use of isothermal titration calorimetry [4-7]. As the years went by, solution calorimetry went from a pioneering technique to a standard technique proposed in textbooks [8]. By reducing the size of the reaction vessel and lowering the detection limit (nanowatt-ITC), calorimetry can be employed for the study of systems where materials are rare, expensive, or available only in limited amounts. Thus, it is not surprising that isothermal titration calorimetry (ITC) is nowadays employed in fields as diverse as inorganic chemistry, biochemistry and supramolecular chemistry. For example, owing to the universality of the signal measured, ITC is well suited for the study of the interaction of protein fragments or even whole proteins with spectroscopically silent metal ions (e.g. Zn^{2+}) that do not possess the spectroscopic signatures characteristic of other metal ions associated with d-d transitions [9].

By contrast, heat, precisely because it is a universal reporter, cannot be linked directly with any specific molecule or part thereof as for example the shift of a specific band in UV-vis spectroscopy and/or the chemical shift in NMR. Most importantly, the determination of the stoichiometry of the reaction via calorimetry becomes rather difficult (or even impossible) for systems in which multiple species are formed, which, in turn, makes it impossible to link the apparent binding constant as well as the associated enthalpy and entropy of binding, to the structure/property of a protein/fragment [10,11].

The present contribution focuses on the applicability of and the caveats to solution calorimetry, with special emphasis on speciation. Examples will be illustrated showing that *i.* experiment design is the basis for results that appropriately describe interactions in solution [12]; *ii.* the apparent binding constant derived via calorimetry, often the only constant accessible when dealing with large biomolecules with several protonation sites, gives an idea of the binding strength only and should not be used to draw conclusion on the structure of species in solution; and *iii.* the apparent binding constant derived via calorimetry may not 'portray' the real situation in solution especially in the presence of systems with multiple species and may lead to misinterpretation of results [13].

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"A. LUCCI" PRIZE

Differential scanning calorimetry of encapsulated food ingredients

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Keywords: encapsulation, differential scanning calorimetry, active ingredients, stability

Encapsulation is a process to entrap active agents within a carrier material and it is a useful tool to improve delivery of bioactive molecules and living cells into foods [1]. Materials used for design of protective shell of encapsulates must be food-grade, biodegradable and able to form a barrier between the internal phase and its surroundings. Among all materials, the most widely used for encapsulation in food applications are polysaccharides. Proteins and lipids are also appropriate for encapsulation. There are some unique applications of Differential Scanning Calorimetry (DSC) to study encapsulated food ingredients [2]. Confirmation of encapsulation, evaluation of encapsulation efficiency, estimation of water content and determination of storage stability are of the greatest importance and can be obtained by this thermal technique. Moreover, the wall materials in encapsulation should be thermally stable in order to protect the bioactive ingredients against heat processing and DSC can be applied to investigate their thermal characteristics. The full potential of DSC in this field will be discussed, together with some of the latest attempts for enhancing thermal stability of certain bioactive ingredients by encapsulation.

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PLENARY LECTURE

How thermodynamics describes DNA stability and regulatory phase space?

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Keywords: DNA stability and recognition, G-quadruplex, transcription regulation, DSC, ITC

In 1953 Watson and Crick presented their double stranded DNA structure that has become firmly engraved in the cultural memory of mankind. DNA is also able to adopt other structures that appear in the context of regulation of ordinary and disease related cellular processes, leading to complex DNA energy landscapes. Here we will show how thermodynamics can be used for estimating the mechanism of DNA folding and structural interconversion processes, determining their driving forces and for predicting DNA transcription regulation properties. This will be demonstrated using two model systems:

(i) G-quadruplexes that form from guanine-rich DNA sequences of some key regions of the genome, including the promoter regions, oncogenes and telomeres. We will address one of the key issues in G-quadruplex formation as why a single guanine-rich sequence may fold into different G-quadruplex structures and interconvert between them depending on the temperature and concentrations of cosolvents and cosolutes [1-3].

(ii) Toxin-antitoxin (TA) modules, bacterial stress response genetic systems, may be a major cause of chronic infections. TA modules encode a stable toxin (T) and an unstable antitoxin (A) responsible for formation of the transcription repressor complexes with DNA. We will explain the molecular mechanism behind the TA module transcription regulation [4,5].

Thermodynamic characterization of these systems is based on global analysis of a wide variety of calorimetric (DSC, ITC) data [1-6]. We will demonstrate how the obtained thermodynamic parameters can be related to structural properties and used to predict the DNA behavior at different conditions (i.e. stability and regulatory phase space).

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INVITED LECTURES

Conservation: heating to know and understand

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Keywords: conservation, DSC, DTA/TG

The philosophical Italian approach from the 1930s has given restoration a meaning closely linked to the humanistic side of thought. Many art historians, among the most evolved, have however understood how the contribution of the sciences is fundamental for a good result in conservation. Moreover, it is evident that the material alteration context of the works must follow, in its life cycle. The rules that govern the behaviour of matter in its relationship with the environment in which it is inserted and is a part of the natural sciences. For artistic materials, then, we must often take into account that more objects are composed of several materials, with obvious problems of different relationships in the behaviour of the interfaces. What is, therefore, the role of the scientist in the process of conservation of cultural heritage?

The most widespread interpretation is to think that the scientist must to be involved in knowing the composition of materials and perhaps their originality or provenance. But this view is very limited and does not include all the knowledge that the natural sciences can give to the conservation of cultural heritage. It is likely that this interpretation is also due to the contribution of most of the work done by scientists, but it has greatly reduced the awareness of the need for the continued presence of this scientific profile in the conservation process. In this conservation context, there are many analytical techniques that contribute to knowledge, but some of them are still little used. This is perhaps due to the lack of a more targeted application of these techniques and their potential. Among these, calorimetry is certainly one of the great absentees or, at least, less used.

The most widespread interpretation is to think that the scientist must to be involved in knowing the composition of materials and perhaps their originality or provenance. But this view is very limited and does not include all the knowledge that the natural sciences can give to the conservation of cultural heritage. It is likely that this interpretation is also due to the contribution of most of the work done by scientists, but it has greatly reduced the awareness of the need for the continued presence of this scientific profile in the conservation process. In this conservation context, there are many analytical techniques that contribute to knowledge, but some of them are still little used. This is perhaps due to the lack of a more targeted application of these techniques and their potential. Among these, calorimetry is certainly one of the great absentees or, at least, less used.

Also with DTA/TG we can find some confusion in the bibliography. Some studies, carried out on mortars, try to express the hydraulicity evaluating the phase transition of the pozzolanic-based compounds, which should take place around 450 °C [2]. But in that thermal interval is often found the decomposition of organic substances. The lack of verification of the presence of any organic additives, typical for some traditions in the mortars making, does not allow to better understand the result and its attribution.

This can suggest that the work to be done by the researchers is to develop appropriate analytical protocol methods of analysis and to make them easily accessible. The analytical capacity of calorimetry experts must give working tools to those who, within the Superintendence, must carry out daily and routine analyses. This would make it possible to use these techniques more widely, also with the creation of an accessible data base with the results and interpretation of the thermogravimetric diagrams, like it's made for FTIR and RAMAN spectra.

An example of practical use for a conservation process, can be done when we try to understand if, or when, a particular action can contribute in the alteration of the matter. Many persons talk about the risks of frost and thaw cycles, defined by the term freezing. The question is used in a general way, especially in northern countries and few have verified the problem when and which are the temperatures of the water in the pores of a specific material freezes. This can be very important, especially for the change that could be induced by the use of certain preservation products, such as consolidates. The possibility to make a study with the DSC [3] enabled us to understand whether this risk is real or not. The result give us a contribute to assess how this risk can interact positively or negatively with the material to be conserved. However, it should also be taken into account that the experiment was carried out on a sample completely soaked in water and that it's possible that in the pores of stones can have only the humidity present in the air. This could be a study to do for a right contribute in the freezing knowledge useful for the conservation.

The integration of analytical results made by calorimetry, may not only be possible with the addition of other techniques, but also with the study of cooking residues, trying to understand if there are differences in the transformations of products according to their composition or the initial ratio of the various compounds. The measure with FTIR of the residual calcination of a mortar, for example, allowed to identify changes in production related to the epochs. Heating generates phase transitions that are related to the internal relationships between calcite and silicates. This generates different products depending on the proportions of the various components. With this result we were able to identify two production sites that used the same starting materials and that the analyses with DTA/TG and XRD were unable to discriminate. It is not excluded that, probably, an expert specialised in thermal analysis would have been able to give the same result, but it must be borne in mind that someone working in the field of conservation can never be such a fine expert in a technique. The complexity of materials and situations makes it necessary for the cultural heritage diagnostician to be helped in the interpretation of data by studies produced by the academic world of research.

In conclusion, we have to consider that the analytical use of calorimetric analytical techniques in cultural heritage studies cannot and should not be typical research tools, but should become a basic tool like others analytical techniques, such as FTIR and SEM-EDS have long been so.

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Thermal analysis applied to polymers: a powerful tool in combination with other techniques to extrapolate chemical structure-property correlations

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Keywords: differential scanning calorimetry, bio-based polyesters, WAXS: dielectric analysis

As is well known, when we speak of thermal analysis, we are referring to a family of measuring techniques sharing a common feature: all them measure a material' s response to heating or cooling (or even, in some cases, to a constant temperature). The goal of thermal analysis is to establish a correlation between temperature and specific physical properties of materials. The most popular techniques are differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), thermomechanical analysis (TMA), dynamic mechanical analysis (DMA) and dielectric analysis (DEA). Polymers are by far the most studied materials with thermal analysis. In this field, thermal analysis is used not only for measuring the actual physical properties of materials, but also for clarifying their thermal and mechanical histories, for characterizing and designing processes used in their manufacture, and for estimating their lifetimes in various environments. For these reasons, thermal analysis instruments are used routinely in laboratories of companies producing polymers and by industries, which manufacture or develop plastic products.

From academic point of view, thermal analysis aims to achieve clear correlations between chemical polymer structure and final polymer properties through the easy and fast determination of the glass transition temperature, the heat capacity jump at the glass transition, melting and crystallization temperatures, heat of fusion and heat of crystallization, and measurements of liquid crystal transitions. Last, but not least, we can also evaluate kinetics of melt as well as glass polymer crystallization. The establishment of these structure-property relations is indeed of fundamental importance to design a new polymer for an intended application.

Herein, we focused on bio-based polyesters (see Figure 1), which revealed to be promising candidates to replace traditional fossil-based plastics still employed today in food packaging, the sector using the biggest amounts of plastic materials and thus producing the largest volumes of plastic waste, with a consequent dramatic environmental impact.

In detail, we devote our attention to poly(butylene isophthalate) (PBI), a 100% bio-based polyester with T_g around room temperature, good mechanical properties, outstanding gas barrier properties, together with easy melt-processability.

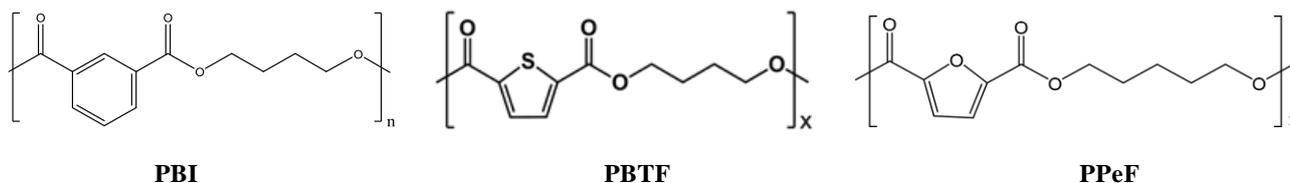


Figure 1. Chemical structure of PBI, PBTF and PPeF.

However, its crystallization rate is too slow in view of its commercial production and application. In this context, we aimed to investigate crystallization rate and lamellar crystals formation for PBI. Then, more specific studies were conducted on crystal nuclei at high supercooling from the melt and in glassy state, as alternatives to the traditional method utilizing heterogeneous nucleators [1,2]. Lastly, glass relaxation and crystal nucleation at temperatures slightly below T_g have been investigated.

Another potentially interesting new 100% bio-based polyester for food packaging application is poly(butylene 2,5-thiophenate) (PBTF) (Figure 1) characterized by outstanding mechanical and gas barrier properties, which have been explained on the basis of polymer microstructure. Two different ordered phases (the 3-D crystalline phase and a 2-D mesophase, this latter originating from π - π stacking, reinforced by the polar character of the thiophenic ring) have been recognized and investigated by means of calorimetric and diffractometric analysis. Their relative amounts were found to depend on the presence of impurities of 2,5-thiophendicarboxylic acid, which acting as nucleating agents favor the crystalline phase formation at the expense of 2-D one [3,4].

Lastly, poly(pentamethylene 2,5-furanoate) (PPeF) (Figure 1) is a superpolymer obtainable from renewable resources, which can be utilized as monomaterial in place of multilayer structure films, currently used when very high gas barrier performances are required to prolong food shelf-life. Interestingly, although amorphous and rubbery at room temperature, PPeF could be processed in form of free-standing film. In terms of functional properties, PPeF shows exceptional barrier and mechanical response, which make it suitable for the production of flexible packaging (flexible films). More in details, the mechanical behavior was typical of elastomers, i.e. low elastic modulus and stress at break, high elongation at break together with an instant shape recovery after breaking, indicating the presence of net points. In order to understand better the origin of these peculiar as well as outstanding properties, a further study combining calorimetric, diffractometric and spectroscopic techniques was carried out. The results obtained evidenced the formation of a particular ordered microstructure, different from the classical crystalline phase, characterized by a lower degree of order (2-D, 1-D instead of 3-D), originating from a partially ordered arrangement of furan rings, favored by intermolecular hydrogen bonds. The existence of such interchain interactions has been proved also through broadband dielectric spectroscopy ad-hoc experiments [5,6].

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Focus on calorimetry and thermal analysis to study oil paint curing

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Keywords: oil paint curing, DSC, TGA, Py-GC-MS

This communication is aimed at discussing the main information that can be obtained on the chemistry of the oil paint curing by means of a methodological approach based on thermogravimetric analysis (TG), differential scanning calorimetry (DSC) and analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS).

Reactions taking place during paint curing are crosslinking, oxidation and hydrolysis. All these reactions occur simultaneously during air-drying of a paint, and the prevail of one over the others is strongly related to the presence of pigments, dryers, additives, determining the final molecular composition of the paint film and, consequently, its stability, hydrophobicity/polar nature and durability. [1]

The molecular characterization of a paint film is a very complex task due to its insolubility and often its knowledge is inferred from the analysis of the nonpolymerized fraction of the oil binder.

Our idea is to study the degree of cross linking/oxidation/hydrolysis taking place in the oil binder during the first period of a paint curing and how and how much the presence of inorganic pigments with different drying properties can modify it. The results obtained can be used to predict the final composition of a totally cured paint network. [2]

In this framework, model paints based on linseed oil and safflower oil (a drying and a semi-drying oil respectively) mixed with two historically relevant pigments - lead white (a through dryer) and synthetic ultramarine blue (a pigment often encountered in paintings with conservation issues) - were investigated.

TG was used to follow the oil curing under accelerated conditions (80°C under air flow). The fitting of the oxygen uptake profiles by a semi-empiric equation allowed to reveal that the first oxygen uptake is followed by two main degradation phenomena with kinetics depending on the oil/pigment combination (Figure 1). The parameters of the equation allowed also to estimate for the first time the mass of oxygen taken by the paint, and the mass of paint that is lost by degradative oxidation. DSC was used to monitor the radical activity of paint layers and to evaluate the stability of peroxides formed. Py-GC-MS was used to characterize the whole organic fraction of the model paintings, including the cross-linked network. [3]

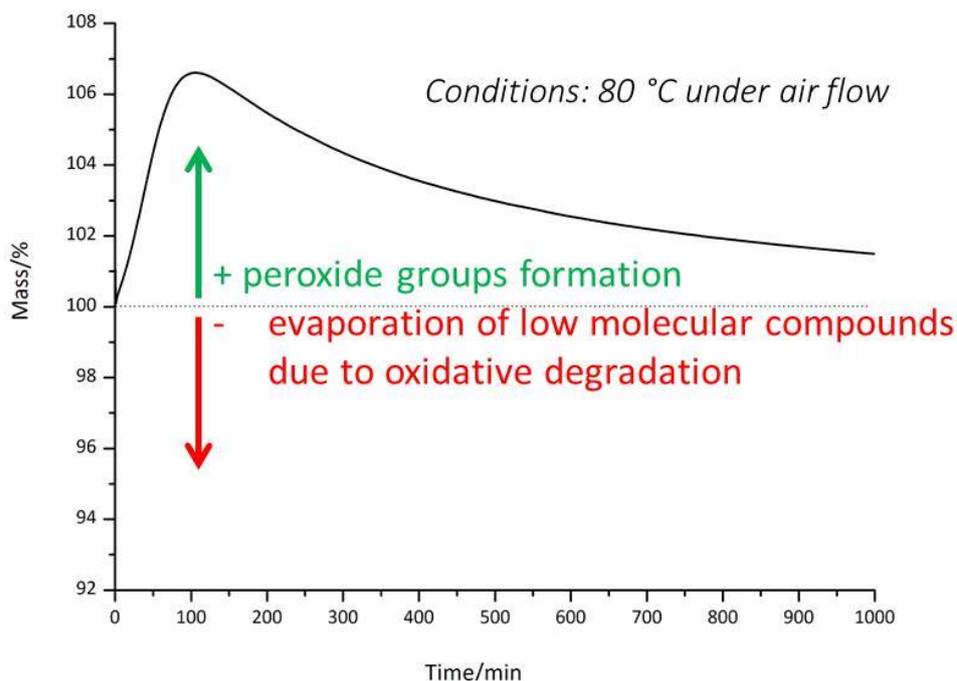


Figure 1. Oxygen uptake curves versus time of linseed oil at 80°C under oxygen flow

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The role of researchers in kinetical calculations

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Keywords: kinetic analysis, non-isothermal thermogravimetry, influence of researcher

According to the current recommendations of the International Association for Thermal Analysis and Calorimetry, ICTAC (International Confederation for Thermal Analysis and Calorimetry) [1], kinetic analysis deals with measurement and parameterization of the process rates and it is carried out for practical or theoretical purposes. In order to get reliable and comparable data it is necessary to follow ICTAC recommendations. However, the published results of the kinetic analysis of the thermal decomposition process for the same polymer materials differ significantly. The question is why - because of non-compliance to ICTAC recommendation or there might be other reasons? The aim of this presentation is to investigate whether the researchers themselves affect the results of kinetic analysis during the computations. For that purpose, four polymers having different degrees of complexity of the thermal decomposition process were analyzed. The kinetic analysis was performed by three researchers: one scientific advisor with tenure, one research associate and one doctoral student. All of them used the same experimental thermogravimetric data and the same software, Netzsch Thermokinetics Professional software. The results indicate that researchers themselves might have a significant influence on the results of kinetic analysis.

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ORAL COMMUNICATIONS

The power behind micro-calorimetry – About leather making and its preservation over the millennia

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This paper is dedicated to the memory of Professor Giuseppe (Pino) Della Gatta, a great pioneer of calorimetry applied to the field of Cultural Heritage.

Keywords: historical and modern leather, collagen, hydrothermal stability, microDSC

Looking deep inside the materials to uncover the secrets of ancient crafts, and the causes and patterns of historical materials degradation provides invaluable clues for extending their lifespan and improving our capacity to communicate rich narratives about the past, as well as to imagine new and more sustainable materials. Dating back thousands of years are numerous examples of ancient technology that leave us awe-struck at the knowledge and wisdom held by people of our past – among them, the raw leather processing technologies. Like other many ancient technologies, its mysteries were partially forgotten, lost to the pages of history, but they are now awaiting to inspire better man-made materials and structures. Here we feature the ancient skin processing history and dozens of amazing artefacts that reflect the brilliance of ancient minds together with their conservation story. The power of a classical technique, micro-calorimetry, multiplied by complementary techniques (NMR MOUSE, ATR-FTIR, Raman, XRF, SEM), teaches us how applying an ancient and beautiful technology can inspire future innovation. Why collagen best survived in ancient parchment and leather than in modern chrome-tanned leather? Clues from leather thermal stability resulted from hydrogen bonding and covalent crosslinking of collagen with traditional tanning agents have suggested us ways to reinforce fragile artefacts. Another question came next. Could we use the stabilization of collagen as had been used in the old age technology of tanning to produce leathers of comparable qualities to those of modern chrome-tanned leather? As alternative tanning technologies are highly sought for curbing environmental pollution from the leather industry (highly criticized globally for its severe environmental and human health harm), both ancient materials and our ancestor's way of living (reduce, reuse, recycle biodegradable) have become very topical trends within the contemporary multi-circular economy.

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Determination of the equilibrium enthalpy of melting of two-phase semi-crystalline polymers by fast scanning calorimetry

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Keywords: Fast Scanning Calorimetry, Rigid Amorphous Fraction, Melting Enthalpy, Furanoates

Polymers can crystallize to different extents, but never entirely. The equilibrium enthalpy of melting ΔH_m^0 [J·g⁻¹] is an extrapolated thermodynamic quantity attributed to crystallizable macromolecules and widely used to characterize polymers in their semi-crystalline state, for it allows estimating the degree of crystallinity by direct comparison with the enthalpy of melting obtained from differential scanning calorimetry. ΔH_m^0 is typically determined by cross-comparing the results obtained by at least two techniques. This work proposes a simplified experimental protocol to estimate the value of ΔH_m^0 by using Fast Scanning Calorimetry (FSC). This approach applies to any crystallizable polymer for which a specific microstructure can be obtained (i.e. a two-phase semi-crystalline microstructure with a negligible amount of rigid amorphous fraction) and that can also be quenched to its fully amorphous state. Such a two-phase microstructure can be obtained on nanoscale samples through an annealing process performed *in situ* on the FSC sensor at crystallization temperatures as close as possible to the melting temperature. The enthalpy of melting is then evaluated from the two-phase model for different crystallization times (i.e. different crystallinities) and the value of ΔH_m^0 is obtained by extrapolating the data to the theoretical 100% crystalline state. This procedure was applied on samples whose values of ΔH_m^0 are already available in the literature, but also on more recent bio-based polyesters whose thermal properties are still under investigation.

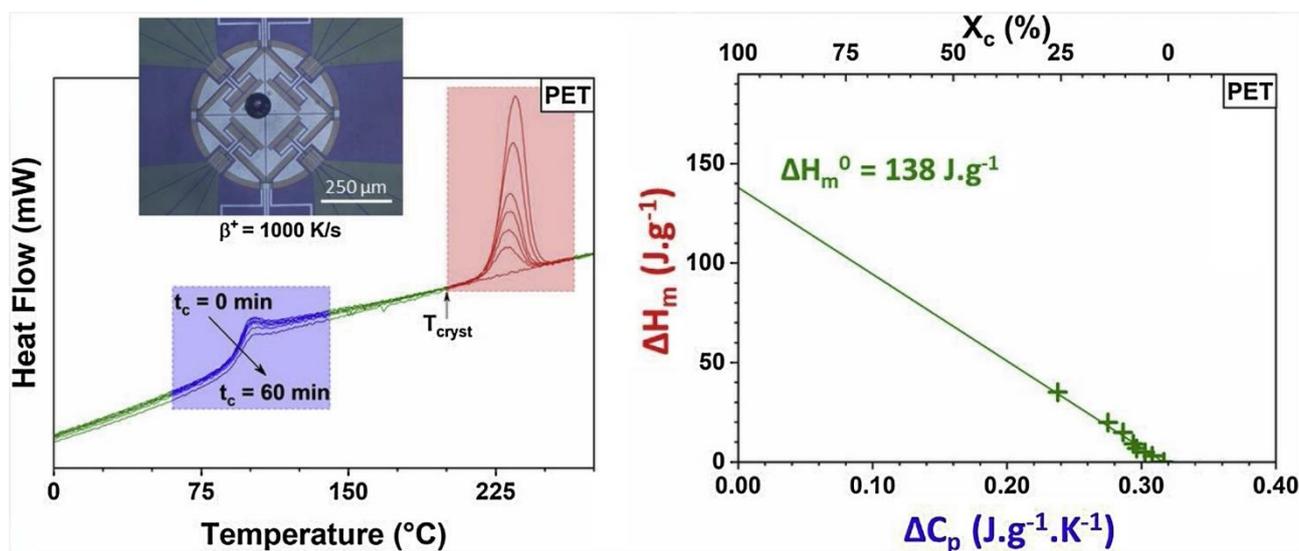


Figure 1. Illustration of the method used to estimate the value of ΔH_m^0 of crystallizable polymers by Fast Scanning Calorimetry. Nanoscale samples were crystallized *in situ* on FSC sensors at selected crystallization temperatures for increasing crystallization times (left); the melting enthalpy measured during the subsequent heating ramp was plot against the heat capacity step at the glass transition (right); the extrapolation provided an estimate of the equilibrium enthalpy of melting ΔH_m^0 .

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Eco-friendly method for keratin extraction from poultry feathers and manufacturing of keratin-based bioplastic in one-pot process

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Keywords: Keratin, Electrospinning, Poultry feather, Biodegradable

Poultry feathers are among the most abundant and polluting keratin rich waste biomasses [1]. Waste-derived keratin is a biodegradable and biocompatible protein with high sulphur content and peculiar properties (e.g. high tensile strength, mechanical stability and rigidity) [2] that make it suitable for the production of useful materials in various application fields such as cosmetic [3], biomedical [4], tissue engineering [5] and added-value bioplastics [6].

Main objective of this research is the development of one-pot process that provide for eco-friendly keratin extraction from poultry feathers and the direct electrospinning of the extract to obtain keratin-based bioplastics.

The keratin extraction process was conducted in acetic acid 70% v/v using innovative coaxial dipole antenna [7] to apply microwave (MW) energy inside the extraction medium. The effect of the extraction time (2 and 5 h) on the extraction yield was investigated and the composition of the extracted solution was determined analysing the amino acid, peptide, and protein contents. The higher extracted peptide/protein yield (25.9 ± 0.9 %w/w) was obtained after 5 h of MW acidic extraction. Keratin-based bioplastics were manufactured via electrospinning technology (50kV, 1 mL/h, 15 cm, electrospinning time 2h) starting from blends of the waste-derived keratin extracts and commercial gelatine 20% w/v with 3-(Glycidyloxypropyl)trimethoxysilane (GPTMS) as cross-linking agent in a ratio of 3% or 6% v/v with respect of the final volume. Thermal properties of the keratin-based electrospun bioplastics were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), while their mechanical and barrier properties were investigated through uniaxial tensile tests and water permeability measurements. Furthermore, these new bioplastics were also structurally and morphologically characterized by attenuated total reflection-infrared spectroscopy (ATR-FTIR) and scanning electron microscopy (SEM).

The mechanical properties show that an increase of crosslinking agent makes the keratin-based bioplastics more stiff but more brittle. This result seems to be confirmed also by glass transition temperatures which are greater of about 10°C for the bioplastics with 6% of GPTMS.

The different extraction times have a less evident effects on mechanical properties with respect to GPTMS: results indicate that passing from 2h to 5h decreases the elastic modulus (-20 to -30%) without affecting the toughness.

The present work illustrates how abundant and underused proteins, such as keratins extracted from poultry feather, can be turned into eco-friendly bioplastics thanks to innovative one-pot extraction process together with advanced manufacturing techniques.

Acknowledgments

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The influence of the initiator as parameter to improve the thermo-mechanical properties and recyclability of thermosets based on epoxidized vegetable oils

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AICAT participation grant

Keywords: Epoxidized linseed oil, Recyclability, Transesterification reaction, Disulfide exchange reaction, Reactivity, Initiator.

Vegetable oils are used since long-time as plasticizers, lubricants, adhesives, paints and coatings. Thanks to their cheapest and abundant availability the oilseeds, as renewable natural resources, are nowadays used as starting monomers to develop bio-materials for industrial applications [1]. The conventional thermosets show excellent properties, but usually they are derived from fossil resources and their recycling is limited by their permanent cross-links making them difficult to be reprocessed.

This work, under H2020 "ECOxy" project- proposes the synthesis of innovative bio-based epoxy thermosets from commercial epoxidized vegetable oil (Epoxidized Linseed Oil) to produce new sustainable thermoset exhibiting recyclability properties.

The epoxy monomer was copolymerized with aromatic diacid crosslinker, containing S-S bonds, in the strategy to design materials with dual exchange mechanism: disulfide metathesis and of transesterifications [2]. To assess the feasibility of the reprocessing, a screening of 10 initiators was tested to probe their effect not only on the cross-linking reaction but also on the recyclability [3,4].

The crosslinking reactions were investigated using differential scanning calorimetry (DSC), *in situ* Fourier Transform Infrared Spectroscopy (FT-IR). The physico-chemical and thermomechanical properties of thermosets and reprocessed bio-materials have been investigated via dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA).

An excellent effect and very good reprocessability was achieved by using Imidazole, as initiator. The thermosets were reprocessed 10 times without losing their thermo-mechanical properties.

Moreover, the thermosets exhibit complete chemical recyclability in 1 N NaOH at 80 °C, after 3 days, without needing additional chemicals.

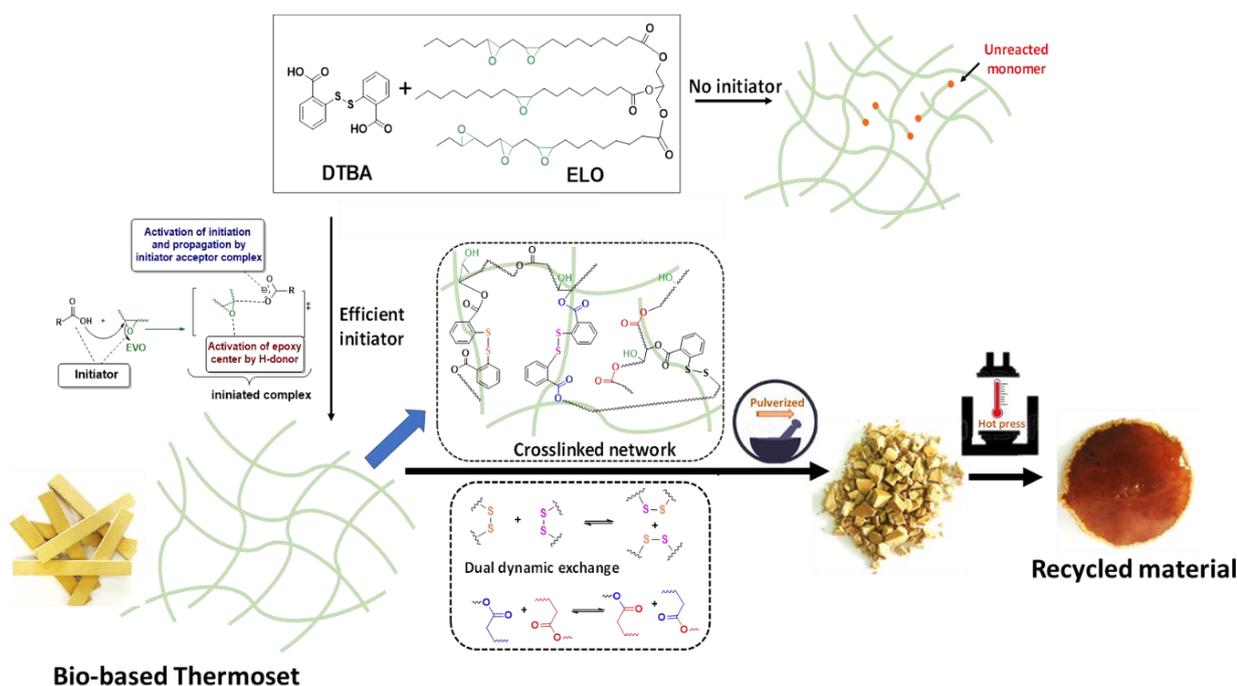


Figure 1. Epoxidized linseed oil (ELO)/2,2'-dithiodibenzoic acid (DTBA) cross-linked structures, and network rearrangement by simultaneous exchange reactions guaranteeing mechanical reprocessing of the bio-thermoset by hot pressing.



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Thermal analysis and electrical performance by Tunneling Atomic Force Microscopy of carbon nanofiber-based nanocomposites

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Keywords: Thermosetting resins, Carbon Nanofibers, Thermal analysis, Tunneling Atomic Force Microscopy (TUNA)

In order to obtain multifunctional structural composites characterized by good thermal and mechanical properties and high electrical conductivity as well as better processability, Carbon NanoFibers (CNFs) are increasingly playing a strategic role in advanced structural applications [1-7]. In this work, epoxy nanocomposites filled with different CNF weight percentages capable to impart electron conduction and high curing degree to epoxy resins have been investigated. The remarkable mechanical properties strictly related to the high curing degree (almost 100%) reached with the chosen formulation and curing treatment, together with the values in the electrical conductivity and the state of the nanofiller dispersion and interconnections, analyzed by Tunneling Atomic Force Microscopy (TUNA) technique, highlight an interesting applicative potential for the formulated material in the aeronautical sector. TUNA technique is a valid tool for the study of the arrangement of charged particles within an insulating matrix and significant information can be obtained not only on the distribution of the nanoparticles but also on the interaction between host matrices and nanofillers. The nanocomposites filled with CNF heat-treated at 2500°C (CNF2500) are characterized by the presence of conductive paths at a relatively very low nanofiber content, causing an increase of conductivity beyond the electrical percolation threshold (EPT) due to an effective connection among carbon nanofibers, which are integrated into the epoxy matrix (T20BD) and become part of the cross-linked structure. The presence of conductive network inside the epoxy resin is clearly visible in Figure 1.

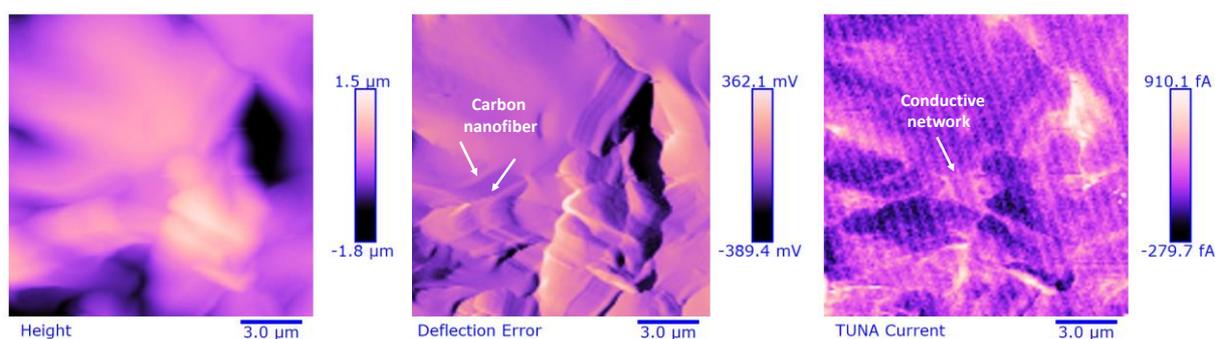


Figure 1. TUNA-AFM height, deflection error, and tuna current images of the fracture surface of the T20BD+1.3%CNF2500 sample.

In this work, the Curing Degree (DC) has been obtained in dynamic (see Figure 2a) and isothermal regime (see Figure 2b). All the analyzed formulations show DC values higher than 92% also in isothermal regime. The nanofiller causes an increase in the efficiency of curing process in isothermal regime, which is usually the real condition of curing in industrial processes [1]. From Figure 3, we can see that the DC of all samples containing embedded CNF2500 is very high compared to unfilled epoxy resin. All CNFs filled epoxy samples reach a value of CD of almost 100%. The results on the resin filled with CNF nanoparticles highlight an interesting behaviour with respect to the curing degree proving the proper formation of the crosslinked network.

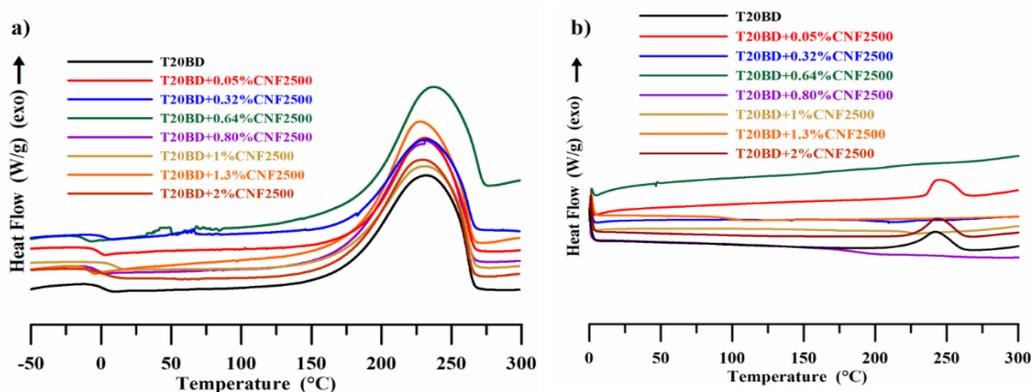


Figure 2. DSC curves of the nanofilled samples: a) in the first run, b) in the second run.

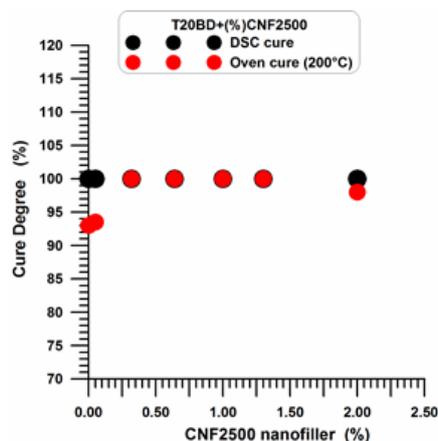


Figure 3. DC values of the CNF epoxy nanocomposites cured under dynamic and isothermal heating conditions.

Acknowledgments

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Analyzing the bulk glass transition in Ultrastable glasses with fast-scanning nanocalorimetry

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Keywords: Fast-scanning nanocalorimetry, Ultrastable Glasses, glass transition

Glasses prepared by physical vapour deposition at substrate temperatures around 0.85T_g present extraordinary thermodynamic and kinetic stabilities, comparable to those of ordinary glasses aged for thousands of years. Such exceptional stability makes these glasses incredibly interesting for a wide range of new applications, including drug delivery [1], organic electronics (Organic light-emitting devices [2], organic field-effect transistors [3] or organic solar cells [4]) and lithography [5], among many others. These glasses are prepared as thin films with thicknesses ranging from 20nm to 200nm generally. The small nature of these samples requires of high sensitivity techniques in order to measure the small amounts of energy that are involved in their thermal processes. In this sense, quasi adiabatic fast-scanning nanocalorimetry has shown to be a very useful tool. The extremely low mass of the calorimetric cells used in this technique allow us to reach very high heating rates (up to 10⁶ K/s) which lets us study thermal processes (such the glass transition) in samples of just a few nanometers with high precision.

In this work we use quasi adiabatic fast-scanning nanocalorimetry to study the characteristics of the homogeneous mechanism by which capped ultrastable glasses transform into the supercooled liquid. The results show that the kinetic stability during annealing treatments increases by a factor 25-50 with respect to the uncapped stable glasses. In addition, we identify that the transition mechanism into the supercooled liquid of these glasses follows a nucleation and growth like kinetics with pre-existing nuclei and a 2D growth of the liquid fraction. Dynamics that previous works reported as the correct framework to describe ultrastable glasses' glass transition through computer simulations [6].

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Calorimetric and fluorimetric interaction studies of Europium(III) complexes with Bovine Serum Albumin

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Keywords: BSA interaction, Europium(III) complex, Isothermal Titration Calorimetry, Biothermodynamics

Lanthanide (Ln(III)) derivatives, mainly Eu(III) and Tb(III) complexes, have been broadly exploited as sensors in physiological conditions for the detection of relevant clinical biomarkers.[1] This can be done thanks to their peculiar properties such as long Ln(III) luminescence lifetime and the so-called antenna effect. The luminescent Ln(III) complex must interact selectively with a target bioanalyte competing with species, such as proteins. Serum albumins, which represent 52% of the protein composition in the circulatory system, play many physiological and pharmacological functions in the delivery of a variety of endogenous and exogenous species. Human serum albumin (HSA) and Bovine serum albumin (BSA) are the most studied serum albumins, and classified as homologous proteins. Changes of the albumin levels in blood could be a sign of several disorders, such as liver disease, neoplasia and more [2].

With the aim to assess the interaction of some Eu(III) luminescent complexes (Figure 1) with the BSA and thus the possible competition with other analytes, fluorescence/luminescence titrations with the cited protein were carried out in this work, the ligands employed differ for their antenna moieties. In addition, the thermodynamics of the interactions were studied by isothermal titration calorimetry (ITC).

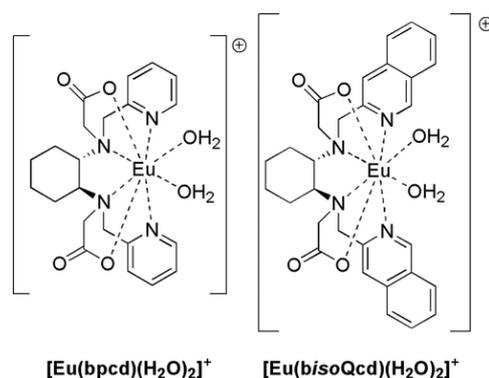


Figure 1. Molecular structure of the Eu(III) complexes for BSA detection

The protonation constants for the ligands alone and their formation constants with Eu(III) have been determined by potentiometric and spectrophotometric techniques [3], the fluorescence/luminescence titrations and ITC titrations of the complexes with BSA have been run at

pH = 7.4 (MOPS buffer). The results obtained by ITC measurements, reported in Fig.2, indicated negative enthalpy values for the interaction with BSA.

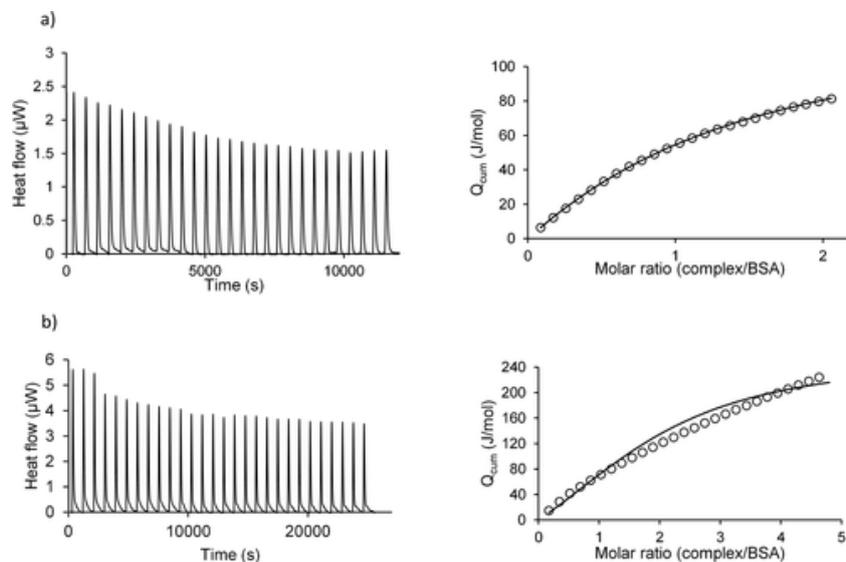


Figure 2. Calorimetric titrations of BSA with (a) Eu(bpcd); b) Eu(bisoQcd). On the right, the experimental (\circ) and calculated (line) Q_{cum} (cumulative heat exchanged/total moles of added reactant) vs complex/BSA molar ratio.

Computational methods provided additional information about the formed adducts: in particular, EuL (L = bpcd and bisoQcd) complexes form adducts with BSA with different stoichiometry, which result from different interaction mechanism. Also, as showed by competitive titrations with site markers (warfarin/ibuprofen/digitoxin) and Molecular Docking/Molecular Dynamics Simulations, the interaction with BSA occurs at different sites for Eu(bpcd) and Eu(bisoQcd) [4].

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Peptide-lipid membrane interaction: influence of free fatty acids-deriving alterations in host membrane's thermodynamic stability

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Keywords: Model membranes, Differential Scanning Calorimetry, Peptide-membrane interaction, Free Fatty Acids

The binding of peptides/proteins to membrane surfaces is crucial in several biological events and is often accomplished through lipid-interacting protein domains. Generally, many peptides have been shown to approach the cell membrane by means of nonspecific interactions [1], which drive, if possible, the subsequent insertion of the peptide's hydrophobic portions within the phospholipid bilayer. However, peptides/proteins functionalities and interaction with membrane also depend on the physicochemical properties of the lipid bilayer itself [2,3]. Therefore, the presence and the effects deriving from external perturbing agents within the cell lipid bilayers might significantly affect the resulting peptide-membrane binding.

In this frame, this work was focused on the effects that the presence of Free Fatty Acids (FFAs), which are naturally present in biological membranes, may have on peptide-membrane interaction [4]. For this purpose, nisin, a small cationic peptide known for its ability of interacting with cell membranes both directly and by a receptor-mediated way [5], was selected as a model for the peptide-membrane interaction study. Furthermore, basing on the thermodynamic information achieved through the previous studies [6,7], a model cell membrane was designed and prepared as reference liposome system by combining specific percentages of DMPC, DPPS and DOPC in order to consider the main compositional aspects (phospholipid headgroup, tails, presence of unsaturations) and to resemble the thermal stability profile commonly observed in both real cell membranes and highly-representative artificial ones in terms of cooperativity and enthalpy contributions to the gel-to-liquid crystalline phase transition. Nisin-vesicle interaction was investigated through micro-DSC and fluorescence spectroscopy in FFAs-free and FFAs-containing liposomes at physiological pH (pH 7.4). The effects of six different FFAs on membrane stability were evaluated, namely two saturated FFAs (palmitic acid and stearic acid), two monounsaturated FFAs (the *cis*-unsaturated oleic acid and the *trans*-unsaturated elaidic acid) and two *cis*-polyunsaturated FFAs (the ω -6 linoleic acid and the ω -3 docosahexaenoic acid or DHA).

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Interaction of calixarene-based micellar aggregates with model antibiotics in neutral aqueous solution: a calorimetric investigation

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Keywords: amphiphilic calixarenes, antibiotics, micelles, driving forces

The entrapment of target molecules in drug delivery systems (DDSs) is an emerging strategy employed to improve the therapeutic efficacy of a drug. For example, old generation medicines, such as antibiotics, may take advantage of the interaction/encapsulation within suitable nanocarriers for overcoming problems associated with antibiotic resistance [1].

Among novel DDSs, polycationic calixarene derivatives which self-assemble in nanoaggregates are emerging as promising nanocontainers for the delivery of antibiotics to bacteria due to their ability to establish electrostatic interactions with the negatively charged bacterial membranes [2]. In particular, a polycationic calix[4]arene amphiphile, CholineC4dod, bearing choline groups and dodecyl aliphatic chains at the cavity upper and lower rim respectively, turned out to be a promising nanocarrier for drug delivery [3].

Despite the general interest in the study of drug-micelle interactions, a quantitative analysis of the species, binding affinity as well as thermodynamic parameters for the recognition/inclusion of a drug with(in) micellar assemblies has rarely been addressed. However, the determination of the strength and nature of these interactions is crucial for the design of novel medicines as well as for the modification or selection of suitable shuttles for target-oriented drug delivery.

The present work deals with the study of the binding features of polycationic calix[4]arene derivatives (CholineC4dod, MedeaC4dod and MedeaC4prop) with ofloxacin, chloramphenicol or tetracycline (Figure 1) in neutral aqueous solution for investigating the capability of micellar aggregates to recognize and host three old generation antibiotics. These molecules were selected as models of antibiotics affected by the onset of resistance phenomena with the aim of offering a contribution to the design and development of effective DDSs for the reevaluation and use of old-fashioned antibiotics.

The examination of solution equilibria and the determination of the binding parameters in neutral aqueous solution were carried out using nano-isothermal titration calorimetry which proved to be an invaluable technique for determining both stability constant and enthalpy change values for host-guest complex formation [4] and/or self-organization of surfactants into micelles by a single experiment [5]. ITC experiments provided key information on the forces driving the molecular recognition processes involving calixarene-based micellar aggregates and the models drugs. The formation of the chloramphenicol-micelle adduct was found to be enthalpy driven, whereas entropy drives the formation of the adducts with both ofloxacin and tetracycline. NMR experiments supported the picture obtained by ITC results about the positioning of the antibiotics within the micellar backbone [6].

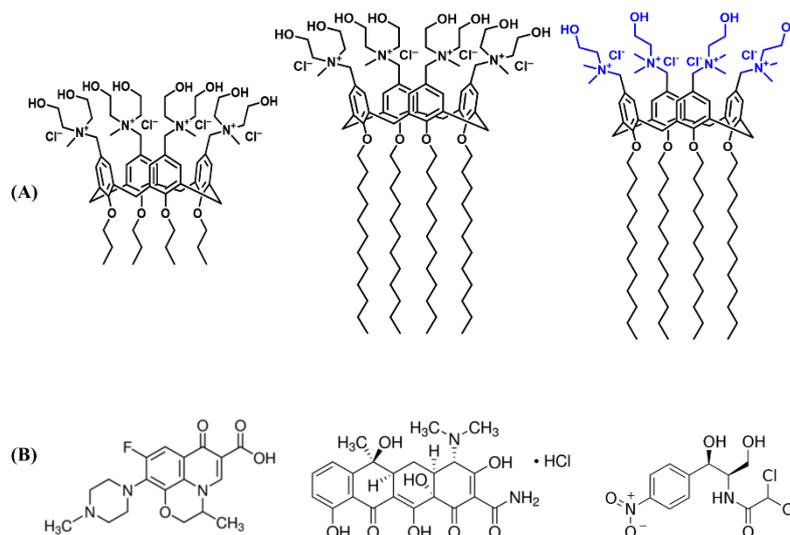


Figure 1. (A) From left to right: MedeaC4prop, MedeaC4dod, CholineC4dod; (B) from left to right: ofloxacin, tetracycline hydrochloride, chloramphenicol

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Thermodynamics of complex formation between hydroxypropyl- β -cyclodextrin and quercetin in different solvents

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Keywords: Quercetin, Hydroxypropyl- β -cyclodextrin, Calorimetry

Quercetin (QCT) is a flavonoid derived from many fruits and vegetables possessing many activities, such as neuro-/cardioprotective, anti-inflammatory and anticancer [1,2]. Unfortunately, the pharmacological application of QCT is severely restricted by its low water solubility and in vivo bioavailability. The therapeutic potential of QCT can be unraveled by enhancing its solubility through the formation of a host-guest complex with hydroxypropyl- β -cyclodextrin (HP β CD) [3,4]. Here we describe the thermodynamic studies on QCT- HP β CD host-guest complex formation under different solution conditions. First of all HP β CD-QCT complex has been obtained in liquid phase using two different buffers at pH = 3.6 and pH = 8.0. Phase solubility and differential scanning calorimetry studies revealed that the best condition for the formation of the complex, with a strong enhancement of QCT solubility, are at basic pH. The affinity constant was calculated by isothermal calorimetry at pH = 8 and was found to be $489 \pm 38 \text{ M}^{-1}$, in good agreement with the value indirectly obtained from phase solubility studies, $394 \pm 101 \text{ M}^{-1}$. The thermodynamics of the formation of the QCT-HP β CD complex in water/ethanol mixtures has been investigated using calorimetric and spectroscopic techniques. The experiments showed that above 0.10 molar fraction molar of EtOH the complex did not form, probably because ethanol competes with quercetin for inclusion within the cavity of HP β CD. Indeed, the low content of ethanol in hydroalcoholic solvents and a slightly basic pH contributed to a better encapsulation of QCT in the cavity of HP β CD.

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Kinetic modeling of the inhibition of lipid autoxidation reaction by isothermal calorimetry

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Keywords: kinetic modeling, antioxidant, COPASI Software, isothermal calorimetry, lipid autoxidation

The aim of this work was to develop a method based on isothermal calorimetry to study the inhibition of lipid autoxidation. For this purpose, styrene was used as a model substrate. The heat evolved during the reaction between styrene and the antioxidants was measured by isothermal calorimetry. The autoxidation reaction was induced by the addition of 2-2'-Azobisisobutyronitrile (AIBN) as a radical initiator. The inhibition of the reaction was controlled by adding increasing concentrations of α -tocopherol at concentrations from 50 to 125 μ M. About 200 ml of samples were loaded in 4 mL glass ampoules and the reaction was monitored in isothermal conditions at 50°C.

The obtained thermograms were then studied to evaluate the rate constants of the autoxidation reaction. A kinetic model was developed by COPASI (COMplex PATHway Simulator) software to evaluate its performance in the simulation of oxidation reactions and the calculation of the inhibitory activity of α -tocopherol.

The results showed an increase in the value of the induction time of styrene oxidation by increasing the antioxidant concentration. COPASI software was able to simulate the oxidation reactions and allowed the experimental data fitting for the calculation of the inhibitory parameters of the reaction. Different parameters were deducted after simulation: the rate of initiation (k_i), the rate of hydroperoxide formation (k_o), the rate of propagation (k_p), the rate constant of termination (k_t) and the rate of inhibition (R_{inh}). Out of all these parameters, the rate of inhibition could be relevant to express the antioxidant activity. The depletion of oxygen, as well as the generation of hydroperoxides, could be followed in the simulated plot. The action of the rise in antioxidant concentration on these parameters was underlined.

Overall, the results of this study showed that the implementation of a kinetic model with COPASI software for the simulation of lipid oxidation gave insight into the understanding of the reaction kinetics for the study of lipid substrates. This approach showed the potentials to underline the action of antioxidants and compare their effects in the protection of food and the improvement of shelf-life.

Bridging heat exchange and surface physics investigations on samples at the nano-scale

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Keywords: Calorimetry, heat exchange, nano-scale, surfaces

The development of atomic-scale engineered systems is booming in the last decades, pushing research to realize new experimental techniques able to characterise them. Regarding the heat exchange, a general method for its direct evaluation in such nanometre-sized samples is not available at present. Calorimetry usually requires samples having mass in the mg range, while nano-devices range in the ng- μ g. Here we report on the development of an original thermometric technique able to detect temperature variations as low as 10 mK in a sample of ~ 10 ng, using a sensitive gold film thermometer (see Fig. 1a) having physical dimensions of about 5×5 mm² [1]. We have assessed the performance of this technique by measuring the enthalpy release during the adsorption process of deuterium (D₂) on a sample of titanium-functionalized monolayer graphene (Ti-MLG). Ti-MLG is a promising material for hydrogen storage applications [2-5], which makes this material a reference system. We show that the sensitivity of our technique allows to detect a hydrogen uptake of $\sim 10^{-10}$ moles, corresponding to ~ 0.2 ng, with a temperature increase of $\Delta T = 0.065$ K (see Fig. 1b) and an enthalpy release of ~ 23 μ J [1].

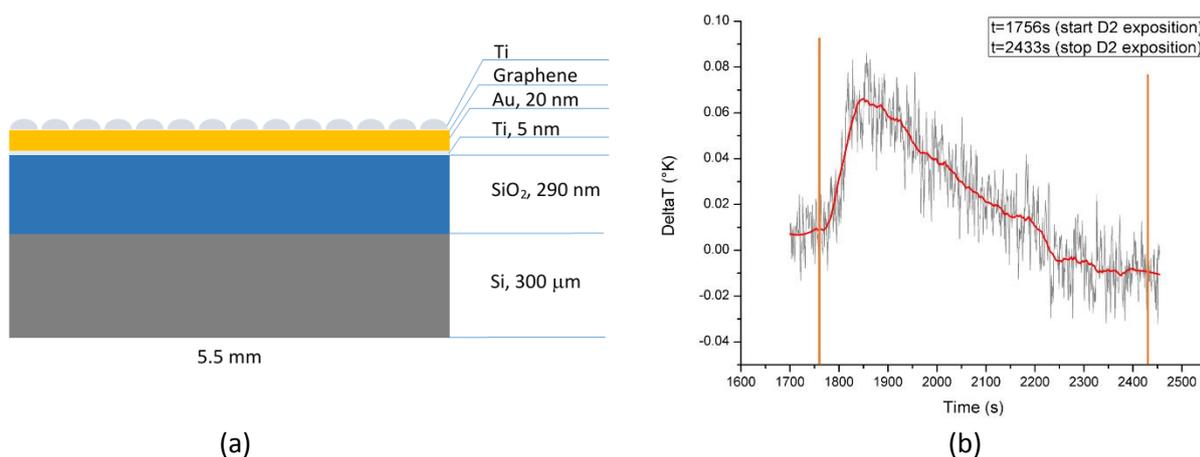


Figure 1. (a) Thermometer structure and graphene sample on it. (b) Thermal signal during the D₂ uptake.

A limitation of the first version of the thermometer is the surface roughness of the gold film on SiO₂, which does not allow atomic resolution imaging with the STM probe. Therefore, we have improved

and upgraded the thermometer and report on the fabrication, characterization, and calibration of an atomically flat, monocrystalline gold film thermometer on mica substrate [6].

Gold re-crystallization is obtained in situ, allowing the successive investigation of the thermometer surface by LEED and with STM imaging. Large gold terraces, exhibiting the herringbone reconstruction (see Fig. 2a), allow achieving a resolution comparable with atomic dimensions during STM imaging of the surface. Moreover, the gold-on-mica thermometer performs about 10 times better than the previous sensor based on a Si substrate (see Fig. 2b). This sensor represents a bridge between calorimetry and surface physics, opening the possibility to investigate simultaneously energy (heat) exchange mechanisms and surface physics with the same physical support. The experimental setup opens a unique perspective in understanding physics and chemistry at the nanoscale.

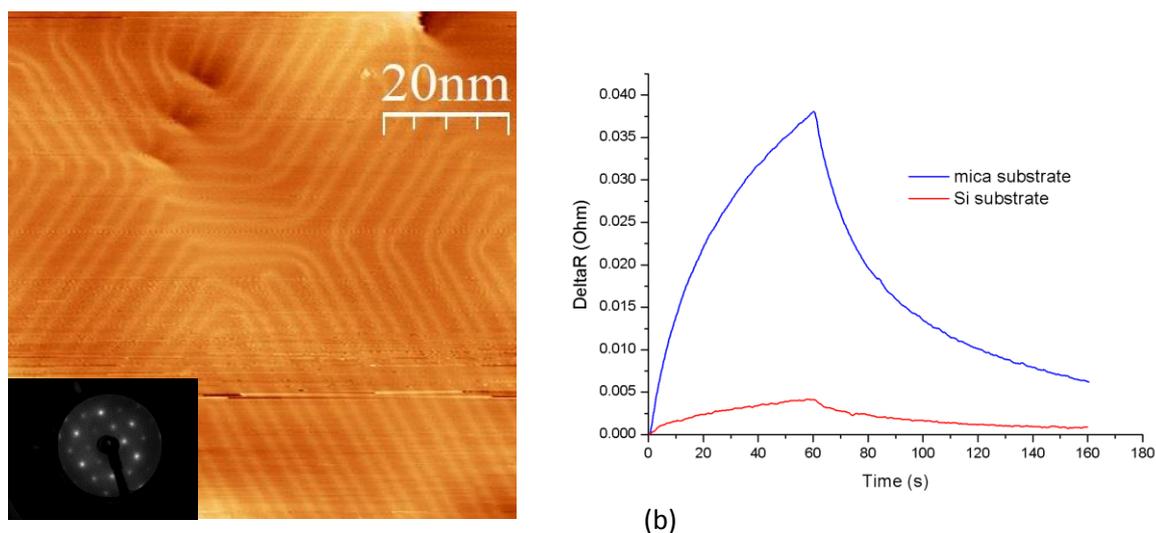


Figure 2. (a) Herringbone reconstruction of the gold film on mica substrate. Inset: LEED shows that the gold film is a single crystal. (b) Comparison between gold-on-Si and gold-on-mica thermometer under the same heating pulse.

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Thermodynamics of non-canonical DNA structure formation

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Keywords: DNA, differential scanning calorimetry, circular dichroism, structural stability

Nucleic acids have the ability to form different hydrogen bonding patterns of varying stabilities. This enables DNA to attain a variety of structural and conformational polymorphic forms [1]. Structurally, DNA can exist in single-stranded form or fold into secondary structures, which include the canonical double helix as well as non-canonical structures such as the G-quadruplex and i-motif species [1,2]. Non-canonical structures in turn encompass an ensemble of conformers depending on the sequence composition and environmental context. In vivo, non-canonical DNA structures may form in important genomic regions and intervene in several biological processes, including the modulation of oncogenes expression, and therefore represent potential anticancer drug targets [2]. By using differential scanning calorimetry and circular dichroism as complementary physicochemical methodologies, we studied the thermodynamics of biologically relevant non-canonical DNA structures. Among these are the G-quadruplexes formed in the *KRAS* oncogene promoter region [3], which is essential for transcriptional regulation of this gene involved in the pathogenesis of several types of cancers. Since the biological consequence of G-quadruplex formation in the *KRAS* promoter element is gene silencing, we considered of primary importance to elucidate the stability and unfolding mechanism of such DNA structures. Overall, our results provide further insights into the thermodynamics governing the formation of non-canonical DNA structures.

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Thermal stability of novel biodegradable protein-polymer conjugates in solution

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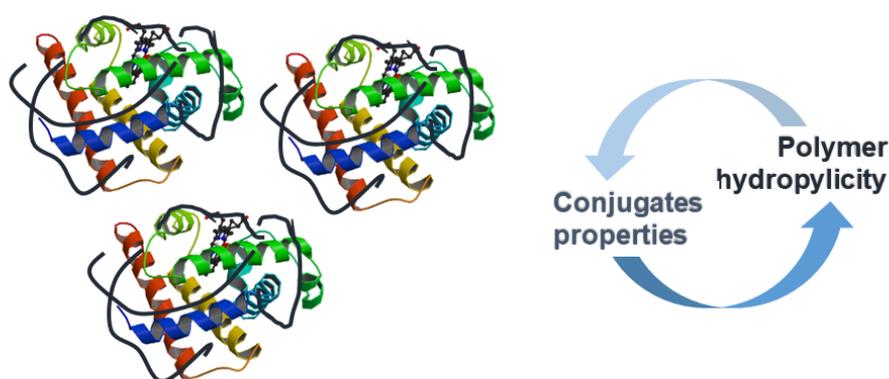
AICAT participation grant

Keywords: Polyphosphoesters, protein-polymer conjugates, *Nano*-DSC, protein thermal stability

Polyphosphoesters (PPEs), an emerging class of biodegradable and biocompatible polymers, have been proposed as promising alternatives to poly(ethylene glycol) (PEG) in the biomedical field [1,2].

We present the synthesis of a set of PPEs with different hydrophilicity and molar mass, used to prepare a novel set of protein-polymer conjugates with the model protein myoglobin [3]. The properties of the conjugates in aqueous solution were evaluated using complementary techniques (UV-VIS spectroscopy, circular dichroism, *Nano*-Differential Scanning Calorimetry and Fluorimetry), with the aim to observe the effect of the polymer attachment on the protein activity, conformation, thermal stability, and resistance to proteolytic agents.

We observed a systematic influence of the polymer hydrophilicity on the protein properties (Figure 1). In particular, the protein activity and thermal stability decreased when decreasing the polymer hydrophilicity. The unfolding process of the protein within the conjugates was studied in detail, observing that, despite the reduction of thermal stability, the more hydrophilic polymers protected the protein toward thermal-induced aggregation and from the attack of proteolytic external agents. On the contrary, the more hydrophobic polymers rendered the protein more vulnerable to the attack of external agents.



Protein-Polymer conjugates (Myoglobin-PPE)

Figure 1. Schematic representation of the protein-polymer conjugates, highlighting the relation between the polymer hydrophilicity and the conjugates properties. Image of myoglobin from the RCSB PDB (rcsb.org) of PDB ID 5CN5, taken from (Barends, T.R., et al.) (2015) Direct observation of ultrafast collective motions in CO myoglobin upon ligand dissociation. *Science* **350**: 445-450.

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Pressure modulation of enzymatic reactions in aqueous two-phase system

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Keywords: kinetics, high pressure, reaction volume changes, biocondensates

Eukaryotic cells are highly compartmentalized structures. The intracellular components are organized into organelles that can be membrane-bound or membrane-less [1]. Membrane-less structures (e.g., nucleoli, Cajal bodies) are formed through liquid demixing of macromolecules which leads in liquid-liquid phase separation (LLPS) and formation of biocondensates. Such biocondensates are highly dynamic structures formed by proteins and/or nucleic acids. They are involved in the modulation of a wide variety of cellular functions, including the fine tuning of enzymatic reactions and protein-ligand interactions as well as the assembly of larger biomolecular units (e.g., ribosomes) [2].

High pressure is a convenient thermodynamic variable that allows to modulate intermolecular interactions between molecules serving as a physical probe for changing the free-energy and conformational landscape of proteins and nucleic acids. In addition, a huge fraction of organisms in the Earth's biosphere is thriving at a depth in excess of 1000 m and therefore is exposed to pressures that can reach 1000 bar level in the Mariana trench, the deepest point in our planet. Hence, high hydrostatic pressure (HHP) studies on biomolecular systems (piezophiles) are also prerequisite for understanding life in the deep sea, an environment which is also the potential birthplace of life on Earth [3,4].

In this study, the combined effects of HHP and LLPS on the hydrolysis reaction of the substrate Ala-Ala-Phe-7-amido-4-methylcoumarin catalysed by α -chymotrypsin is reported [3]. As LLPS mimetic, we used an aqueous two-phase system (ATPS) formed by PEG and dextran polymers. Our data show that the partitioning of both enzyme and substrate in the dextran-rich phase has a deep impact on the reaction rate. The turnover number is drastically reduced compared to the rate observed in neat buffer at ambient conditions. Conversely, no effect on the binding affinity between the interacting partners was observed. In neat buffer, pressure application leads to a significant acceleration of the reaction. Interestingly, we found that the ATPS is able to counterbalance the effect of HHP on this reaction and the enzymatic reaction becomes completely pressure-insensitive when carried out in the ATPS. The results are interpreted invoking volume diagrams of the reaction. The findings are relevant for understanding cellular processes of piezophiles and might have significant bearings on biotechnological applications using liquid-liquid phase separation and pressure in concert for modulating enzymatic reactions.

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Thermogravimetry coupled with Chemometrics as an innovative screening test for the first level diagnosis of hereditary erythrocyte membrane defects

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Keywords: Thermogravimetry, chemometrics, erythrocyte membrane defects, hemolytic anemia

Thermogravimetric analysis (TGA) coupled with chemometrics proved to be able in hematological investigations and in particular in the detection of β -thalassemia and sickle cell anemia: hereditary hemolytic anemias caused by genetic defects in the synthesis of hemoglobin. [1-3]

In this study, the TG/Chemometrics approach was proposed to perform the first level diagnosis of hereditary hemolytic anemias resulting from red blood cell (RBC) membrane alterations: Hereditary Spherocytosis (HS) and Hereditary Elliptocytosis (HE).

Current screening protocol involves a complete blood count followed by a combination of expensive and specific laboratory tests and require many time to make a diagnosis. Therefore, an alternative and cost-effective diagnostic tool able to provide a quick identification of individuals affected by HS and HE defects is needed.

Few microliter of whole blood samples collected from healthy individuals and patients were analyzed by thermogravimetric analyzer and the resulting TG curves were processed by chemometric techniques. The Partial Least Squares-Discriminant Analysis (PLS-DA) algorithm was used to develop and validate a prediction model able to detect HS/HE defects. In addition, the optimized model was tested on patients with a confirmed diagnosis of spherocytosis or elliptocytosis obtained by the molecular analysis.

Results were found to be in accordance with the genetic diagnosis proving the ability of the optimized model to recognize patients with different clinical manifestations in less than one hour.

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Effect of Porosity on the Thermal Conductivity of 3D Printed Parts by Fused Filament Fabrication (FFF)

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Keywords: additive manufacturing, fff, fdm, thermal conductivity, porosity

Fused Filament Fabrication (FFF) is the most widely used process among Additive Manufacturing (AM) techniques.

One of the major issues in FFF printing is the presence of porosity inside the printed parts. In fact, the presence of voids involves a significant decrease in mechanical properties, making FFF components not comparable to the parts obtained by Injection Moulding [1,2].

Several works have focused on the porosity prediction of FFF parts [3-5]. In the field of FFF composite materials, a recent application is the printing of metal and ceramic filled filaments [6,7]. The final metal or ceramic part is first printed (green part) and then subjected to debinding and sintering treatment in order to remove the polymeric binder and to obtain the highly dense final part in metal or ceramic.

To obtain good final sintered parts, it is essential to predict and limit shrinkages. To do this, the porosity of the green part must be very low. In this work, the thermal conductivity of the FFF green parts was related to their porosity. The stainless steel filled filament, Ultrafuse 316L from BASF, was investigated. To introduce a known macroscopic porosity, samples with different infill percentage (0, 50 and 100%), shaped in squares of 12.7 x 12.7x 3 mm³ of dimensions, were printed by using a Zortrax M200 (Zortrax, Olsztyn, Poland) (Fig. 1).

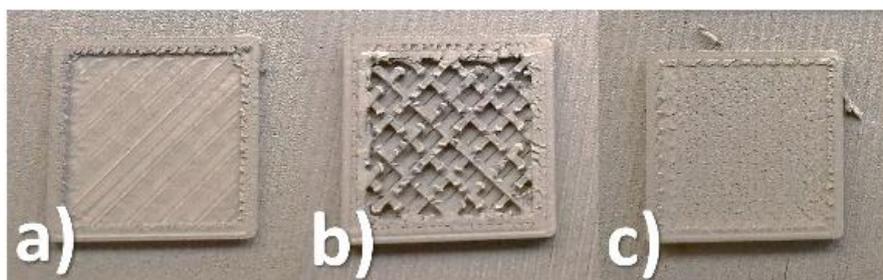


Figure 1. Cross-sections of green parts samples with different infill percentages: a) 0%; b) 50%; c) 100%.

The samples were coated with graphite and introduced into the instrument for thermal conductivity tests, a Laserflash LFA467 Netzsch (Netzsch, Verona, Italy), Fig. 2b.

The thermal conductivity was calculated by applying formula (1).

$$(1) \alpha = \frac{k}{\rho \cdot C_p}$$

where α is the thermal diffusivity ($\text{m}^2 \cdot \text{s}^{-1}$), k is the thermal conductivity ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$), ρ is the density ($\text{kg} \cdot \text{m}^{-3}$) and C_p is the specific heat capacity ($\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$).

The C_p of the material was calculated by DSC analysis, using a Mettler DSC1 Star System (Mettler-Toledo, Milan, Italy), shown in Fig.2a.



Figure 2. a) DSC and b) Thermal conductivity test apparatus.

In conclusion, the knowledge of thermal conductivity has allowed us to estimate the degree of porosity inside the 3D printed parts as a function of the temperature variations. This characteristic is very important, for example, for the estimation of shrinkages in those processes where porosity and temperature influence the final dimensions of the parts, such as in the sintering process.

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Soft magnetic alloys and composites: thermal analysis

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Keywords: Thermal analysis, soft magnetic, alloy, composite

Soft magnetic alloys and composites are topics of technological research interest due to its multiple applications. Likewise, the control of the processing conditions permits the development of the desired amorphous or nanocrystalline microstructure in order to improve the magnetic and thermomagnetic response. Soft magnetic alloys and composites will play an important role to improve energy efficiency of energy conversion devices. They are mostly Fe, Co and / or Ni-based compounds. Among the magnetic properties to be optimized, it is worth highlighting: magnetization of saturation, coercivity, remanence, magneto-impedance, saturation polarization, magneto-crystalline anisotropy, losses. In addition to complementary resistance to corrosion and resistivity.

Thermal analysis techniques are used in the characterization of these alloys and composites to determine their characteristic temperatures (including magnetic or structural transformations), as well as their thermal stability [1]. On the other hand, thermodynamic parameters can be determined such as: the enthalpy and entropy change of a transformation, or the specific heat [2]. Thermogravimetry makes it possible to find oxidation processes and thermomagnetometry the Curie temperature of these alloys. In the case of bulk alloys and composites, their thermomechanical response is analyzed by measures of dilatometry or thermomechanical analysis.

This work shows thermal analysis results for soft magnetic alloys and composites: a) Fe based soft magnetic alloys produced by mechanical alloying, b) Ni-Mn shape memory alloys produced by rapid solidification and c) soft magnetic composites with polymer matrix (as shown in Figure 1).

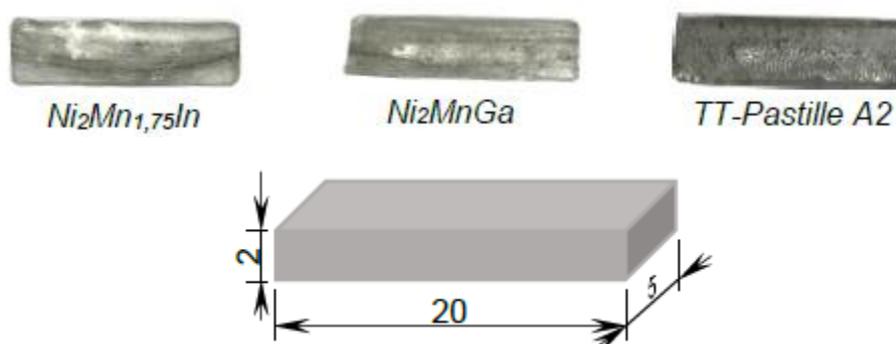


Figure 1. Some composites produced for this study (characteristic lengths are given in mm).

Furthermore, complementary comparison with data from the scientific literature has also been performed.

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Thermochemical energy storage in composite materials: MOFs impregnated by hygroscopic salt

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Keywords: thermochemical storage, Metal-Organic-Framework

The recovery and storage of waste heat sources and the use of sustainable renewable energies would contribute to decrease dependency on fossil fuels. Energy storage systems have therefore been developed in order to reduce the discrepancy between demand and supply. In particular, thermochemical heat storage systems, using reversible sorption/desorption reactions, offer high energy storage density over variable amounts of time with minimal heat losses [1]. Water sorption storage systems using hygroscopic salts, such as CaCl_2 , inside a porous matrix (composite salt porous matrix (CSPM)) are widely used [2]. These composite materials allow the storage of energy (solar or from any other source) during dehydration (charge) and its release during hydration (discharge). Among porous materials, Metal-Organic-Frameworks (MOFs) have recently been of particular interest because of their high sorption capacity due to a very high surface area and tunable properties [3].

This work proposes a calorimetric study of the heat storage/release and water sorption/desorption capacities of CSPM materials. Aluminium fumarate-based MOFs impregnated by different amounts of CaCl_2 (25, 37, 58 wt.%) were synthesized (MOF- Ca_x , figure 1). Materials were subjected to analysis by TG-DSC coupled to humidity generator during successive hydration/dehydration cycles. DSC analysis showed that after impregnation, the heat storage/release capacity of MOFs gradually increases with the amount of salt until reaching 1840 kJ kg^{-1} for MOF- Ca_3 sample (MOF + 58 wt.% of CaCl_2). A concomitant increase in water sorption/desorption capacity, determined by thermogravimetric analysis is observed (figure 1). Besides, storage properties of MOF- Ca_3 decrease by only 6% after 3 dehydration/hydration cycles, and remain stable thus showing high stability.

These materials have been further investigated in order to determine the impact of aluminium fumarate impregnation on structural and textural properties and on hydrophilicity/hydrophobicity balance. High heat and water storage capacities and stability are not the only important parameters for the choice of the storage material. The adsorption rate and desorption activation energy are also primordial data, therefore a kinetic study of hydration and dehydration steps has been performed.

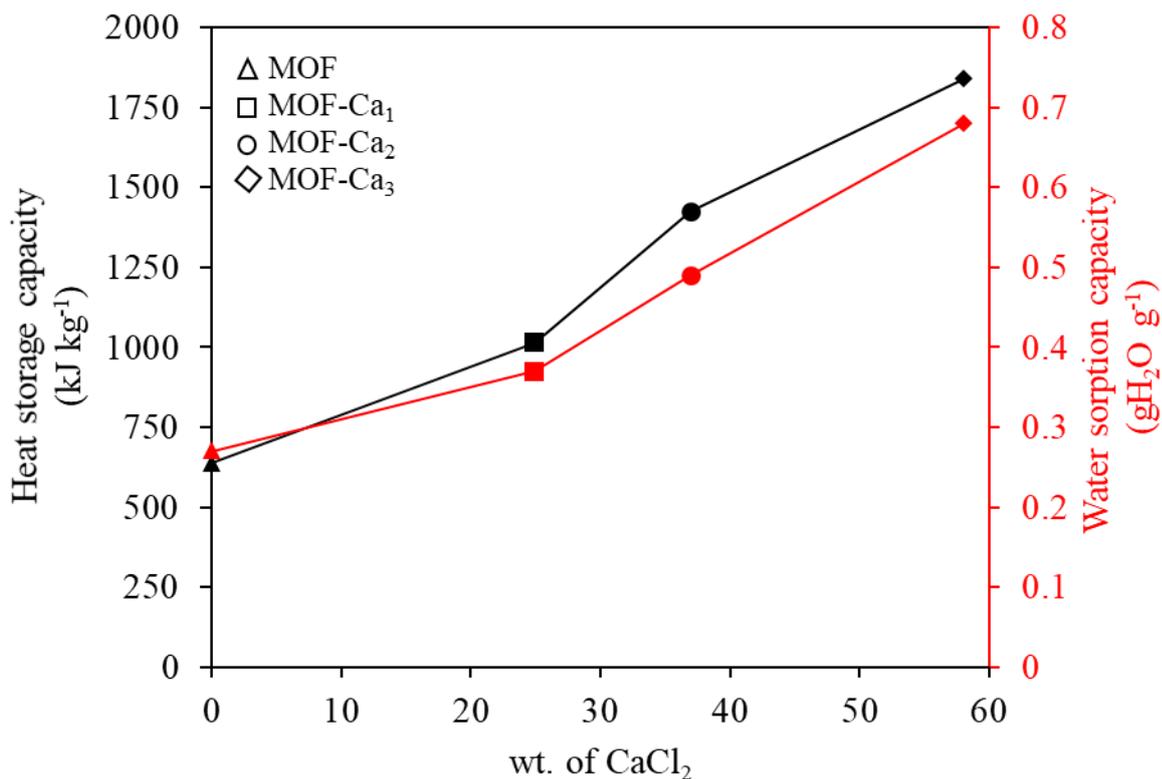


Figure 1. Water sorption and heat storage capacities of composite materials as a function of deposited amount of CaCl₂

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Thermal properties of photocatalytic and gas sensing carbon nanostructures and nanocomposites

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Keywords: Carbon nanostructure, Semiconductor oxide, Nanocomposite, Atomic layer deposition

Our aim was to tune the photocatalytic and gas sensing properties of various carbon nanostructures by coating them with atomic layer deposition (ALD) grown oxide nanofilms and nanoparticles. As substrates, OH functionalized fullerene (C₆₀-OH), OH functionalized carbon nanotubes, graphene oxide (GO) synthesized with the improved Hummers method, carbon nanospheres obtained hydrothermally as well as carbon aerogels were used. Onto them, TiO₂, ZnO and Al₂O₃ thin films and nanoparticles were deposited by ALD.

The preparation and functionalization reactions of carbon nanomaterials were thoroughly monitored by thermal analysis (TG/DTA-MS). In addition, the thermal stability of the as-prepared carbon nanostructures in inert atmosphere was checked to determine what the maximum possible temperature was for the ALD reactions. The annealing in air was studied to determine what heating conditions are needed to remove the carbon cores to obtain hollow oxide nanomaterials. Besides thermal analysis, the nanomaterials were analyzed by XRD, SEM-EDX, TEM-ED, FTIR, Raman, XPS, UV-Vis.

Based on these studied we found that the C₆₀-TiO₂ composite was the first example of ALD prepared single molecule fullerene/oxide composite. The other depositions also meant the extension of the use of the ALD onto these important substrates. The photocatalytic and gas sensing of the as-obtained nanocomposites was investigated. Unexpectedly, amorphous TiO₂ grown by ALD had photocatalytic activity on these substrates - usually TiO₂ is considered to have photocatalytic activity only in crystalline state. The gas sensing of the substrates was considerably modified by the deposited oxide layers and multilayers.

TECHNICAL COMMUNICATIONS

See what is really happening within your furnaces.

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Keywords: Optical camera, TG-DTA, Colour Analysis

Although thermal analysis techniques like DSC, STA, DMA and TMA have been around for a long time, it's always been a challenge to know what is really happening to our samples during an experiment. Being able to see what is happening within the furnace of a thermal analysis instrument can provide valuable information such as sample positioning, size/shape and colour change.

Understanding thermal analysis results can be challenging especially when you don't have much experience with the technique. It can also be laborious to explain the different thermal analysis techniques to people without experience. Being able to see the sample during a measurement helps to either understand results or explain them clearly. Figure 1 clearly shows the reason of why an increase of sample mass in a TGA measurement was measured between 350 °C and 400 °C. Images 4 and 5 show that it is due to gases trapped within the sample which are bursting out and caused the sample to move.

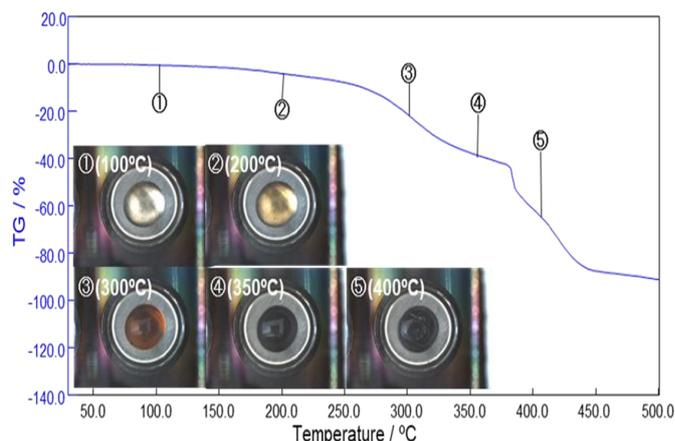


Figure 1: A TGA curve shows an artefact between 350 °C and 400 °C which is explained by visible image 4 and 5.

Being able to see your sample change during a thermal analysis experiment can also provide insight on its dimension change as well as its crystalline form. Figure 2 shows DSC results of Carbamazepine Form I. We can clearly see the melt of form one as well as the recrystallisation to form 3 which is followed by its melt. The visible images confirm the change in crystalline form. Visible images can also allow you to measure changes in shapes and dimensions during thermal analysis.

Another important parameter which can be measured with visual images is sample colour change during analysis. Some materials will go through wanted or unwanted colour change over specific temperature range. Measuring the effect over time or temperature while collecting visible images in a thermal analysis instrument allows accurate temperature control, study of thermal behavior as well as colour changes which couldn't be measured otherwise. Colour analysis is done using pixel colour information which allows the use of colour models such as RGB, Lab, CYMK. Figure 3 shows the effect of temperature on a thermal paper using CYMK. Even if the weight loss

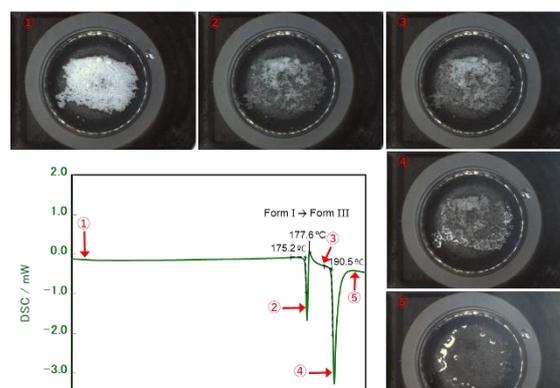


Figure 2: A DSC result of Carbamazepine form 1 showing its melt, recrystallization to form 3 and its melt. Each thermal changes are captured by the visible image.

is minimal, we can observe the changes of colours through the visible images as well as with the CYMK values. Another example is the undesirable effect of heat on materials over time or due to temperature change is shown in Figure 4: a sample of a polypropylene material which change from white to yellow from 200 °C to 300 °C even if no weight loss is observed. The increase in b value from the Lab colour model shows that the material is getting yellow above 200 °C. The use of colour models is essential to remove the arbitrary measurement if the colour measurement was done by an analyst. Since each of us sees colour slightly different, analyst one could give a different answer to analyst two. By using colour model, we improve consistency.

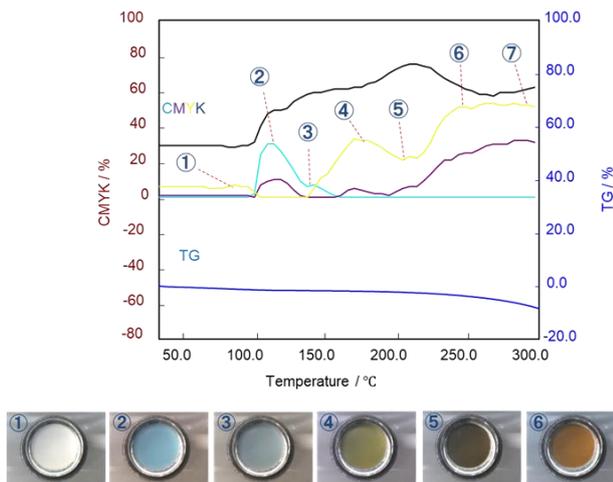


Figure 3: Thermal paper going through colour changes during a TGA measurement. Colours are captured by the visible image and changes are also showed using CMYK colour model.

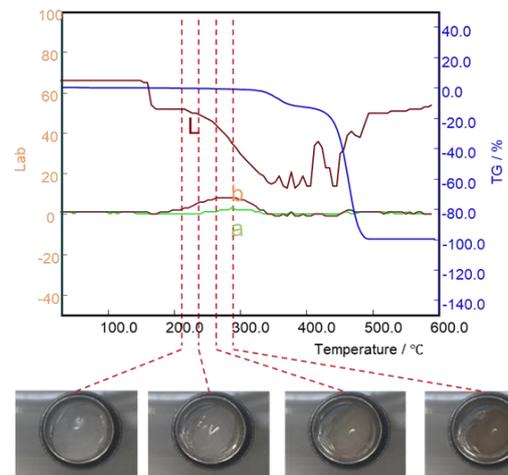


Figure 4: The effect of temperature on a polypropylene sample. Lab colour shows that samples becoming yellow above 200 °C as the b value increases.

There are many more applications where visible images in combination with thermal analysis which are still to be discovered. This presentation will go through the advantages of being able to see the samples while using thermal analysis techniques (DSC, STA, DMA and TMA). Real examples will be used to show the power of the techniques and it will also cover the extra information which can be extracted from a visible image (e.g. RGB values).

Study of Nylon 66 Degradation by Hyphenated TGA-MS and TGA-FTIR-GC/MS Techniques

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Keywords: TGA, Nylon66, Mass Spectrometry, FTIR

Nylon 66 has a wide range of applications due to its mechanical and chemical properties. It is very often used in the form of films and fibers [1].

The thermal degradation of polymers in general and of Nylon 66 in particular is useful in assessing both the behavior of the tested material and the off-gas products, for safety reasons [2 – 3].

Thermo-Gravimetric Analysis (TGA) is a common technique for testing the degradation path of Polymers and the amount of solvents or humidity absorbed. Nylon 66 is known to be particularly hygroscopic.

In order to understand the composition of the off-gases, additional techniques can be applied by directly collecting the fumes coming from the TGA furnace. Mass Spectrometry (MS), Gas Chromatography plus Mass Spectrometry (GC-MS, see Fig. 1) and Fourier Transform InfraRed Spectroscopy (FTIR, see Fig. 2) have all distinct advantages and can all be hyphenated (that is: combined) with the TGA analysis in order to get a full compositional and quantitative profile of the off-gases.

In this work we report the results [4] of a complete Nylon 66 analysis with a TGA Discovery 5500 by TA Instruments coupled with an iS50 FTIR by Thermo Scientific Nicolet and a 5977B GC-MSD by Agilent.

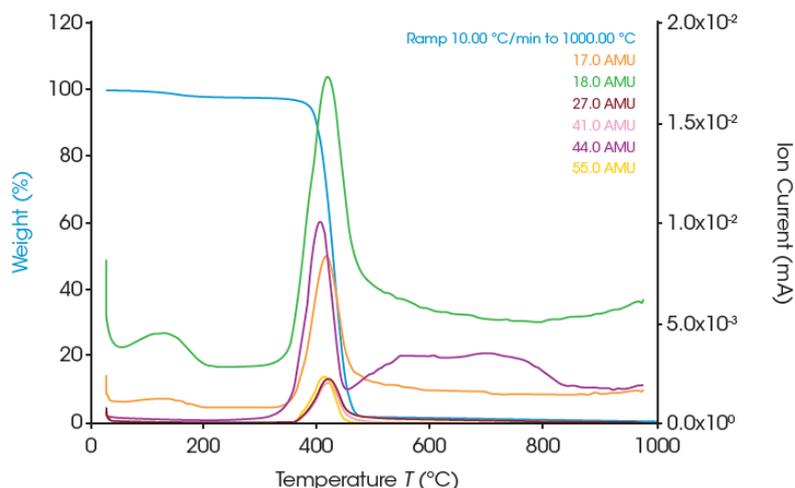


Figure 1. TGA – MS profile of Nylon 66 with selected m/Z signals

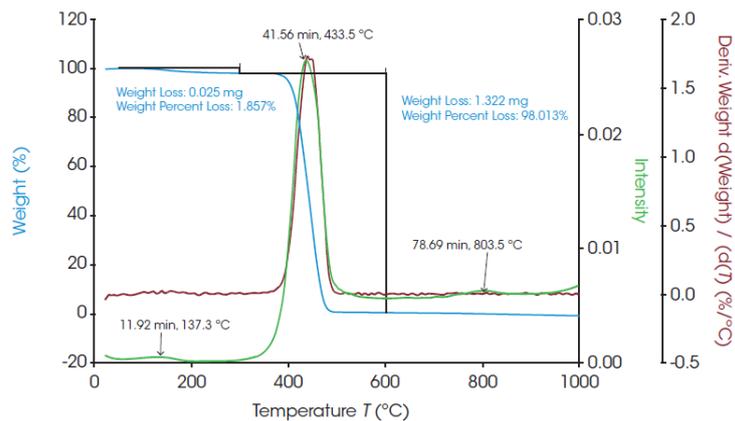


Figure 2. TGA – FTIR profile of Nylon 66 showing Gram – Schmidt curve

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AI-Artificial Intelligence for your Thermal Analysis Software

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Keywords: AI, Autoevaluation, Identify, Superposition

AUTOEVALUATION and IDENTIFY

It is possible to identify substances manually by comparing their characteristic data with literature sources or with previous measurements, but it is far more effective to automatize this process and to use databases for comparison purpose. Learn here how the NETZSCH software can do this for you!

Melting temperature, enthalpy, decomposition, onset, peaks, glass transition, thermal conductivity and all the common thermal transition could be use to “fingerprint” a compound, polymers and pharma above all.

Glass transition temperature [°C] -85/95 to 105/(125)	<h1>ABS</h1>			Density [g/cm ³] 1.03 to 1.07
Melting temperature [°C] -				Thermal conductivity [W/(m·K)] 0.15 to 0.20
Melting enthalpy [J/g] -	Decomposition temperature [°C] 420 to 428	Young's Modulus [MPa] 2200 to 3000	Linear thermal expansion coefficient [*10 ⁻⁶ /K] 80 to 100	Specific heat capacity [J/(g·K)] 1.26 to 1.68

Figure 1. Show an example of a dataset from a single polymer, a single entry in a library

From different “fingerprint” you can build a library, and from a library an automatic search-match software named IDENTIFY

Artificial intelligence can help in auto-classify the transitions, curve recognition, identify the thermal path, and above all compensate all the influencing factors just like scanning rate, atmosphere and crucibles.

Within a few clicks, the current evaluated measurement curve is compared to several libraries (which can be pre-selected). The library material that shows the greatest similarity has the highest probability of being the unknown sample. Libraries can easily be created by users as well as edited and expanded. Possible library entries are measurements and literature data.

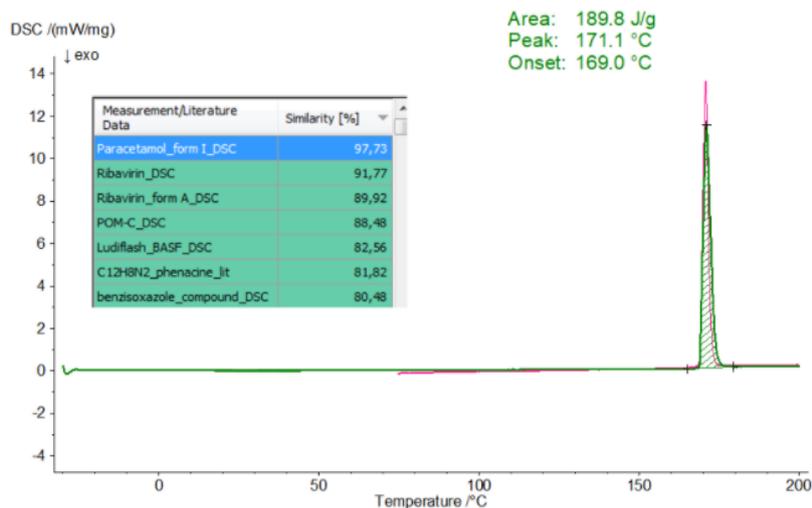


Figure 2. One-on-one comparison of a DSC measurement on Paracetamol (green) with database entries (measurement conditions of the paracetamol measurement see text). The leading position of the corresponding hit list (marked in blue) depicts the data base entry with the highest similarity. The corresponding DSC curve is shown in pink.

SUPERPOSITION

Drug-excipient compatibility studies constitute an important phase in the development stage (pre-formulation) of dosage forms. They provide information whether physicochemical interactions happen between API (active pharmaceutical ingredient) and excipients.

The *SuperPosition* software feature of the *Proteus*[®] analysis software calculates the curve that would be obtained for a mixture if **no interaction** between the two (or more) components occurred. By comparing the measured DSC/TGA curve of the mixture and the calculated curve obtained with *SuperPosition*, one gets fast conclusions about eventual interactions between both ingredients. ***SuperPosition* simulates the curve of a mixture**

Figure 2 depicts the DSC curve of a mixture containing 3% alpha-lactose monohydrate, 45% cellulose and 19% corn starch (blue curve). The pink curve is the curve calculated by *SuperPosition* on the basis of the DSC measurements carried out on the single components. This software feature is able to calculate the curve resulting from a mixture of 2 or more substances with desired mass ratios.

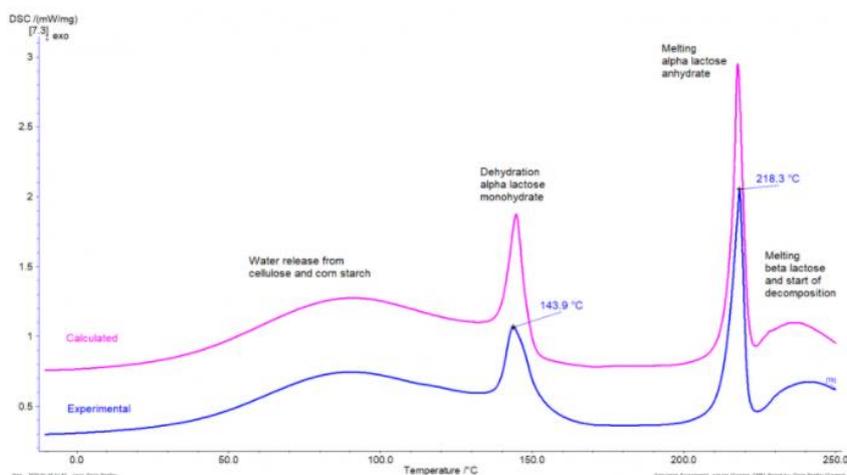


Figure 3. Comparison of the measured DSC curve of the mixture (blue curve) with the calculated curve obtained by *SuperPosition*

Chip-based Calorimeter for fast heating and cooling rates inclusive related investigations

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Keywords: DSC, Calorimetry, Chip-DSC

In 125 years, the storage capacity of the punched card up to the SD card with 2 Terabytes of storage has grown by a factor of 25 billion. Due to the ongoing progress in nanotechnologies there will be a further optimization and “miniaturization” in the near future for sure. LINSEIS thermal analysis is following this trend and is introducing its LINSEIS Chip-DSC, a miniature of one of its most established previous measuring instruments, to the market. The sensor combines DSC, furnace, sensor and electronics in a miniaturized housing. Due to the miniaturized design, pushing the boundaries high heating and cooling rates as well as temperature modulation almost from room temperature are possible. For this reason, common but also some new investigations can be performed fast and with little effort. Exiting new opportunities arise for both scientific research and day to day quality control.

In our talk, we will present our latest product development and discuss the innovation of differential calorimetry. In particular, the influence of rapid heating and cooling rates and associated investigations should be the focus.

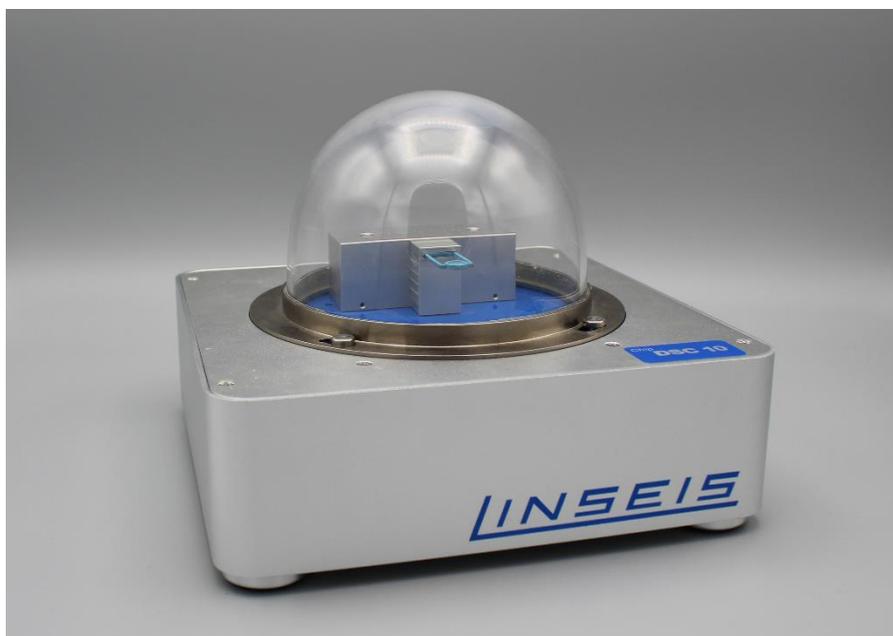


Figure 1. LINSEIS Chip-DSC 10 with a footprint of 20 x 20 cm

POSTERS

Thermo-mechanical performances of Mater-Bi filled with Halloysite nanotubes

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Keywords: Halloysite, nanocomposites, bioplastics, DMA

The aim of this study is the design and preparation of Mater-Bi/halloysite nanocomposite materials that could be employed as bioplastics alternative to the petroleum derived products. The biocomposite materials at variable halloysite content (from 0 to 30 wt%) were prepared by using the solvent casting method. We investigated the mechanical behaviour and the thermal properties of the prepared nanocomposites in order to estimate their suitability as biocompatible packaging materials. The thermo-mechanical characteristics were correlated to the nanocomposites' morphologies, which were studied by Scanning Electron Microscopy (SEM). As a general result, the physico-chemical performances of Mater-Bi were improved by the presence of small amounts of nanotubes, which evidenced a homogenous distribution in the polymer matrix. The strongest enhancements of the thermal stability and tensile properties were achieved for Mater-Bi/halloysite 10 wt%. A further addition of nanotubes determined the worsening of both thermal stability and mechanical behaviour.

The attained knowledge represents the starting step for the development of packaging films composed by Mater-Bi and halloysite nanotubes.

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A new approach to elucidate impact of metal-based driers on industrial oil paint air-curing process

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Keywords: oil paints, metal-based driers, oxygen uptake, air-curing process

Paint consists of finely divided pigment particles dispersed in an organic fluid binder [1]. When a drying oil - a plant oil rich in triglycerides of polyunsaturated fatty acids - is used as a binder, the paint is an oil paint [1]. The air-curing process, during which a liquid oil paint layer converts to a durable film, is known as autoxidation [2]. The autoxidation of oil paints entitles the formation of peroxide species which evolve according to two main competitive phenomena - cross-linking and oxidation [3,4], of which cross-linking is fundamental for obtaining a durable film. Autoxidation of oil paints is a very slow process. In order to reduce the drying time, metal-based driers were introduced into paints formulations [5]. If the effect of driers on the drying time of the paints is known, the kinetic of curing process and the interaction among components are still not clear, particularly when complex oil paint formulations are concerned. In order to fill this gap, the present study aims to investigate the role of different metal-based driers on the oxygen uptake kinetic of realistic oil paints.

The research was carried out in collaboration with Golden Artist Colors, Inc. Four customized cadmium red paints with known and realistic formulations was prepared by Golden Artist Colors, Inc. The seven paints had the same amount of alkali refined linseed oil, cadmium red pigment (cadmium sulfoselenide), additives (CaCO_3 and bees wax) and same amount of different driers. The paint formulation without drier was tested as reference. Calcium (Ca^{2+}), cobalt (Co^{2+}) based driers were tested alone and the synergistic effect of cobalt-calcium was also investigated. The curing of each paint formulation was followed by thermogravimetric analysis under accelerated conditions. Paints were cured at 80 °C in a thermobalance under a constant and controlled air flow. The oxygen uptake profiles are reported in Fig. 1.

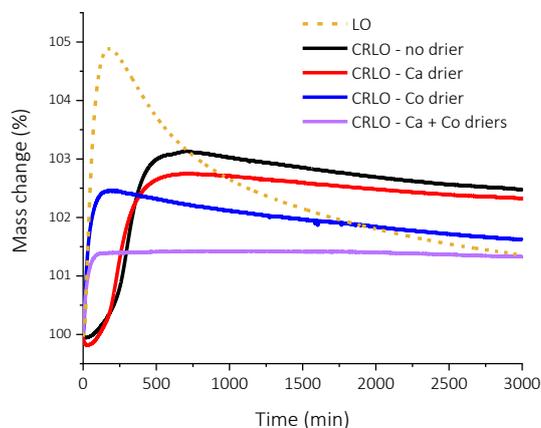


Figure 1. Oxygen uptake curves versus time of alkali refined linseed oil alone (yellow dash line), cadmium red paint without drier (black solid line), cadmium red paint with calcium drier (red solid line), cadmium red paint with cobalt-calcium driers (purple solid line). Curves are normalized for the oil content.

The oxygen uptake curve shape is a balance between the mass increase due to the oxygen addition, and the mass loss, due to evolution of low molecular weight compounds formed.

The oxygen uptake profiles show that the main effect is played by the pigment: cadmium red increases the induction time and decreases the maximum of mass uptake of linseed oil.

Calcium drier alone does not affect so much the curing process of cadmium red paint formulation. While cobalt based driers strongly affect the curing process. The semi-empiric equation used to fit experimental data revealed that all the oil paints, except that containing cobalt-calcium drier, show an oxygen uptake followed by one or two degradation phenomena with kinetics depending on the oil/dryer combination (Figure 1). In cobalt-calcium drier containing oil paint two distinct oxygen uptake steps are present: the first, more rapid, and the second much slower, at higher time.

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Characteristics of late Neolithic pottery of the Zau Culture: analysis of pottery samples from Iernut-Site II (Mures County, Romania)

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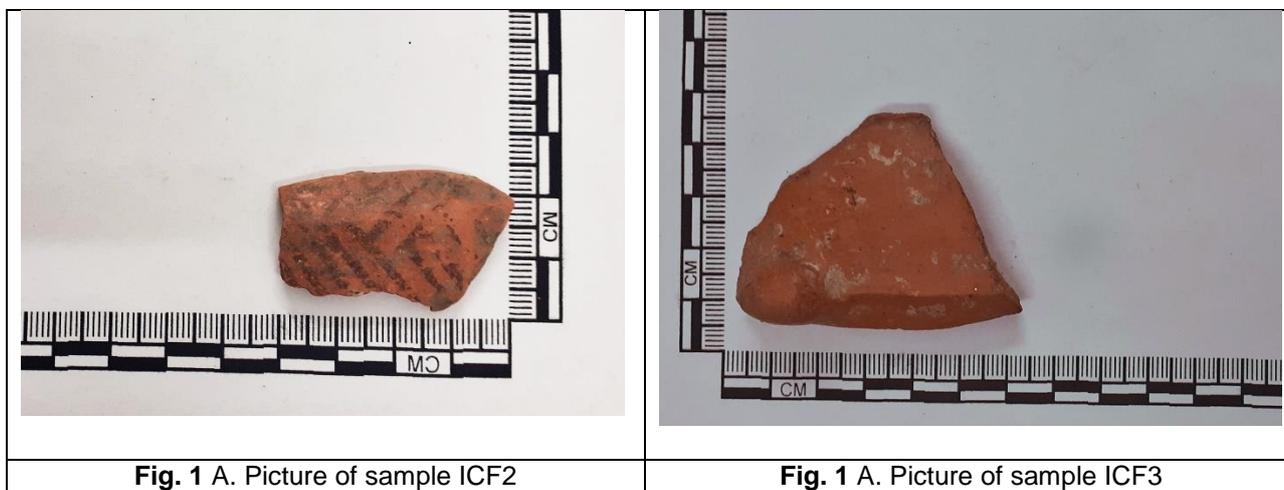
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Keywords: Neolithic pottery, archaeological research, thermogravimetric analysis, FT-IR/UATR spectroscopy, SEM, EDAX, XRF and XRD analysis.

The study contains results from analyzed samples, coming from 5 pottery shards from the Iernut – Site II archaeological site, located on the Iernut-Chețani segment from the Transilvania Highway (Sector 2A Ogra-Câmpia Turzii). The 5 shards, dated to the Neolithic period, specifically to phase IV of the Zau Culture (4750-4450 BC), are representative of the two main category types associated the site, red fine pottery and black pottery, respectively, while being representative for the types (fine, semifine and coarse) [1-3]. In figure 1 A and B. are present the picture with 2 ceramic samples.



The techniques use (TG/HF, FT-IR, SEM, EDAX, XRF and XRD) are complementary and suited for the purpose of the study, which was to determine production technology within the main categories associated with Iernut – Site II and the Zau Culture (Phase IV) [4-6]. The results are present in Fig. 2.A and B.

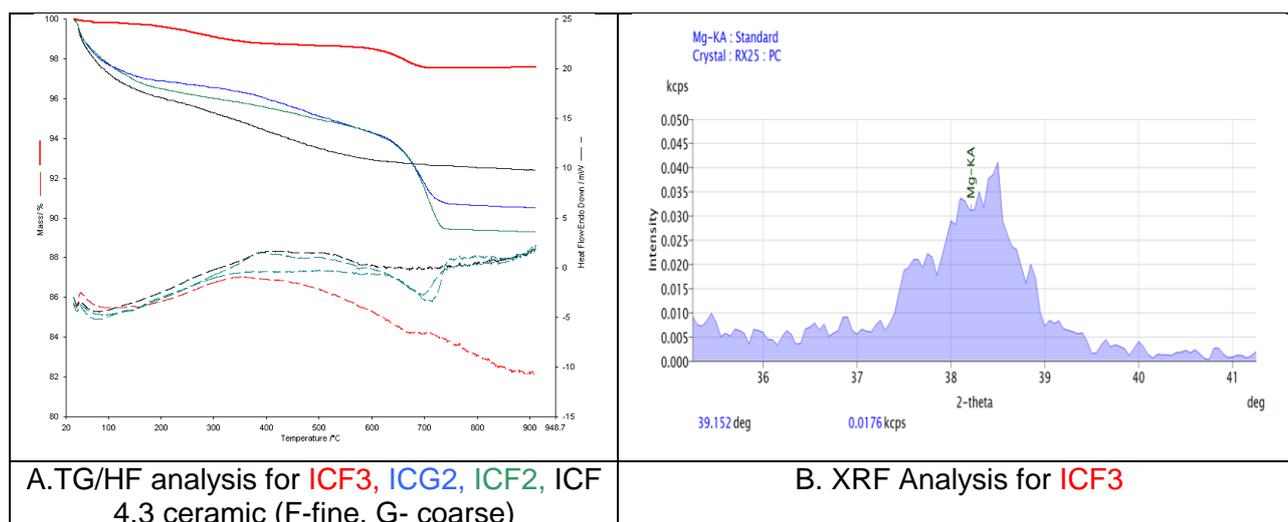


Figure 2. The results for A. TG, DTG and HF curves obtained in 30-900 ° C temperature range with 10 ° C·min⁻¹, B. XRF analysis for ICF3.

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Regarding the technology and origin of late Neolithic and Eneolithic pottery: analysis of pottery and soil samples from the Foeni Tell-Orthodox Cemetery (Timis County, Romania)

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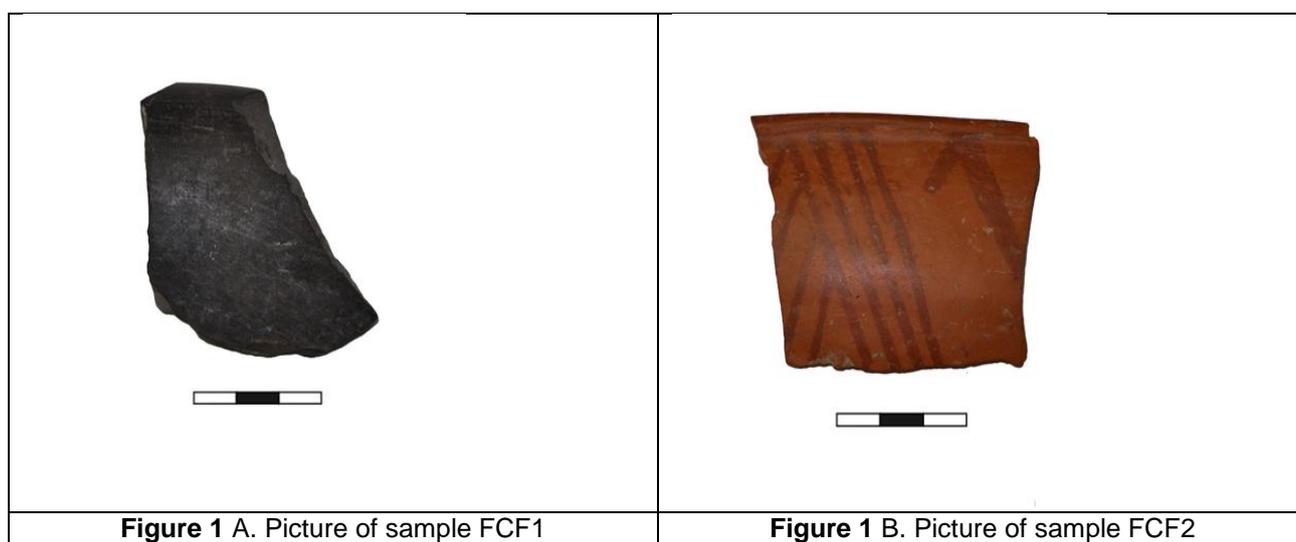
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Keywords: Eneolithic pottery, archaeological research, thermogravimetric analysis, FT-IR/UATR spectroscopy, SEM, XRF and XRD analysis.

The study aims to analyze pottery samples from the archaeological site Foeni Tell – Orthodox Cemetery, located in the western edge of Foeni (Timiș county, Romani), a late Neolithic, early Eneolithic multi-stratified site (three phases, covering the period 4720-4457 cal BC), also inhabited during the early Bronze Age and Middle Ages. The analyzed samples come from 20 pottery shards, belonging to the Foeni cultural group (4920/4675-4580/4460 cal BC, corresponding to the later period of the Vinča culture, from the end of phase C to the end of phase D), and are representative of the categories (black, red, painted) and types (fine, semifine, coarse) pottery associated with the cultural group. Also analyzed were soil samples from the site [1-4]. In figure 1 A and B Picture of sample FCF1 and FCF2 are presented.



Complementary techniques were used in the analysis (TG/HF, FT-IR, SEM, XRF and XRD) in an effort to ascertain details regarding production technology and origin of the raw materials used in making the pottery [1, 5, 6]. The results are presented in fig. 1 A and B.

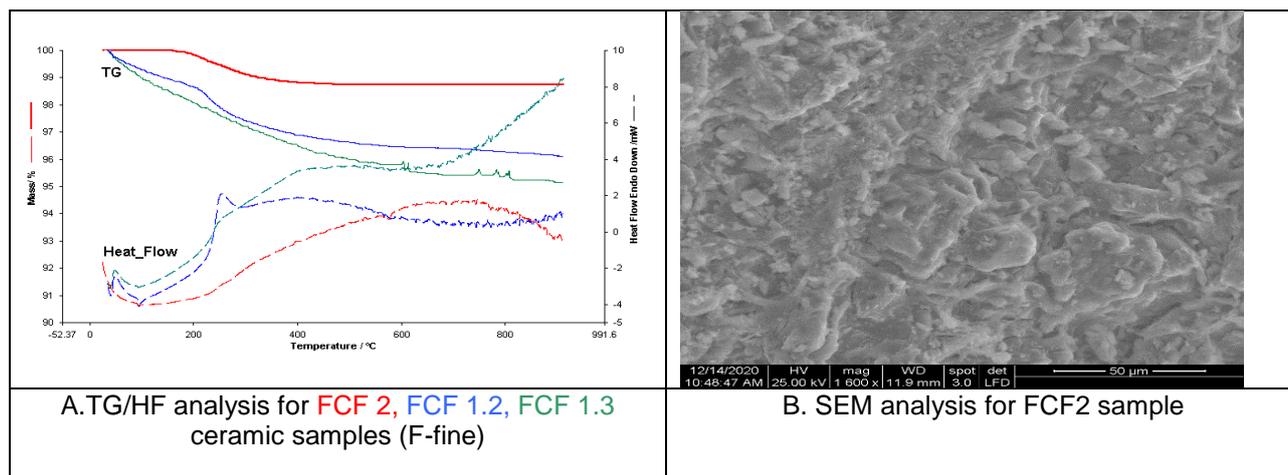


Figure 1. The results for A. TG, DTG and HF curves obtained in 30-900 °C temperature range with 10 °C·min⁻¹, B. XRF analysis.

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DSC to reveal structural changes in egg white submitted to hyperbaric storage at room temperature

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Keywords: egg white, hyperbaric storage, differential scanning calorimetry, protein structure

Egg white is well-known for being a protein-rich, highly technologically valuable food. Due to its high water activity and pH, it is an extremely perishable matrix, which is generally submitted to refrigerated storage (4 °C) to inhibit microbial growth [1]. Reportedly, refrigeration is characterized by considerable economic cost and environmental impact, making it a highly energy intensive storage technology [2].

Hyperbaric storage has been proposed as an efficacious and sustainable alternative to refrigeration, since it has virtually zero-energetic impact [3]. This technology implies storage of the product at room temperature under moderate hydrostatic pressure ($P < 250$ MPa) (HS-RT). However, moderate hydrostatic pressure might induce structural modifications in food components, including egg white proteins [4], potentially leading to significant changes in consumer acceptability and technological functionality.

In this framework, differential scanning calorimetry (DSC) is well known as a sensitive and fast tool to investigate the changes in protein structure and stability [5]. The aim of this work was thus to study the effect of HS-RT on the structural properties of egg white proteins by means of DSC. To this aim, egg white samples were packaged in plastic pouches and stored in a HS-RT pilot plant at 200 MPa at room temperature for up to 28 days. Analogous control samples were represented by egg white stored at 4 °C and shell eggs stored at room temperature. In particular, 25 mg of egg white were carefully weighed in 40 μ L aluminum pans, which were heated from 45 to 98 °C at 5 °C/min by means of a DSC 3 Star[®] System differential scanning calorimeter (Mettler-Toledo, Greifensee, Swiss). An empty pan was used as a reference in the DSC cell. Transitions peak temperatures (T_{peak}) were extrapolated and transitions enthalpy was calculated by integration of normalized peak areas.

A distinct endothermic event, ascribable to unfolding of conalbumin ($T_{\text{peak}} = \sim 66$ °C) was clearly detectable in egg white thermograms (**Figure 1**). Transition enthalpy of this peak decreased during storage under hyperbaric conditions, indicating progressive unfolding of conalbumin, which was not observed in the controls under refrigeration and in shell. A broad thermal phenomena attributable to ovalbumin unfolding was also detected, in the temperature range 75-95 °C (**Figure 1**). The multiple peak appearance of this thermal event was related to the occurrence of ovalbumin in two additional forms other than the typical one ($T_{\text{peak}} = \sim 80$ °C): S-ovalbumin ($T_{\text{peak}} = \sim 90$ °C) and an intermediate ovalbumin form ($T_{\text{peak}} = \sim 85$ °C) [6].

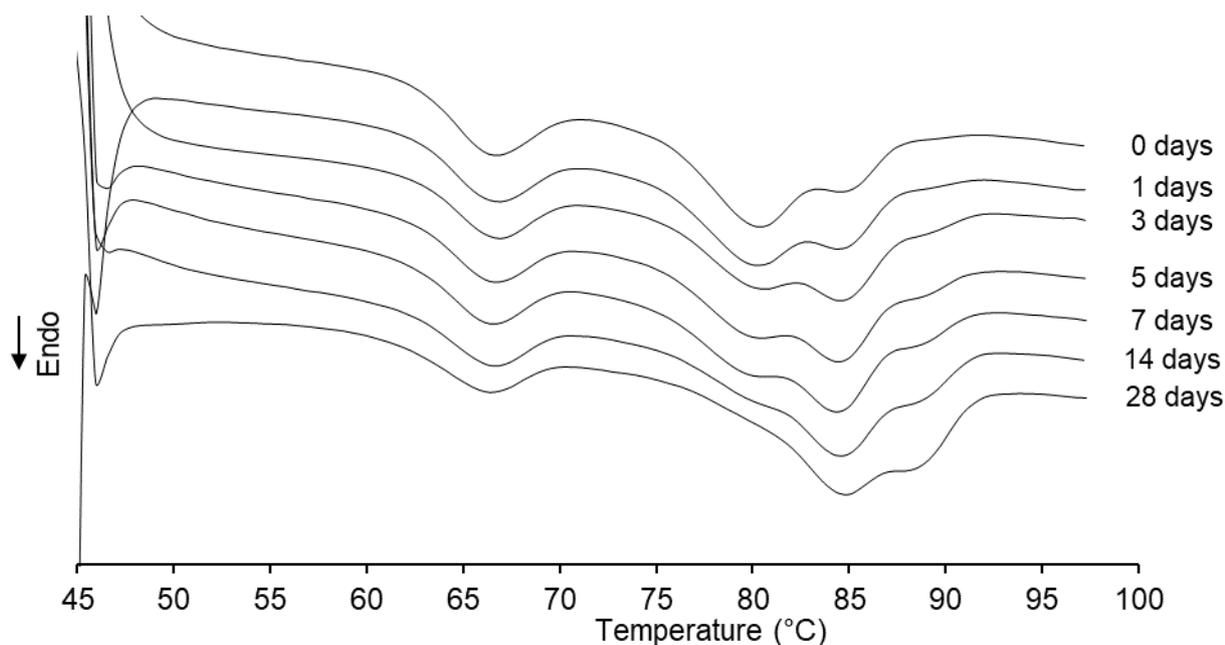


Figure 1. DSC thermogram of egg white samples as a function of storage time under hyperbaric conditions (200 MPa)

The enthalpy of this complex ovalbumin peak increased as a consequence of the progressive and spontaneous conversion of ovalbumin into S-ovalbumin. A similar evolution was observed in shell eggs, while less intense conversion of ovalbumin was detected under refrigeration. The formation of S-ovalbumin, which is known to be more heat-stable than native ovalbumin, could be responsible for changes in techno-functional properties of egg white, including its gelling capacity [6].

DSC resulted an efficacious analytical technique to study the effect of a novel storage technology, such as HS-RT, on thermal stability of protein-rich food ingredients.

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Application of DSC analysis to study oil gelation

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Keywords: oleogel, crystallization, network formation, structure, olive oil

Over the last decades, overweight and obesity have reached critical levels all over the world, increasing risks of life-threatening diseases, such as cardiovascular disease and cancer [1]. This has been mainly attributed to eating habits including a high consumption of palm oil or hydrogenated fats rich in saturated and trans fatty acids. The EU is asking for actions and strategies to improve the nutritional value of lipid-containing foods, thus assuring healthier and more sustainable diets, ultimately reducing health-related costs.

One of the most innovative and promising ways to face these issues is oil gelation (oleogelation). This is a relatively novel strategy by which liquid oils are structured into semisolid materials, called oleogels, by exploiting the structuring ability of defined molecules in oil [2].

The interest in oleogels has increased dramatically in the last decade due to their potential as replacers of hard stock fats in different foods, such as bakery products, ice-cream, chocolate-based products [3], [4]. Beside their potential use as fat-replacers, oleogels have been recently proposed as functional components able to modulate lipolysis as well as the delivery of bioactive lipophilic molecules [5], [6]. This aspect could open new horizons for their use as a tool to improve food health functionality as well as energy management deriving from lipid ingestion.

Based on these considerations, the present research studied the effect of gelator molecules on the structural properties of oleogels obtained by using sunflower oil (SO) or extra virgin olive oil (EVOO). To this aim, a selection of gelators, *i.e.*, rice wax (RW), monoglycerides (MG), ethyl-cellulose (EC) and γ -oryzanol and β -sitosterol (PS) were considered at 10% w/w concentration.

In this context, differential scanning calorimetry (DSC) analysis was applied to characterize the oleogelators and oleogels thermal properties as well as to study their destructuring behavior upon heating. Beside thermal properties, to better study system structure, macro- and microscopic appearance as well as oil absorbing capacity, and rheological properties were evaluated.

Both SO and EVOO were efficiently gelled by the selected molecules, showing self-standing appearance and good capacity to bind oil. However, the gelator type definitively affected the gel macro and micro characteristics. Considering thermal properties, all oleogels revealed a broad endothermic peak with lower T_{peak} as compared to neat gelators. This behavior was expected and is attributable to the initial disaggregation of the network in oil followed by the melting of crystals [7].

Beside other analytical methodologies needed to characterized oleogel structure, DSC analysis resulted fundamental to understand the susceptibility of oleogel structure to temperature changes. This information is crucial in the attempt to use oleogel in food applications, being foods subjected to different temperature changes during food processing.

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Oxidative stability of linseed oil encapsulated by particles from gas saturated solution technique

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Keywords: isothermal calorimetry, particle from gas saturated solutions technique, encapsulation, oxidative stability

In this work, isothermal calorimetry was used to evaluate the oxidative stability of microcapsules produced by encapsulation of linseed oil in glycerol stearate as a food grade wall material. The microcapsules were produced by particle from gas saturated solutions technique (PGSS), an innovative encapsulation methods based on supercritical fluids where carbon dioxide was used as solvent.

The encapsulation was performed by loading the glycerol stearate (~80%) and linseed oil (~20%) in a melting chamber saturated with CO₂ at 55°C for 30 minutes at a constant pressure of 10 MPa. To improve the oxidative stability of the linseed oil, microcapsules were also produced by adding β-carotene to the formulation as natural antioxidant. The concentrations used ranged from 0.2 to 1.6 mg of β-carotene per gram of linseed oil. For all the samples, the melted mixtures were sprayed into a cyclone chamber at ambient temperature and pressure. The depressurization cooled the droplets and turned them into powder crystals.

The oxidative stability of the microcapsules was monitored by isothermal calorimetry. About 100 mg of samples were loaded in 4 mL glass ampoules. The heat flow signal generated during the oxidation process at 40°C was recorded. The analysis was combined with the measurement of the oxygen consumption carried out with an oxygen sensor and the generation of peroxides by the determination of the peroxide value during the oxidation of the samples.

The results showed that linseed oil was oxidative stable for 20±5 hours. The encapsulated linseed oil improved the oxidative stability of the oil up to 78±3 hours, almost 4 times more compared to the not encapsulated oil. The addition of β-carotene, as natural antioxidant, to the formulation reported an inhibition activity by delaying the oil oxidation. Depending on the concentration of β-carotene, ranging from 0.2 to 1.6 mg per gram of linseed oil, the stability of the microcapsules was extended to 96±3 and 176±5 hours, respectively. The oxygen consumption as well as the peroxide value and confirmed the results obtained by isothermal calorimetry.

Overall, our findings highlighted the potential of producing powder microcapsules by PGSS technique and the possibility to study their oxidative behavior by isothermal calorimetry.

Why does thermomagnetic resonance affect cancer growth? A non-equilibrium thermophysical approach

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Keywords: Biothermodynamics; Bio-thermomagnetism; Cancer; Symmetry breaking

Recently, the low frequency thermomagnetic effects on cancer cells have been analyzed both theoretically [1,2] and experimentally [3-5]. It has been explained by an equilibrium thermodynamic approach, but two related open problems can be highlighted:

- (i) Does there exist a magnetic interaction or do there exist any other processes?
- (ii) Do there exist also thermal effects?

Here, we introduce a non-equilibrium thermodynamic approach to respond to these questions. The results obtained point out that:

- (iii) The effect produced by the electromagnetic wave is just a consequence of the magnetic interaction;
- (iv) The interaction of the electromagnetic wave causes also thermal effects, even if there have been applied low frequency electromagnetic waves;
- (v) The presence of the magnetic field generates a symmetry breaking in the Onsager's coefficients with a related perturbation of the stationary state of the cancer.

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Plant-derived stilbenoids as antimicrobial agents: interaction of resveratrol-derived monomers and dimers with model cell membranes

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Keywords: Model membranes, Differential Scanning Calorimetry, Stilbenoids, Antimicrobials

Food contamination with pathogenic microorganisms, such as *Listeria monocytogenes*, *Salmonella enterica*, *Staphylococcus aureus*, and *Bacillus cereus*, is a common health concern. Unfortunately, the overuse and the misuse of antimicrobial agents in humans and animals have been leading to resistance mechanisms, which currently represent a recognized public health problem worldwide [1].

In this frame, natural products have always been a source of inspiration for new drugs and may represent a turning point in alleviating the antibiotic crisis. Stilbenoids are both woody constitutive metabolites and phytoalexins, which are substances produced by plants as means of protection against microbial infections and stress factors. Resveratrol and resveratrol-derived monomers and oligomers (stilbenoids), which can be extracted from several botanical sources such as grapes, cranberries, etc., have been shown to exert various biological activities [2,3].

Literature reports the evaluation of the antimicrobial activity of a collection of resveratrol-derived monomers and dimers against a panel of several foodborne pathogens, showing a variegated pattern of efficacies in terms of minimum inhibitory concentration (MIC) and minimum bactericidal concentration (MBC) depending on both the chemical structure (shape and substitution pattern) and the nature of the microorganisms (gram-positive vs gram-negative). In some cases, morphological modifications on the cell membranes and leakage of intracellular content has been shown, suggesting that the cell membrane might be the principal biological target of such compounds [4].

In this scenario, starting from thermodynamic information about cell membranes recently reported by some authors [5,6], this study aimed at the investigation of the direct interaction of selected polyphenolic compounds with a model cell membrane in order to gain further insights on the possible molecular mechanisms lying under of the antimicrobial activity. The panel of tested compounds consisted in three specific monomer/dimer/dehydro-dimer sequences, namely 1) resveratrol / (\pm)-*trans*- δ -viniferin / dehydro- δ -viniferin, 2) pterostilbene / (\pm)-pterostilbene-*trans*-dihydrodimer / pterostilbene-dehydro-dimer, 3) resveratrol / (\pm)-*trans*- ϵ -viniferin / viniferifuran, hence including those compounds that have shown the highest and the lowest antimicrobial activities. The analyses were carried out through an integrated approach combining micro-DSC and mono and bidimensional NMR spectroscopy. DSC experiments were performed on Small Unilamellar Vesicles (SUVs) constituted by 2:3 DPPC:DSPC with incorporated polyphenols at physiological pH (pH 7.4) and results were well supported by complementary NMR data.

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Differential scanning calorimetry: a powerful technique in I-motif DNA secondary structure characterization

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I-motifs are non-canonical DNA secondary structures which are very interesting from a pharmaceutical point of view. They form in cytosine rich filaments that are not randomly distributed in the genome, but they are enriched in the promoters of oncogenes where they regulate the transcription. I-motifs are high organized tetra helices formed by two parallel duplexes held together by cytosine-cytosine⁺ base pairs (CC⁺) and intercalated in an antiparallel manner. With three hydrogen bonds, the energy of the CC⁺ is relatively high, but its stability is also highly dependent on pH as it requires the hemi-protonation of cytosines to form. [1]

In contrary to how it might appear, the change in enthalpy between the I-motif folded and unfolded states is not strongly affected by the stacking interactions between the intercalated couples of cytosines which are very weak, but it approximatively depends just on the amount of hydrogen bonds of the folded state. Indeed, in addition to the hydrogen bonds of the base pairings, there is a peculiar C-H-O hydrogen bonding network between the backbones of the narrow grooves which is determinant in the energetic properties of I-motifs. [2]

Based on this, the folding enthalpy is a consistent parameter to estimate the length of the I-motifs core and consequently the number of base pairings. [3]

Here, we present a work in which the combination of differential scanning calorimetry (DSC), circular dichroism spectroscopy (CD) and electrophoretic techniques allowed us to derive the thermodynamics and predict a folding topology of an I-motif forming sequence which is 37 nucleotides up the transcription starting site of the promoter of the Epidermal Growth Factor Receptor oncogene (EGFR-37C). Furthermore, with DSC, we highlighted that the apparently useless 5' and 3' tails control the kinetic of folding by interacting with nucleotides of the second loop. In fact, removing the tails or a single nucleotide mutation in the second loop drastically changes the kinetic folding behavior.

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Exploring the conformational stability of the ribotoxin-like protein ageritin

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Keywords: Differential Scanning Calorimetry, protein stability, denaturant-induced unfolding

Ageritin represents the prototype of a new ribotoxin-like protein family, recently identified in basidiomycetes [1]. This enzyme has different structural features compared to canonical ribotoxins isolated from Ascomycetes fungi [2] and is characterized by a strict metal ion-binding requirement for its ribonucleolytic activity [3]. Ageritin displays cytotoxic activity against several human malignant cell lines as well as antifungal activity [4], characteristics that make this enzyme a promising candidate for application in biomedical and agricultural field.

In this contribution we report a thorough analysis of the native protein conformational stability, both at a physiological pH of 7.4 and at acid pH values (6.0 and 5.0) similar to those of cancer cells [5], performed by differential scanning calorimetry (DSC) and fluorescence measurements. In addition, the stability of a modified form of the protein, obtained by alkylating the only cysteine residue in the sequence, was also investigated.

DSC results indicate that ageritin possesses a high thermal stability at all pH values explored. The alkylation procedure reduced the melting temperature by more than 20 °C. This dramatic change is probably caused by the disruption of a putative zinc-binding site [3].

A detailed thermodynamic analysis is reported for the protein at pH 5.0, where the thermal unfolding is completely reversible. The denaturant-induced unfolding of ageritin was performed by using steady-state fluorescence measurements, revealing a very high resistance against the GuHCl denaturant action.

The overall results points out to the important role that metal cation binding has on the high thermal stability of ageritin.

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Dynamical evaluation of novel biodegradable protein-polymer conjugates in the solid state

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Keywords: Protein-polymer conjugates, protein dynamics, Differential Scanning Calorimetry, polyphosphoesters

The covalent attachment of synthetic polymers to protein-based drugs, forming the so-called protein-polymer conjugates, is one of the most promising strategies followed in the last years to enhance the lifetime of drugs in the human body [1]. The majority of the works present in the literature on protein-polymer conjugates is focused on their synthesis and biochemical evaluation, either *in vitro* or *in vivo*. However, on a more fundamental level, a better comprehension of the structure and the dynamics of the items could help to rationalise the impact of the polymer on the protein properties and orientate the design of future candidates.

In this frame we present an extensive evaluation of the dynamics of a novel class of protein-polymer conjugates, made by the protein myoglobin and biodegradable polyphosphoesters (promising substitutes of the gold standard poly(ethylene glycol) in the biomedical field [2]). We used a complementary approach of Differential Scanning Calorimetry and neutron scattering spectroscopy [3], observing the samples in the solid state.

Different studies performed at various timescales (ps, ns, s) revealed that the protein and the polymer chains in the conjugates mutually influence their dynamics, enhancing each other fluctuations. The shape of the conjugate is dependent from the effective space that the polymer chains have to lie on the protein surface. Overall, we shed the light on the establishment of interactions protein-polymers, at the basis of the observed properties.

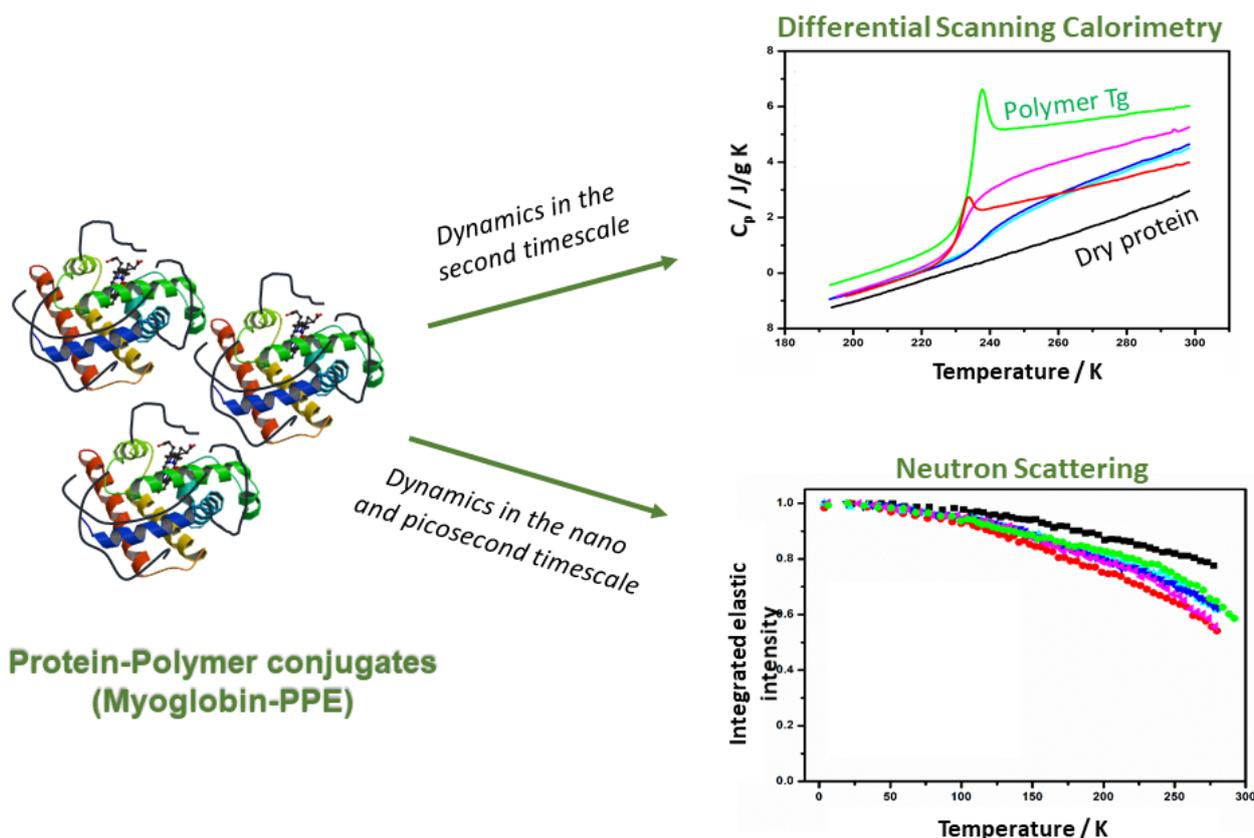


Figure 1. Schematic representation of the protein-polymer conjugates, highlighting the techniques that permitted the biophysical study in the solid state (Differential Scanning Calorimetry and neutron scattering spectroscopy). Image of myoglobin from the RCSB PDB (rcsb.org) of PDB ID 5CN5, taken from (Barends, T.R., et al.) (2015) Direct observation of ultrafast collective motions in CO myoglobin upon ligand dissociation. *Science* **350**: 445-450.

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Thermal behaviour of ceramics obtained from the kaolinitic clays of Terra Alta, Catalonia, Spain

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Keywords: Kaolinitic clays, firing, thermal analysis

Determining the optimal firing temperature for a clay is essential to produce a quality ceramic with the strictly necessary energy consumption. The mineralogical, textural and colorimetric evolution of a clay with temperature will determine its industrial use within the scope of ceramic materials. Each mineral phase has its thermal evolution and with it its role in the firing process of a ceramic. To determine this temperature, the evolution of the properties of the ceramic obtained at different firing temperature must be assessed to determine their optimal treatment conditions.

In the region of Terra Alta, southern Catalonia, Spain there are important kaolinitic clay deposits whose mineralogy has already been studied previously [1]. In the present work, its thermal properties and its evolution were studied to determine the optimum temperature of treatment in obtaining ceramics.

Mineralogy of the raw samples and ceramic paste fired at several temperatures was determined by X-Ray Powder diffraction (XRPD). Plasticity was determined by the Atterberg limits: liquid limit (LL), plastic limit (PL) and plasticity index (PI), using the Casagrande method.

Thermal properties were determined by simultaneous differential thermal analysis and thermogravimetry (DTA-TG) and dilatometry. The coefficient of thermal expansion was obtained at a heating rate of 10°C/min between 20°C and 400°C.

The sintering behavior was evaluated by gresification diagrams, which present the variation in properties of ceramics as a function of firing temperature. The gresification curve was obtained to predict the maximum firing temperature of the raw clay, since it allows to determine when the balance between the hardness and the minimum possible porosity was achieved. The firing characteristics were obtained by heating the samples up to several temperatures from 1050 °C and 1300°C at a heating rate of 2 °C /min and with a holding time of 2 hours.

The colour properties were measured and the raw kaolinitic clays and in the fired samples in the CIEL AB space using a colorimeter.

The mineralogy of the raw materials consists mainly of kaolinite (13-27 wt.%) and quartz (48-86 wt.%). Minor illite, hematite, K-feldspar and calcite also occur. The fired clays are mainly composed by quartz, cristobalite and mullite, with minor hematite and rutile. Mullite starts to appear at 1050 °C. SEM observations show that porosity is nearly negligible in samples fired from 1150 °C.

The ATD of these clays shows an endothermic peak at about 570 °C produced by the transformation of kaolinite into metakaolinite, and an exothermic peak at 990 °C related to the mullite crystallization.

The analysis of the sintering process determined from the firing curves that are obtained with the dilatometer allows to establish the firing and cooling velocity for a clay, as well as its coefficient of expansion, which is essential for the ceramic manufacture.

The evolution of the water absorption and linear contraction were determined from the gresification curve. From 1100 °C the water absorption decreases steeply, due to an increase to of liquid phase,

which penetrates into the pores and close the porosity. At this temperature, the firing shrinkage increases progressively to 15% up to 1200°C and from this point this parameter decreases.

The colour of the kaolinitic clays from Terra Alta vary according their hematite content, being from white to reddish. In the fired samples, the chromatic coordinate a^* of the fired kaolinitic clays increases between 1100 and 1125°C (Figure 1). This fact can be attributed to the destruction of the structure of illite, causing the release of iron, which will produce the reddish colours [2]. The decrease in the chromatic coordinate a^* at high temperatures could be due to the formation of mullite, which can capture the hematite causing whiter or cream tones [2].

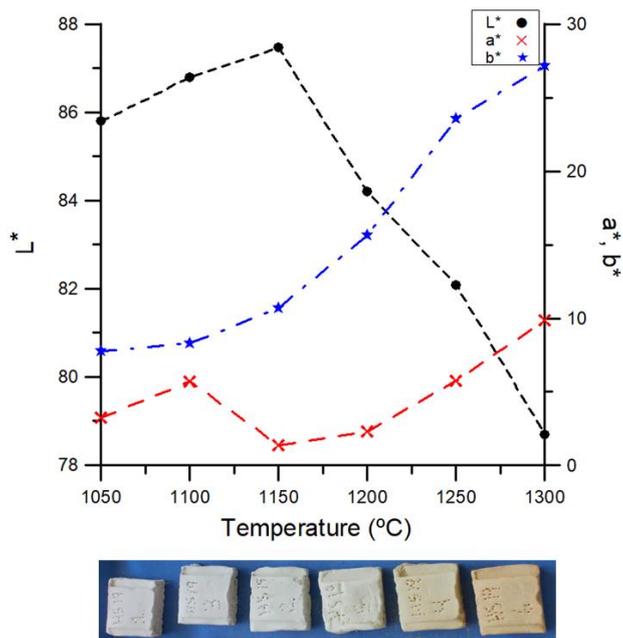


Figure 1. Evolution of the colour parameters with the firing temperature.

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Volatility study of syringic acid and methyl syringate

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Keywords: Syringic acid, Methyl syringate, sublimation vapour pressures, fusion

Syringic acid (SA, 4-hydroxy-3,5-dimethoxybenzoic acid) is a naturally occurring phenolic compound present in spices, olives, grapes, pumpkin, honey, red wine [1] and in fruits of edible plants and mushrooms [2]. SA has an extensive therapeutic application due to its anti-inflammatory, antioxidant, hepatoprotective, anti-diabetic, antihyperlipidemic, cardio and neuroprotective properties [1,2]. Besides usage in pharmacological field, SA has greater industrial uses in photocatalytic ozonation and bioremediation [1]. Methyl syringate (MS, methyl 4-hydroxy-3,5-dimethoxybenzoate) is an efficient phenolic mediator for bacterial and fungal laccases [3] and an activator of the chemosensory ion channel TRPA1 [4]. The vapor pressures of the crystalline phase of both compounds were measured using the mass-loss Knudsen effusion technique [5] over the temperature ranges $T = (387.2 - 409.4)$ K for SA and $T = (337.1 - 359.2)$ K for MS. Their standard molar enthalpies, entropies and Gibbs energies of sublimation, at reference temperatures, were derived from the experimental results. Their temperatures and molar enthalpies of fusion were also determined using differential scanning calorimetry. The contributions of the carboxylic, methyl ester, methoxy and hydroxy groups to the values of the sublimation properties of the compounds studied were confirmed accordingly to our previous predictions [6].

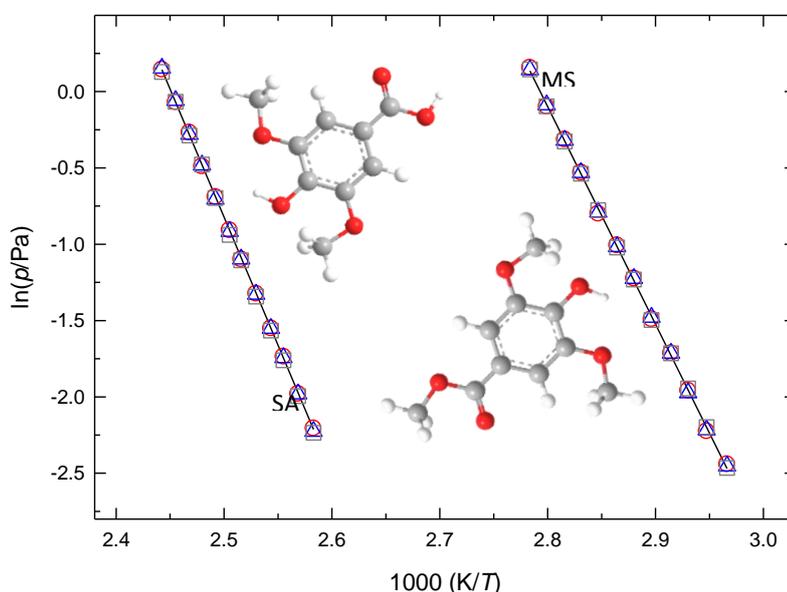


Figure 1. Plots of $\ln p$ against $1/T$ for syringic acid (SA) and for methyl syringate (MS): \circ , small effusion orifices; Δ , medium effusion orifices and \square , large effusion orifices.

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Dynamic mechanical properties of MWCNTs/epoxy composite for aerospace applications

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Keywords: Carbon nanotubes; Thermal analysis

The present paper analyzes the dynamic mechanical properties of multiwalled carbon nanotubes (MWCNTs)/epoxy composites for structural applications. The composites were prepared by dispersing MWCNTs into an epoxy resin based on TetraGlycidyl-MethyleneDiAniline (TGMDA) and both epoxy precursor and composite were cured with 4,4'-diaminodiphenyl sulfone (DDS) [1-2]. Morphological investigation indicates good levels of CNT dispersion into the epoxy mixture. The electrical behaviour of the formulated composites and their high values in the storage modulus and glass transition temperature are very promising in the field of aerospace applications. The epoxy matrix was obtained by mixing TGMDA with 1,4-Butandiol diglycidylether (BDDGE) monomer at a concentration of 80%: 20% (by wt) epoxide to flexibilizer. DDS was added at a stoichiometric concentration with respect to the epoxy rings. Epoxy blend and DDS were mixed at 120 °C and the MWCNTs were added and incorporated into the matrix by using a ultrasonication for 20 minutes (*Hielscher* model UP200S-24KHz high power ultrasonic probe). All the mixtures were cured by a two-stage curing cycles: a first isothermal stage was carried out at the lower temperature of 125 °C for 1 hour and the second isothermal stage at higher temperatures up to 180 °C or 200 °C for 3 hours. These samples are named TBD-CNT(X%)(Y °C) where X is the CNT percentage and Y is the temperature of the second stage. Figure 1 shows the AFM micrograph of TBD-CNT(0.64 %)(200 °C). The image clearly shows that the nanofillers were well dispersed in the polymeric matrix, forming a homogeneous structure in which CNTs uniformly cover the entire surface. Similar results have been obtained for lower concentrations of MWCNTs and curing cycles up to 180°C. The obtained results demonstrate that the method used for CNT dispersion into the epoxy mixture was very efficient for this investigated composite.

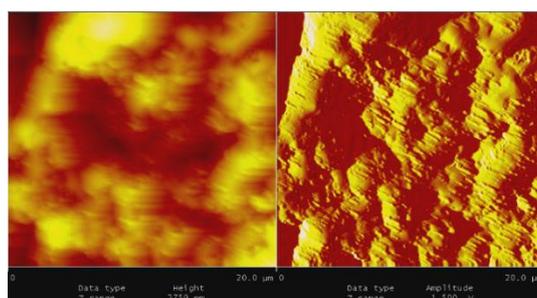


Figure 1. Tapping mode AFM image of TBD-CNT(0.64 %)(200 °C) sample.

Figure 2 shows that the incorporation of a small percentage of MWCNTs (0.32% by weight) causes an increase in the elastic modulus value in range of temperature between -60 and 180 °C. The different temperature of the second stage of the curing cycle changes the curve profiles at temperature higher than 70 °C. For the lower temperature of the curing cycle (second stage), the nanofilled composite shows a non progressive decrease in the value of the elastic modulus with an unforeseen increase between 210 and 240°C before again decreasing. This behavior is very likely due to an increase in the cross-linking density during the heating. This increase is not observed from the pure resin (unfilled sample) with the same history of the curing cycle, see sample TBD(180 °C).

We can explain this behavior if we assume that the inclusion of carbon nanotubes well dispersed inside the matrix causes a reduction of the cross-linking density in a fraction of the epoxy matrix in close contact with the nanofiller. This also explain two peaks in the $\tan \delta$ of the sample TBD-CNT(0.32%)(180 °C) indicating the presence of a lower temperature glass transition (at 215 °C), beside the main transition at the same temperature as the pristine resin (260 °C). It is likely that the presence of this second lower transition is due to unreacted molecular segments that cause inhomogeneities from regions of varying crosslink density; since the samples TBD-CNT(0.32%)(180 °C) and TBD(180 °C) are formulated with the same stoichiometry and curing history, the lower cross-linking density can be ascribed to the nanoinclusions. This secondary peak, active at a lower temperature disappears for the same composite cured up to 200 °C, see sample TBD-CNT(0.32%)(200 °C). A more effective curing cycle at higher temperature up to 200 °C allows to overcome the drawback due to the inclusion of nanofiller inside the epoxy matrix. It was also observed that a different percentage of MWCNTs (data not reported here) is reflected in both the location and magnitude of the transition peak at lower temperature. These results indicate that, for the nanofilled composites, the curing history must be optimized with respect to the unfilled formulations.

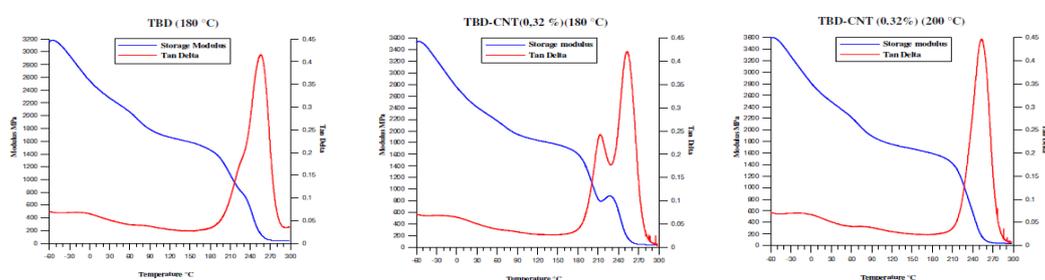


Figure 2. Storage modulus (MPa), and Loss factor ($\tan\delta$) of the pure epoxy (graphic on the left) and the composites 0.32 wt% MWCNTs solidified up to 180 (graphic in the middle) and 200 °C (graphic on the right), respectively.

CONCLUSIONS

MWCNT/epoxy composites based on the TGMDA were prepared. The addition of MWCNTs causes the formation of resin fraction with a decrease in the cure degree, as evidenced by the presence of a lower transition in the spectrum of $\tan \delta$. The incorporation of a small concentration of MWCNTs causes an increase in the elastic modulus value with respect to the unfilled epoxy matrix. The reinforcement effect of MWCNTs in the storage modulus is strong enough to compensate the decrease of the hydrogen bonding in the regular packing of the polymer chains due to the nanoinclusions that space out the polar sulfone groups (the proximity of these groups should favour hydrogen bonding contributing to an increase in the storage modulus).

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Thermogravimetric analysis of local Sicilian clays

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Keywords: clay, thermogravimetric analysis, geopolymer.

As part of the Sicilia Eco Innovative Technologies (SETI) project, a study was started for the preparation of new geopolymeric materials from natural nanomaterials [1] and their subsequent chemical-physical characterization.

Geopolymers are polymeric materials that present an amorphous network of aluminosilicates and they are formed as a result of a geopolymerization process with an alkaline activating solution, leading to the formation of three-dimensional structures with Si-O-Al bonds [2].

They offer new prospects for environmental rehabilitation [3, 4], in fact in this first step of the project, different natural clays, emerging in different sites of the Sicilian territory, have been characterized by thermogravimetric analysis (TGA). These clays have compositional characteristics suitable for the production of geopolymers and high heterogeneity due to the different ratios of abundance between minerals, carbonates and silicates.

The thermal analysis carried out on the natural clays, using the software TA Universal Analysis, has allowed to verify their thermal stability; in particular, information on the various mass losses of each sample, the temperatures at which they occur have been obtained and they have been correlated with the mineralogical nature of each samples.

The same characterization was performed on a sample of refractory bricks and calcarenite observing on both a degradative process at high temperature, consistent with the decarbonation of calcium carbonate with CaO formation. From the mass losses it was also possible to estimate the calcium carbonate content of the two samples examined.

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Dy-Al-Si systems: experimental study of the liquid-solid phase equilibria in the Al-rich corner

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Keywords: Al-Si alloys, rare earth, thermal analysis.

The effect of dysprosium addition to the Al-Si system, concerning the thermal equilibria in the Al rich corner, has been experimentally studied.

Investigation of the R-Al-Si (R: rare earth elements) systems is prominent for a deep knowledge of the transformations occurring during the solidification pathway of foundry aluminum based alloys, that are relevant for industrial applications. There are presently limited information regarding the liquid-solid equilibria at the (Al) rich region of the different R-Al-Si systems. These data, along with the ternary systems isothermal section, are needed to outline the design, plan and develop of new Al-Si based alloys.

The industrially Al-Si alloys have usually a composition next to the binary Al-Si eutectic point and mischmetal (alloy of rare earth metals, whose typical composition includes approximately 50% Ce, 25% La and smaller small amounts of Nd and Pr) is often added instead of pure rare earths [1,2].

The constitution of the alloys and the liquidus surface projection have been determined by means of differential thermal analysis (DTA), scanning electron microscopy (SEM), electron microprobe analysis (EDXS) and X-ray powder diffraction (XRPD). The isothermal section of the Dy-Al-Si system have been previously investigated [3] and the following intermetallic compounds, some of them showing variable composition, were found: DyAl₂Si₂ hP5-CaAl₂O₂ structure type, Dy₂Al₃Si₂ mS14-Y₂Al₃Si₂ structure type, Dy₂Al_{1+x}Si_{2-x} (0≤x≤0.25) oI10-W₂CoB₂ structure type and Dy₆Al₃Si tI80-Tb₆Al₃Si structure type. In the system investigated have been identify four regions of primary crystallization: DyAl_{3-x}Si_x, Dy₂Al₃Si₂, DyAl_xSi_{2-x} and (Si).

In figure 1 shows the experimental results for an alloy in the DyAl_{3-x}Si_x primary crystallization part of the system.

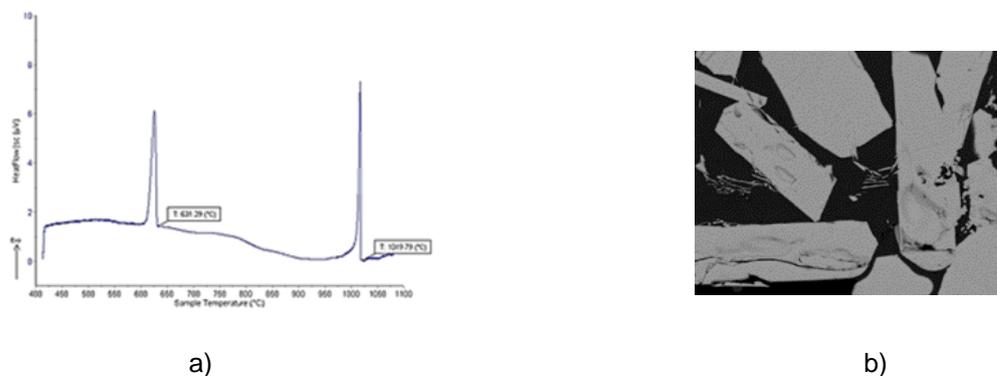


Figure 1. Experimental results for a sample at 16.5 at%Dy-79.0 at.%Al a) DTA cooling curve b) Back scattered electrons (BSE) images of the Dy-Al-Si alloy samples primary light DyAl_{3-x}Si_x surrounded by eutectic decomposition: DyAl_{3-x}Si_x (light smaller particles) + dark (Al).

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DTA/TGA and XRD investigation of Lithium tetragermanate synthesized via sol-gel

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Keywords: Lithium tetragermanate, sol-gel, DTA/TGA, XRD

Lithium tetragermanate gel was synthesized via sol-gel method [1]. A flow-chart indicating the preparation procedure and the compositions employed is given in Fig. 1. Water-free ethanol was obtained by distillation with metallic sodium of commercial anhydrous ethanol, since the $\text{Ge}(\text{C}_2\text{H}_5\text{O})_4$ (TEOG) is a very water-sensitive reagent and to permit the control of TEOG/ H_2O . Bi-distilled water was used for hydrolysis reaction. The alcoholic solutions were prepared in a drybox at room temperature. The alcoholic solution of TEOG was mixed at 0°C with a water-alcoholic solution of lithium hydroxide. Under these conditions complete gelation occurred at room temperature in two days. The obtained gel appeared homogeneous. The gelled system was held for one day more at room temperature before drying. The gel was fully dried in air at 50°C in an electric oven for one day. After these treatments, an amorphous powder was obtained.

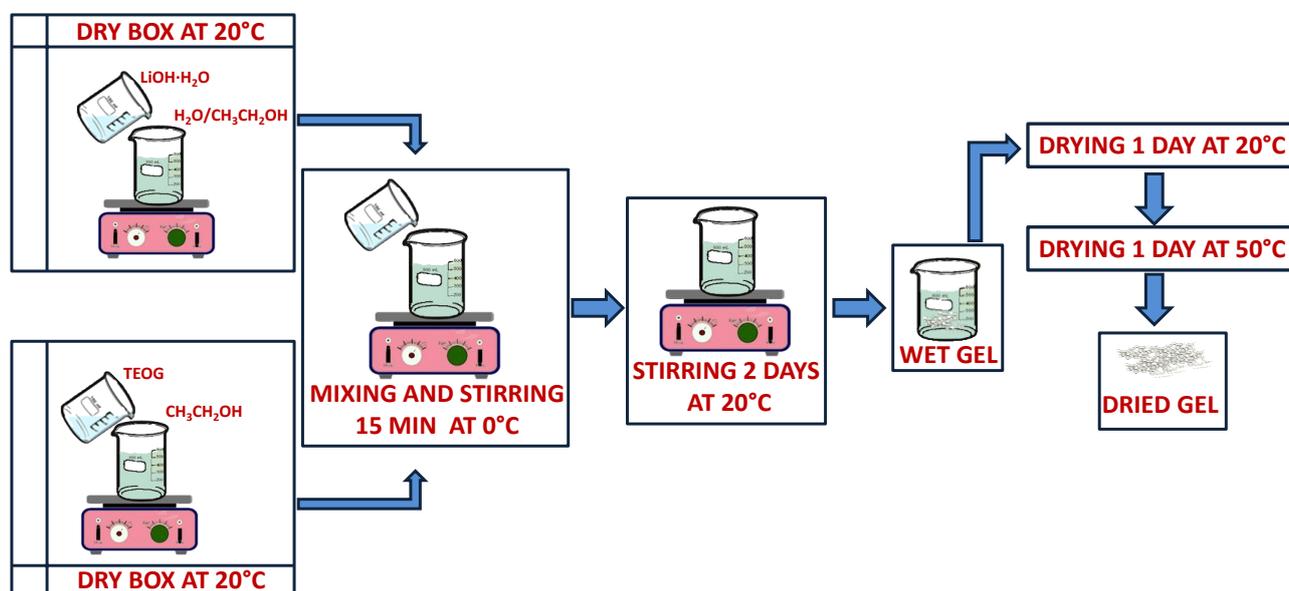


Figure 1. Flow diagram of Lithium tetragermanate preparation procedure.

The gel behaviour was examined by differential thermal analysis (DTA), simultaneous thermogravimetric (TGA) and X-ray diffraction (XRD). Fig. 2 shows the TGA and DTA curves of the dried gel. A large endothermic peak, from room temperature to about 250°C , appears on the DTA curve, with a maximum at about 150°C , and a simultaneous weight loss occurs in the TGA curve. The weight loss was 14.9%. These effects were due to evaporation from open pores of the water and alcohol physically trapped in the gel. No appreciable effects were observed on TGA and DTA

curves in the range of 250-500°C, due to the absence of organic substances which can be produced in sol-gel processing [1,2]. The DTA curve of the gel exhibits a slope change that may be attributed to the glass transition. The inflection point of the DTA curve was taken as the glass transition temperature ($T_g = 532^\circ\text{C}$). A high and sharp exothermic peak appears, just above the T_g , on the DTA curve at the temperature of 565°C. At a higher temperature, 604°C, the DTA curve exhibits a second exo-peak, smaller than the first one. The presence of two exothermic effects on the DTA curve of the studied gel suggests a crystallization process in two steps. The XRD diffraction patterns (data not shown) of the dried gel, the dried gel heated in the DTA furnace up to the temperature of the first exo-peak and the dried gel after a DTA run carried out from room temperature to 700°C, revealed that the powder has broad humps characteristic of the amorphous state of the dried gel. The broad reflections of the dried gel heated in the DTA furnace up to the temperature of the first exo-peak were attributed to $\text{Li}_2\text{Ge}_4\text{O}_9$ and GeO_2 microcrystallites, while the reflections of the dried gel after a DTA run corresponded to $\text{Li}_2\text{Ge}_4\text{O}_9$ and $\text{Li}_2\text{Ge}_7\text{O}_{15}$ crystals. The values of activation energy for the two stages are found to be 557 and 405 kJmol^{-1} [3]. Activation energies are comparable with those reported with conventional melt glasses from oxides.

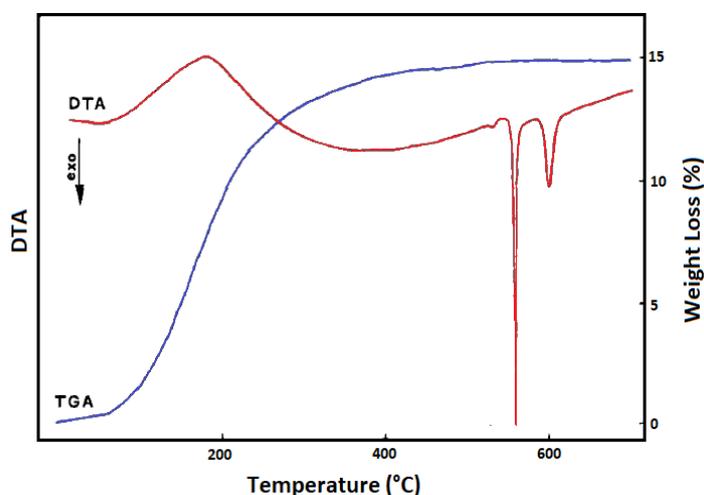


Figure 2. DTA/TGA curves of the dried gel, recorded in N_2 at $10^\circ\text{C}/\text{min}$.

Acknowledgements

The work was financially supported by V:ALERE 2019 grant support from Università degli studi della Campania "L. Vanvitelli" of CHIMERA.

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Tales of Polymorphs:

Effect of Manual Grinding on Diclofenac Acid Nanocrystals

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Keywords: Polymorphism, Diclofenac, Grinding, Polymorphic Transformations

The presence of different polymorphic forms of a drug is very important in the preparation of pharmaceutical solid forms at the pharmaceutical industry [1]. The study of the thermal properties and the energetic aspects of the crystalline lattices of these forms are important for understanding the variations of the chemical-physical properties. In particular, they influence important parameters such as solubility and dissolution rate of the drug and therefore, the technological and biopharmaceutical properties. Of particular interest are the changes in the crystalline structure of polymorphs after the grinding process.

2-(2-[(2,6-dichlorophenyl)amino]phenyl)acetic acid (DCF), also known as diclofenac acid, (Figure. 1) is a molecule belonging to the category of nonsteroidal anti-inflammatory drugs (NSAIDs) that has anti-inflammatory, analgesic, antipyretic activity [2].

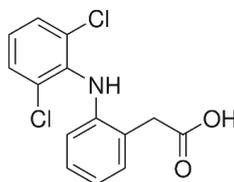


Figure 1. Diclofenac acid molecular structure.

Three polymorphic forms of DCF are known: two are monocline and are called HD1 ($P2_1/c$ space group) and HD2 ($C2/c$ space group) [3]. The two forms are very similar, the molecules present centrosymmetric dimers linked by hydrogen bonds between the oxygen atoms of the carboxyl group (Figure 2 and 3). The third polymorph (HD3) is orthorhombic ($Pcan$ space group) and it does not show any intermolecular hydrogen bond [4]. Literature reports about the co-grinding of DCF with carriers for the preparation of sustained release systems, which observed minor crystallinity changes after the grinding process [5, 6]. This slight difference from the single crystal structure was attributed to the presence of the matrix adversely affecting the quality of the data. To our opinion, it can be related to the manual grinding process that was used to get a powder sample suitable for XRPD analysis.

Therefore, aim of our work was to verify whether the grinding process (either manual or by mill apparatus) could allow changes in the crystal structure and in the molecular conformation of the polymorphs. To this end, we used X-ray Powder Diffraction (XRPD), Fourier Transform Infrared Spectroscopy (FT-IR) and Differential Scanning Calorimeter (DSC), to study the HD1 and HD2 polymorphs of DCF before and after manual grinding. Of particular interest were the thermograms of DSC samples showing endothermic peak due to the incongruent fusion of DCF [7].

Our study perfectly fits with the recent emergence of grinding, either manual or by ball milling equipment, as an attractive way to access and process polymorph forms [8].

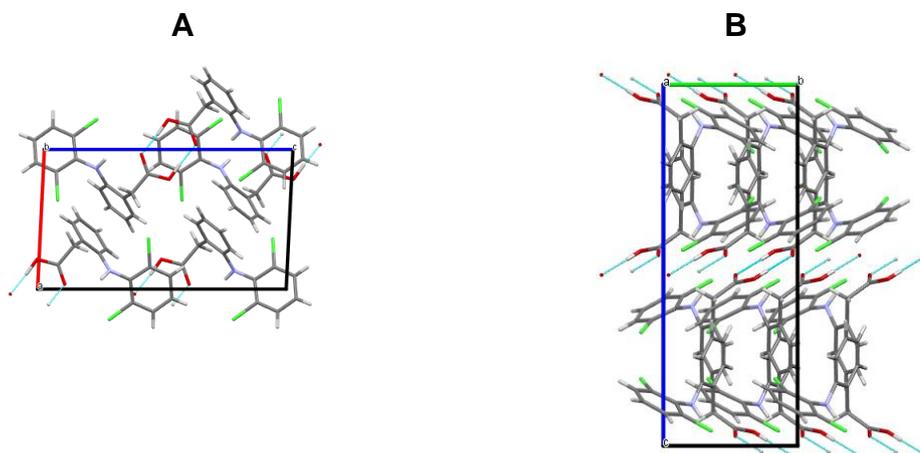


Figure 2. A) HD1 unit cell. View down crystallographic b axis. B) HD2 unit cell. View down crystallographic a axis. H-bond in turquoise color.

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The Studies of the effect of MgO and TiO₂ on the crystallization process of fly ash derived glass

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Keywords: Fly ash, Glass-ceramic, Differential Thermal Analysis, X-ray Diffraction

Nowadays there is a tendency, toward the research, to reuse coal fly ashes, produced by the coal-burning power plant, to protect the environment. In the present work the nucleation and crystal growth processes of fly ash derived glass-ceramic, improved by MgO and TiO₂, were studied. The high viscosity of melted glass obtained from fly ash [1] was reduced adding MgO whereas TiO₂ was used to enhance the nucleation mechanism. The analysis was carried out by Differential Thermal Analysis (DTA), Thermal Dilatometry (TD), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

DTA curve of as-quenched samples, (a) Fig.1, shows a glass transition with a $T_g=730$ °C and two exothermic peaks at 820 °C and 975 °C, respectively. The samples, subjected to a heat treatment at 730 °C for 2 h (b), 4 h (c), 8 h (d) of Fig. 1, show a decrease of the first exo-peak whereas the second one was not affected by heat. Curve (d) also shows a glass transition at the temperature of 940°C that indicates the presence of the phase separation. This is also confirmed by the dilatometry analysis (Fig. 2) in which curve (b) shows a glass transition at 900°C.

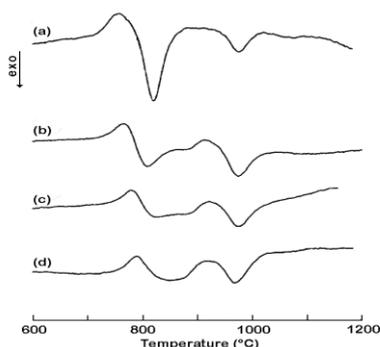


Figure 1. DTA curves. as-quenched glass(a) and heated at 730 °C for 2 h(b), 4 h (c), 8 h(d).

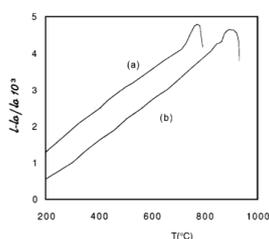


Figure 2. Thermal expansion of as-quenched (a) and 8 h at 730°C heated sample.

XRD analysis (Fig.3) of the as-quenched sample (a) and of that heated 8 h at 730 °C (b) show a still amorphous structure. XRD pattern of the glass heated to 820°C (temperature of the first DTA exo-peak in (c) of Fig.1) does not exhibit a crystalline structure with only a small reflection peak, while the sample heated to 975 °C (temperature of the second DTA exo-peak in (d) of Fig.1) is more crystallized.

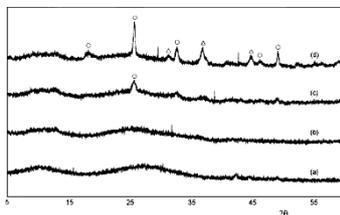


Figure 3. X-Ray diffraction patterns of (a) as-quenched, (b), heated 8 h at 730°C, heated up to 820°C and (d) heated up to 975°C sample.

Following the results, two heat programs were proposed to turn glass into glass-ceramic material:

Program 1: 730 °C (8 h) → 900 °C (8 h) → 1020 °C (20 h)

Program 2: 850 °C (4 h) → 950 °C (8 h) → 1020 °C (20 h)

In both programs, the crystalline phase is produced in the second step and the formation of anorthite and cordierite is observed in the third step, but they have a different glass-ceramic morphology. SEM micrographs of the Program 1 and 2 treated samples (Fig. 4) show an amorphous high viscosity phase and a crystallized low viscosity phase. Finely, the thermal expansion coefficients of two heat-programs glass-ceramic materials are lower than that of as-quenched and the heated 8 h at 730°C glass.

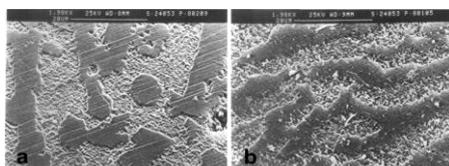


Figure 4. SEM photomicrographs of sample treated with program 1 (a) and treated with program 2 (b).

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Acrolein production by oxidative coupling of a mixture of biosourced alcohols over spinel catalysts: influence of magnesium substitution by transition metals

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Keywords: acid-base properties; spinel catalysts; acrolein production; adsorption microcalorimetry

Acrolein is the simplest unsaturated aldehyde widely used in the chemical industry. Thanks to the conjugation of vinyl with a carbonyl group, acrolein possesses a high degree of reactivity which makes it a very good intermediate for numerous syntheses such as acrylic acid, methionine, or biocides. Nowadays, the major way of synthesis of acrolein is by propylene oxidation. However, considering the need of reducing greenhouse gas emission and finding more environmentally friendly methods of production, new processes have been developed to produce sustainable acrolein from renewable resources [1-2]. In this respect, oxidative coupling of biobased alcohols is becoming an interesting alternative method to replace fossil-fuel based propylene production.

By oxidative coupling of alcohols, acrolein is produced in a two-step process, the first stage concerns the oxidation of methanol and ethanol to formaldehyde and acetaldehyde respectively on a redox (FeMoOx) catalyst. It is followed, in a second stage, by the aldolization and dehydration of the mixture of aldehydes on an acid/base catalyst to obtain acrolein.

Aldolization reactions are known to be driven by acid/base properties. Then, enhanced yield and selectivity towards acrolein should be obtained by improving the cross-aldolization reaction on tuned acid/base catalysts [3-4]

The aim of the present study is to produce acrolein in a single reactor from alcohols (methanol/ethanol) thanks to the development of catalysts with a good balance between acidic and basic sites. To increase selectivity in acrolein without formation of too much COx, spinel catalysts where magnesium was partly or totally substituted by transition metals, supplied by Baikowski, were investigated. The acidic and basic properties of the catalysts were determined by adsorption microcalorimetry of NH₃ and SO₂ probe molecules, respectively. The experiments were performed at 150 °C in a Tian-Calvet heat flow calorimeter (C80 from Setaram, Lyon) linked to a volumetric line equipped with a Barocel capacitance manometer for pressure measurements. This apparatus allows to obtain the number, strength, and strength distribution of the active sites. Besides, to study the affinity of catalysts for the reactants, adsorption microcalorimetry of formaldehyde and acetaldehyde has been done following the same protocol as for NH₃ and SO₂ but at a lower temperature (80°C). Then, catalytic reaction was performed in oxidative conditions to study how the basic and acidic properties can influence the catalytic activity.

Among spinel catalysts, the best results were displayed by (0.8Mg ; 0.2Mn) Al₂O₄ with 31 % yield at 285°C (GHSV 5000 h⁻¹) directly followed by (0.8Mg ; 0.5Mn) Al₂O₄ with 30% acrolein yield.

It appears that acrolein production seems to be depending on the cationic species, increasing with ionic radius.

Successive adsorptions of acetaldehyde and formaldehyde using adsorption microcalorimetry were performed to further investigate the mechanism of adsorption. Results are shown in Fig 1. These

experiments evidenced the isolation of acetaldehyde by formaldehyde at the surface of the catalyst thus explaining the absence of crotonaldehyde (which is the product of self-aldolization of acetaldehyde) and the predominance of acrolein in the final products [5].

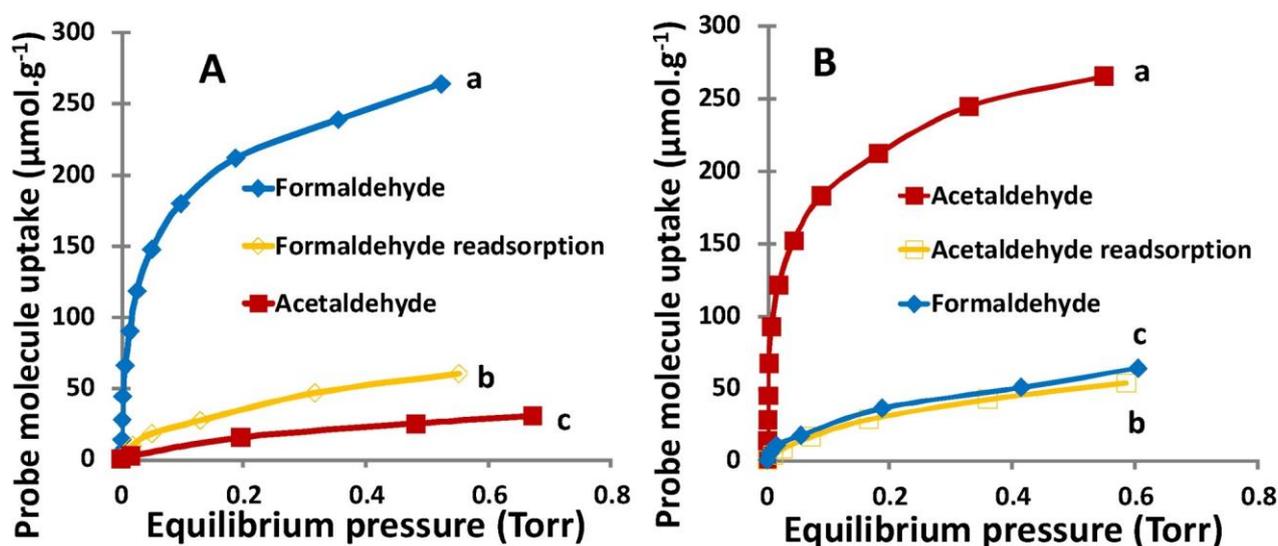


Figure 1. A: Isotherms of formaldehyde adsorption (a) and readsorption of formaldehyde (b) followed by adsorption of acetaldehyde (c) at 80 °C on (0.8 Mg ; 0.2 Mn) Al₂O₄ ; B: Isotherms of acetaldehyde adsorption (a) and readsorption of acetaldehyde (b) followed by adsorption of formaldehyde (c) at 80 °C on (0.8 Mg ; 0.2 Mn) Al₂O₄. [5]

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Thermogravimetric analysis as a tool for *Layered doubled hydroxides (LDHs)* characterization

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Keywords: Layered double hydroxides (LDH), TG

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

Where M and N are respectively a divalent and a trivalent cation, A is an anion with n charge, x is the molar ratio N/(M+N) and m is a value between 1 and 4 depending on the hydration degree of the compound. The prototype structure of this class of materials is the hydrotalcite, in which in the layer of octahedral $M(OH)_2$ some divalent cations were replaced with trivalent cations leading to a positive charged excess, that is neutralized by an anion hosted in the interlayer and connected by weak bonds as shown in figure 1.

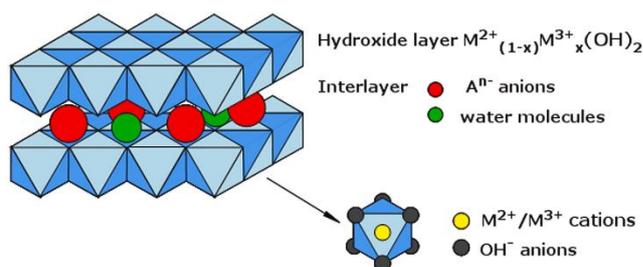


Figure 1. Structure of layered double hydroxide [1].

The interlayer is very flexible and could host different compounds as anions, cations and not charged ones. These properties combined with the wide range of possible combination of M, N and A make these materials very interesting as catalyst and anionic sponge [2,3]. LDHs are also promising materials for energy storage systems in particular in supercapacitors [4] and metal ion batteries [5].

In this work the compound $[(Mg_{0.66}^{2+}Fe_{0.33}^{3+}(OH)_2]^{0.33+}(Cl_{0.33}^{-})^{0.33-} \cdot mH_2O$ has been synthesized for waste waters remediation purpose, owing to its ability to catch pollutant anions releasing Cl^{-} and its simple synthesis procedure by coprecipitation.

The synthesis pathway is very easy but could lead to a compound affected by the presence of CO_3^{2-} , probably at the interlayer in substitution of Cl^{-} . This anion is more stable in the structure and less exchangeable, causing a decrease in the exchanging performances. To avoid the presence of carbonate the synthesis can be carried out under inert atmosphere, all over the entire process, implying an increase in costs and equipment.

The presence of carbonate is not easily detectable by X-Ray Powder Diffraction (XRPD) due to the low crystallinity and turbostratic nature of LDHs, so it could be investigated by TG analysis coupled with an FT-IR analysis. As the TGA, during heating at 200°C occurs a thermal transformation involving the carbonate and the hydration water causing the evolution of CO_2 [6] with subsequent formation of an intermediate compound, which transforms into a mixed oxide at higher temperature. Furthermore, carbonate is active at the IR analysis and its presence could be easily investigated by this technique through the presence of two absorbances at 1460 and 1360 cm^{-1} .

Goal of this work is the study of the TGA and IR results to characterize the compounds obtained under different synthesis conditions, in order to set up the best procedure to obtain the MgFe-Cl LDH required for remediation purposes.

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Energetic and structural properties of organic crosslinker molecules (pyridine 2,3-dicarboxylic anhydride and pyrazine 2,3-dicarboxylic anhydride) from theoretical calculations

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Keywords: Thermochemistry; Theoretical composite methods; Gas-phase enthalpy of formation; Reactivity

The structural characteristics of pyridine-2,3-dicarboxylic anhydride and pyrazine-2,3-dicarboxylic anhydride make them relevant organic crosslinkers. For this reason, they are well known as important raw material and intermediate used in organic synthesis, pharmaceuticals, agrochemicals and dyestuff [1].

The standard molar gas-phase enthalpies of formation, at $T = 298.15$ K, of the two organic crosslinkers were calculated in this work by means of the composite G3(MP2)//B3LYP approach, making use of several different group substitution reactions (isodesmic and homodesmotic reactions). According to our experience in the computational study of heteropolycyclic compounds [2], this type of theoretical procedure generates reliable gas-phase enthalpy values of formation, in good agreement with the experimental data.

The computational study was also extended to the attainment of the dipole moments, electrostatic potential surfaces, and the frontier molecular orbitals for pyridine-2,3-dicarboxylic anhydride and pyrazine-2,3-dicarboxylic anhydride, allowing us to infer about their reactivity.

The main structural difference between the organic crosslinker compounds (the presence of pyridine and pyrazine rings in their structures) will be also compared in energetic terms.

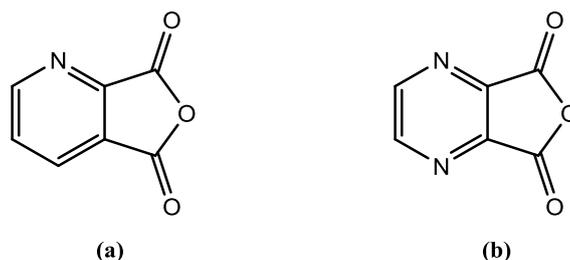


Figure 1. Molecular structures of pyridine-2,3-dicarboxylic anhydride (a) and pyrazine-2,3-dicarboxylic anhydride (b).

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Thermal behaviour of kaolin from San José, Oruro, Bolivia

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Keywords: Kaolinitic clays, firing, thermal analysis

Kaolin is widespread as result of alteration in hydrothermal ore deposits. Often, this constitutes an important economic complement. This is the case of the San José Sn-Ag deposit from the Central Andean Tin Belt. This deposit is related to a Miocene porphyry body hosted in a metasedimentary sequence of Silurian age. A widespread advanced argillic alteration occurs in the San José deposit, which is exploited for kaolin. This study presents a chemical, mineralogical and thermal characterization of the San José kaolinitic deposit to evaluate possible applications.

The San José kaolinitic rocks are white silty materials that outcrops in several locations along 3 km in a NW-SW fringe in the SW of Oruro city. Samples of the kaolinitized rocks in a quarry of about 70x50m were undertaken. The particle size shows a bimodal distribution, with modes at 0.4 μm and the second at 10 μm . Different size fractions were separated. Particles < 60 μm were introduced in 1l of a solution with defloculant and separated by sedimentation the particles between 2 and 20 μm and particles lower than 2 μm were obtained filtering the solution. Detailed grain size distribution has been obtained using a Coulter Electronics LS230 particle counter. The chemical composition of major and trace elements was determined by X-ray fluorescence (XRF). Mineralogy was obtained by powder diffraction X-ray (XRD) using oriented and non-oriented aggregates. Quantitative determination of phases was obtained by the Rietveld refinement method. Fourier Transform Infrared spectroscopy (FTIR) was used to complete the mineralogical characterization.

Thermal properties were determined by differential thermal analysis-thermogravimetry (DTA -TG) and dilatometry.

In the kaolinitic materials of San José SiO₂ content ranges from 64 to 69 wt %, Al₂O₃ varies from 19 to 20 wt % and K₂O ranges from 4.032 to 5.51 wt %. In addition to minor amounts of Fe₂O₃ (0.61 to 1.11 wt %) and TiO₂ (up to 0.64 wt %) and lower amounts of Na₂O, CaO, MgO and P₂O₅.

Mineral phases determined are mainly quartz (54-57 wt %), kaolinite (6-8 wt %), K-feldspar (3-19 wt %), muscovite (16-27 wt %), plagioclase up to 3 wt %, alunite up to 5 wt % and gypsum up to 2 wt %. The fraction <63 μm contains from 20 to 27 wt % of kaolinite.

The FTIR spectrum of the San José kaolin presents the typical bands of kaolinite, corresponding to structural bonds: tetrahedral silica (Si-O), octahedral aluminium (Al-O and Al-OH) and SiO₄-Al₂O₃ bonds (Si-O-Al). In the region between 3800 and 3600 cm⁻¹ the most characteristic absorption bands of kaolinite appear, corresponding to structural water and Al-OH stretching vibrations. These characteristic bands appear at 3698, 3673, 3650 and 3623 cm⁻¹. The theoretical doublet between 3694 and 3619 cm⁻¹, which appear at 3698 and 3623 cm⁻¹ in San José, reveals a well ordered kaolinite structure [1]. Bands at 1113, 1030 and 994 cm⁻¹ correspond to Si-O stretching, a band at 920 cm⁻¹ is attributed to Al-OH bending vibrations and at 790 and 765 cm⁻¹ are attributed to OH deformation [1].

ATD curves show an endothermic peak at ~520°C, caused by the release of kaolinite OH groups and also to a transition phase from α -quartz to β -quartz and an exothermic peak at ~980°C related to the crystallization of mullite. TG curves show a first weigh loss of <1 wt %, mainly due to removal

of moisture. The main endothermic peak is associated with the main weight loss in the TG, about 3.5 wt %. The exothermic peak is related to a small loss of weight. The total mass loss up to 1300 °C is about 8 wt %.

Dilatometric analysis show the dimensional changes obtained during heating and cooling processes of kaolin (Figure 1). In the heating process, there is a small expansion between 500 and 520 °C, due to the high Al³⁺ content. The dilatometric curves show a shrinkage about 890 °C produced by the collapse of metakaolinite into a spinel-like structure. Another shrinkage starts at 1010 °C, at the beginning of the sintering, when the spinel-like phase is transformed to mullite and amorphous SiO₂ [2,3]. In addition, at 550 °C a polymorphic transformation of β - α quartz is reflected in the cooling curve.

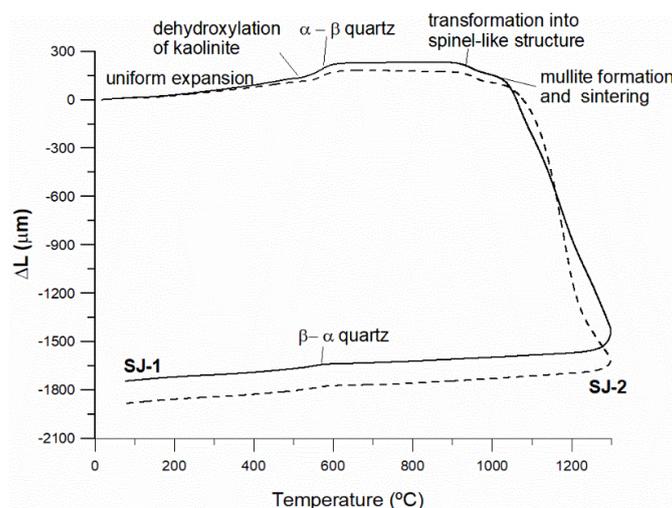


Figure 1. Dilatometric curves of Kaolin from San José.

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Multitechnique studies of the thermal behaviour and thermodynamic properties of hybrid lead halide perovskites

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Keywords: Lead halide perovskite decomposition; Isoconversional analysis, Mass Spectrometry, thermal and thermodynamic properties

In the last decade, lead halide (PbI_3^-) perovskites have proved to be one of the most interesting light harvesting materials, reaching unprecedented conversion results both as such and in tandem with silicon [1]. To date, large-scale technological applications of these materials are seriously limited from their low thermal and intrinsic/extrinsic thermodynamic stability. Various approaches are currently proposed to overcome these limitations, such as modifying chemical composition both in the cation and in the anion portion or protecting the device by suitable encapsulation techniques.

Understanding the degradation behaviour of prototypical materials of this class of compounds, as well as assessing the thermal stability of new variants is very important to achieve the goal of identifying materials with desired long-term stability properties. Furthermore, the determination of thermodynamic properties related to the thermal and chemical degradation, including enthalpies and Gibbs energies of decomposition, heat capacities and enthalpies of formation is of great help in assessing both the perovskite intrinsic stability and the reactivity towards water, oxygen and other agents.

In this context, our group succeeded in applying a multitechnique approach to investigate the thermal stability, heat capacities/phase transitions and thermodynamic properties of several lead halide perovskites and their halide precursors [2,3]. Our approach is based on the combined use of differential thermal analysis (DTA), differential scanning calorimetry (DSC), X-ray diffraction and effusion-based technique (Knudsen Effusion Mass Spectrometry, Knudsen Effusion Mass Loss), the latter aimed at investigating the gas species released under close-to-equilibrium degradation conditions (Fig.1). The use of DTA-TG enabled us to study both the solid phase transitions and the weight loss under open-surface dynamic heating conditions. Moreover, DTA measurements performed at different heating rates were analyzed by the isoconversional method to determine the kinetic parameters of the decomposition process. The so-obtained activation energies were compared with those derived from XRD spectra collected on samples treated at different temperatures under air (Fig.2).

Starting from the prototypical methylammonium compound (MAPbI_3), we explored the effect on thermal properties caused by increasing methyl substitution as well as replacing alkylammonium with the formamidinium cation. The decomposition kinetics was studied and the gas-releasing decomposition reactions were identified by KEMS. Preliminary results on the inorganic CsPbI_3 are also reported.

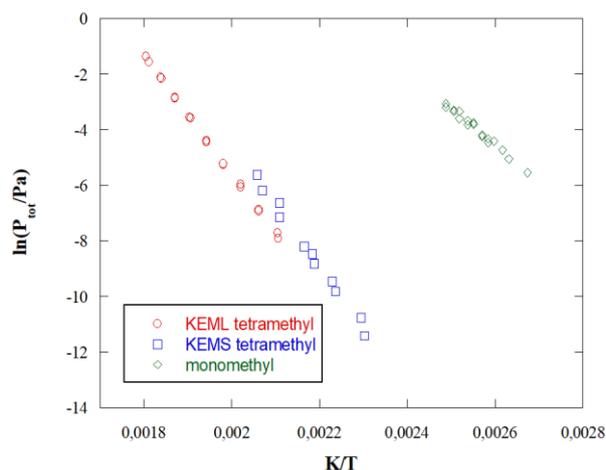


Figure 1. Total pressure as a function of the temperature for the dissociation reaction of $N(CH_3)_4PbI_3$ measured by KEMS and KEML, compared with the corresponding values for $CH_3NH_3PbI_3$.

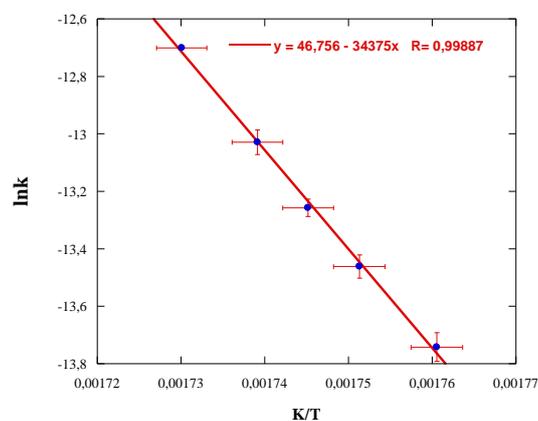


Figure 2. Arrhenius plot obtained by Rietveld quantitative phase analysis of $N(CH_3)_4PbI_3$ samples isothermally treated at 295, 297, 300, 303 and 305.

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A study of the main reactions occurring at the electrodes of Li-ion cells during the thermal runaway

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Keywords: Lithium ion, batteries, reaction kinetics, DSC, thermal runaway

A Li-ion cell is composed by a carbon-based negative electrode (NE), a porous polymeric membrane (usually high-density polypropylene and/or polyethylene) which keep the electrodes electrically apart allowing the passage of Li-ions, and a positive electrode (PE) made of lithium transition metal oxides (LiMO_2 , M=Co, Ni, Mn or Al). All is immersed in a mixture of organic solvents (dimethyl carbonate, DMC, ethyl methyl carbonate, EMC, ethyl carbonate, EC) in which a lithium salt (LiPF_6) is melted. To produce the electrodes, metal current collectors (Al for the positive electrode and copper for the negative electrode) are coated with active material, polymeric binder (usually polyvinylidene fluoride, PVDF) and small amounts of carbon with a high surface area [1].

In recent years, Li-ion batteries have been widespread used in many applications from electric vehicles to energy storage systems, but they have also been the source of several serious accidents. In fact, under electrical, mechanical or thermal abuse conditions a thermal runaway can occur with a consequent uncontrollable increase in pressure and temperature which can lead to fires and explosions [2].

This work wants to analyze the mechanism of the reactions that take place during the thermal runaway occurring at the anode and the cathode, in order to individuate adequate solutions to avoid/mitigate these reactions. To this aim Panasonic's NCR18650 lithium-ion cylindrical cells (LiNiCoAl oxide), previously charged at different state of charge (30-100%), are disassembled and each electrode of the cell is analyzed by Differential Scanning Calorimetry.

DSC test results has shown that at the cathode the first reaction occurs in the range of temperature 372 - 407 K. This reaction is recognized as the decomposition of SEI (Solid Electrolyte Interphase), a protective film that forms during the first charge of the cell, consisting of the products of the reactions between the electrode and the electrolyte. It is usually found at the anode, but some authors have also noted the formation of this film on the positive electrode [1, 3].

This step leads to an increase in temperature up to 443-473 K. Then the positive electrode reacts with the solvent. But the reactions involved may vary a lot, depending on the chemical nature of the positive electrode. For example, LiCoO_2 electrodes exhibit a high heating rate above 453 K while other chemistries such as LiFePO_4 or LiMn_2O_4 have higher stability showing a very limited exothermic peak at higher temperature (493 K-523 K) [1].

The mechanism behind these reactions is not yet clear, some authors have proposed for metal oxide electrodes a mechanism in which the positive active material releases oxygen at a high temperature that could oxidize the solvent, or it can react with the binder used for the manufacture of the electrode [1, 4-5].

Two main exothermic reactions take place at the anode during heating: i) the decomposition reaction of the SEI layer (377-403 K) and the exothermic reaction between the lithiated anode and the PVDF binder (565-602 K) [6].

In literature, few papers have evaluated the kinetic parameters of the main exothermic reactions that occur in Li-ion cell [7-8] while others have determined the kinetic parameters of the decomposition reactions of negative and positive electrodes through DSC tests [9-12].

In this work the kinetics of the identified reactions were evaluated using isoconversional methods and compared with the values available in the literature. The results show an important relationship between the cell's initial state of charge and the progress of reactions.

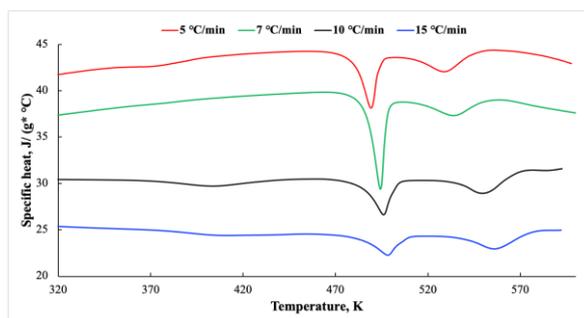


Figure 1. Cathode of 30%SOC NCR18650 Li-ion cell

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Experimental and computational thermochemical study of 2-mercapto-1,3,4-thiadiazole

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Keywords: Calorimetry, Enthalpy of formation, Enthalpy of sublimation, Tautomerism

Thiadiazole is a five-membered heterocyclic system containing two nitrogen atoms and a sulfur atom, with an important role in different practical applications [1]. Those heteroatoms can occupy different positions in the ring, being the 1,3,4-thiadiazole isomer one of the most interesting ring systems (Fig. 1a). In particular, mercapto-substituted thiadiazoles possess a relevant structural characteristic, i.e., the existence of thiol and thione tautomeric forms (Fig.1b). The tautomerisation influences the reactivity of the thiadiazoles therefore, this study is expected to be a contribution to clarify this topic.

The present work reports an experimental and computational thermochemical study on 2-mercapto-1,3,4-thiadiazole (McT). We present the results for the energy of combustion of McT, at $T = 298.15$ K, obtained from rotating-bomb calorimetry measurements. The corresponding enthalpy of sublimation was measured by high-temperature Calvet microcalorimetry. The standard ($p^0 = 0.1$ MPa) molar enthalpies of formation of McT, in condensed and gaseous states, were derived from the parameters previously determined. The gas-phase enthalpy of formation was also determined from high-level molecular orbital calculations at the G3(MP2)//B3LYP level of theory. The results obtained are discussed in terms of energetic-structural relationships, and the evaluation of the tautomeric equilibrium is also presented.

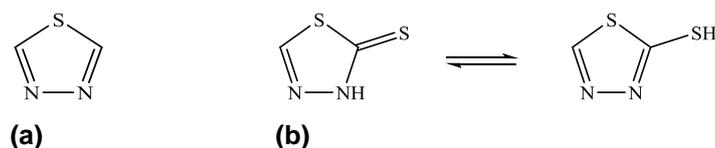


Figure 1. Molecular structure of 1,3,4-thiadiazole **(a)** and thione/thiol tautomeric forms of 2-mercapto-1,3,4-thiadiazole **(b)**

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Thermochemical study of cinnamate derivatives

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Keywords: Calvet microcalorimetry, combustion calorimetry, cinnamate derivatives, thermochemical study

The olfactory properties of fragrances are desirable for products like perfumes, essential oils, shampoos and cosmetics, among many others. However, the everyday use of fragrance products, as well as their presence in various environments, constitute a concern in understanding their reactivity [1-3].

The aim of this work is to evaluate and discuss the energetic properties of ethyl (*E*)-cinnamate and ethyl 2,3-dihydrocinnamate (Figure 1), performing experimental and computational studies, in order to provide reliable data for the analysis of their environmental risk assessment. This research follows a series of previous works [4, 5].

This communication reports the massic energies of combustion of ethyl (*E*)-cinnamate and ethyl 2,3-dihydrocinnamate, measured by static bomb combustion calorimetry and the corresponding enthalpies of vaporization measured by Calvet microcalorimetry technique. These results are used to derive the enthalpy of formation of these cinnamate derivatives, in the liquid and gaseous phases, at $T = 298.15$ K.

The values derived from the experimental measurements and from the complementary computational studies of ethyl (*E*)-cinnamate and ethyl 2,3-dihydrocinnamate, will be analysed in terms of their structural characteristics.

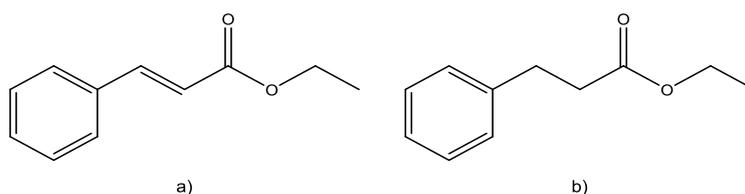


Figure 1. Structural formula for a) ethyl (*E*)-cinnamate and b) ethyl 2,3-dihydrocinnamate.

Acknowledgments

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Ni-Mn-Sn Heusler alloys: thermal cycling

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Keywords: Thermal analysis, thermal cycling, Ni-Mn-Sn, Heusler

Magnetic shape memory alloys of the Ni-Mn-Sn system are characterized by having, in a range of compositions, the highly ordered austenitic Heusler structure. On the other hand, these alloys usually have a martensitic transformation in addition to magnetic transformation (from ferromagnetic to paramagnetic). The shape memory effect is controlled by changing the temperature, the applied magnetic field and/or the pressure, as it occurs in traditional shape memory alloys, but also by varying the magnetic field up to moderate field values [1]. One of its potential applications is in magnetic cooling devices. Multiple studies have been conducted on the thermal and thermomagnetic response of these alloys in a first heating and cooling cycle [2]. However, it is necessary to carry out the study of its response after a high number of cycles.

The characteristic temperatures of phase transformation were measured by differential scanning calorimetry (DSC) with heating and cooling rates of 10 K/min (an example is given in figure 1). Likewise, thermomagnetic analysis by vibrating sample magnetometry (VSM) was applied to check the thermomagnetic response. Thermal cycling was performed at low temperature with a liquid nitrogen reservoir in some alloys of the Ni-Mn-Sn system.

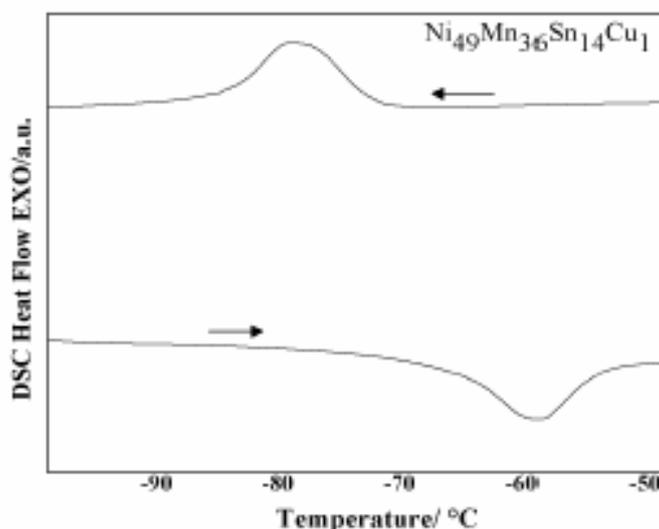


Figure 1. DSC cycling scans of a Ni-Mn-Sn alloy.

The results show a shift on the martensitic transformation temperature (between 10 and 50 K, depending of the alloy) and a reduction of around the 25% in the magnetization of the ferromagnetic phase after multiple cycles. The biggest change occurs during the first three thermal cooling-heating cycles.

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Epoxy Resin Formulation for 3D Printing by Liquid Crystal Display (LCD)

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Keywords: additive manufacturing, LCD printing, epoxy, polymer blends, thermomechanical properties

In the Additive Manufacturing (AM) landscape, resin photopolymerization printing is showing great results in terms of engineering applications [1-3]. There are several techniques and materials used. In the present work, the VAT polymerization process has been studied, in particular the Liquid Crystal Display (LCD) printing.

Following the investigation of previous works [4], new epoxy resin-based blends have been studied, with the aim of improving the printability of the resin without compromising the thermomechanical properties of the printed part.

Different mixtures have been formulated and studied depending on the percentage of diluent, to observe the impact that the addition of epoxy resin has on the commercial resin. In particular, Diglycidyl ether of bisphenol A (DGEBA) mixed with Diethyltoluene Diamine (DETDA) was added due to the easy processing in liquid form at room temperature. Thermomechanical analyzes were carried out on the resulting mixtures.

The best printing conditions were assessed with various speed cure tests (SCT). The characterization of the epoxy-resin blends for knowing the exposure times was carried out by using the statistical methodology of the Design of Experiments (DoE).

The heat treatment was optimized from 4.5 to 3 hours, printed parts having a glass transition temperature (T_g) equal to 114 °C were obtained and the exposure time was decreased from 30 to 15 s.

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Thermal behavior study of a hybrid halide perovskite precursor. The case of tetramethylammonium iodide

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Keywords: tetramethylammonium iodide, lead halide perovskites, heat capacity, thermal stability

Tetraalkylammonium halides have received great interest in the past due to their valuable properties, with particular reference to the low clustering tendency that makes them ideal chemical standards for ESI(+)-IMS/MS [1]. In addition, tetraalkylammonium cations, considered as the archetypal hydrophobic cations, combine in many environmental and biological processes both charge and hydrophobicity [2]. In particular, tetramethylammonium iodide ((CH₃)₄N⁺I⁻), denoted as TMAI) can be considered as a simpler model to study the thermal decomposition pathways of tetramethylammonium lead iodide (Fig. 1) [3], belonging to the class of perovskites currently considered with great expectations as possible light harvesting materials for photovoltaic devices.

Prior to test it for this application it seems important to investigate its thermal stability by means of thermal analysis experiments, where the possible occurrence of degradation processes at low temperature must be monitored. On the other hand, the absence of acidic hydrogens, due to the presence of quaternary nitrogen, makes this compound stable to moisture.

In this study, we report the experimental determination of the molar isobaric heat capacities in the range 25-255 °C by differential scanning calorimetry (DSC), and thermal behavior study of TMAI by means of simultaneous thermogravimetry-differential thermal analysis (TG-DTA) experiments under inert (Ar) atmosphere up to 500 °C. Previous studies [4,5] hypothesized that thermal decomposition involves the bond breaking of C-N, according to the following mechanism:



Our measurements revealed that no mass loss is observed in the TG curve up to about 290 °C. A single step of mass loss is evidenced between 300 and 450 °C, accompanied by an endothermic effect. The reaction mechanism, described in the light of the gases evolved upon heating in the suitable temperature range according to the analysis of MS spectrum recorded at 406 °C confirmed the evolution of gaseous (CH₃)₃N, while CH₃I is not detectable.

In order to complete this investigation a kinetic study of the thermal decomposition has been carried out using two different isoconversional methods, namely the integral Kissinger-Akahira-Sunose (KAS) and the incremental method [6,7], being the latter applicable even in the case of significant variable activation energy with the degree of conversion.

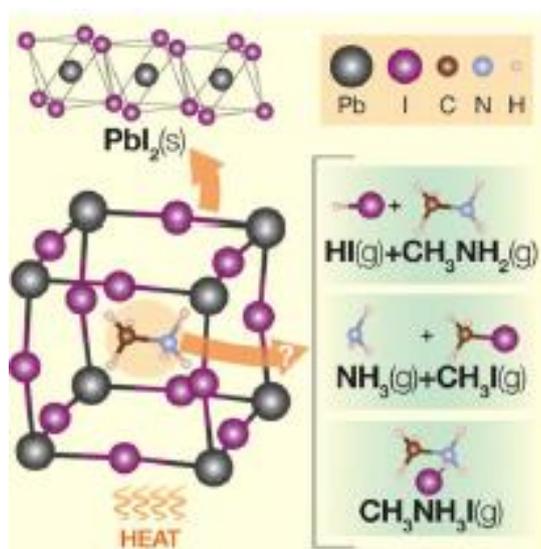


Figure 1. Thermal decomposition pathways of tetramethylammonium lead iodide [3].

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Investigation of kinetics, thermal behaviors and evolved gases of gel explosive

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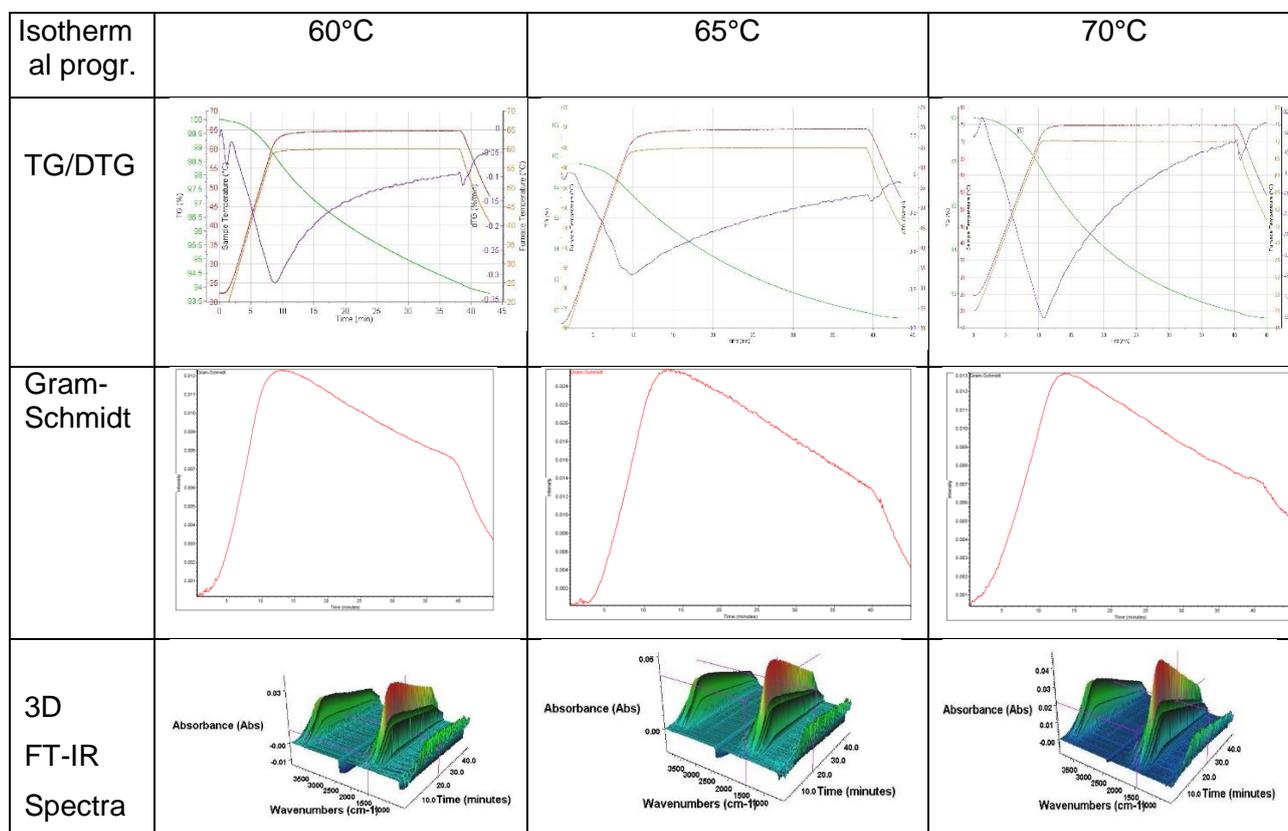
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Keywords: explosives, thermal analysis, kinetics of volatile

The research work was done using a gel explosive, in which the main ingredients are: ammonium nitrate, methylammonium nitrate, sodium nitrate, aluminum powder and the main goal of paper is to investigate kinetics, evolved gases and thermal decomposition behaviors in order to determine an equation for kinetics decomposition.

The isothermal program comprises three stationary stages, respectively: 60°C, 65°C and 70°C, using different increasing ramps, for a period of 30 minutes, following the types of volatiles by FTIR-TGA Coupling. The non-isothermal program was performed with the following increasing ramps: 2,5 °C, 5°C, 10°C, 15°C and 20°C, the maximum temperature of oven being set up to 70 °C. Helium was used as a carrier gas, at a flow rate of 30 ml/min.

The samples were analyzed using the Labsys Evo TGA equipment coupled with a Fourier - Transform - Infrared (FTIR) spectrometer Nicolet IS 50.



Thermal analysis is a technique consisting in measuring the mass variation of a sample over a well-established temperature program, in a controlled atmosphere. Sample heating is performed at a constant speed set by a temperature program, the mass changes being measured with a very sensitive balance [1].

The gases are transferred from the TGA instrument using a heated transfer line to prevent the possibility of condensation. With such a combination, the sample can be inserted into the TGA instrument without any form of chemical or physical change. Applying sequential FTIR analysis adds a new TGA dimension by adding to the measurement the specificity it otherwise lacks [2], [3].

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Comparative thermal and hyphenated analysis of different mortars samples from Deva region

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Keywords: Thermal analysis, infrared spectroscopy, XRD, analysis of mortars, EDS, SEM, historical analysis.

During the Dacian kingdom period (1st century BC – 106 AD), the nobility began using a type of „noble dwelling” for habitation, called „tower-houses” (referencing the medieval keep). Buildings designated as such are usually situated within a fortified area, though there are exceptions [1,2]. Thermal analysis and infrared spectroscopy are used in the study of various mortar samples clearly attributed to different historical periods in south-western Transylvania (Romania)(Figure 1). The results obtained will clarify the character of certain samples, several medieval mortar samples, another from possible mortar from the Dacian kingdom period, while another was not even certain to be mortar. The results may contribute in the successful identification of the construction techniques used in the buildings from where the samples originate. The area under investigation is of great importance for Romanian culture, so restorers have to find and produce mortars similar to those used in the building of our monuments[3,4]. The thermoanalytic curves obtained in the case of possibly Dacian and medieval mortars are presented in the following.



Figure 1. Mortar samples

FTIR Spectra were collected in the 4000-650 cm^{-1} spectral range, using a PerkinElmer SPECTRUM 100 (UATR-FTIR). The thermal behaviour for all of the samples was recorded using a heating rate of 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ until 1300 $^{\circ}\text{C}$ on a TG/DTA Diamond thermobalance produced by Perkin Elmer in quartz crucibles (Pyris software Perkin-Elmer). Surface morphology (SEM) and elemental analysis (EDS) were investigated by scanning electron microscopy [5]. The thermal analysis for samples 1, 2, 3 and 4 are presented in figure 2.

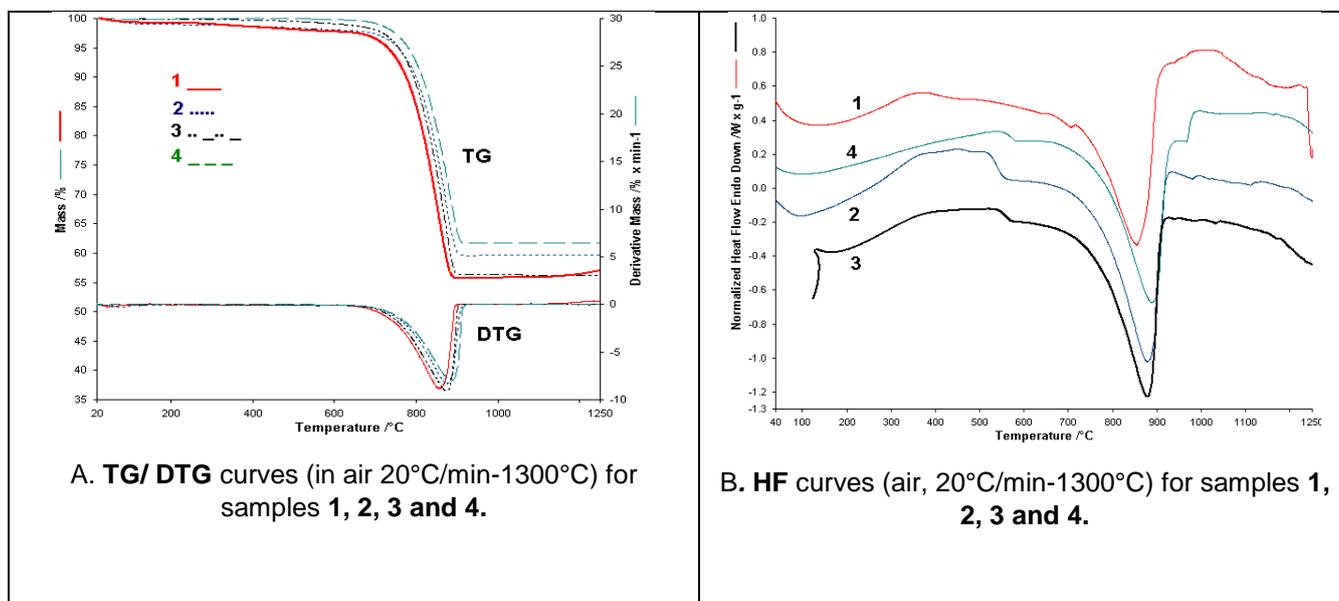


Figure 2. The thermal behaviour of the four samples, the TG and DTG curves, respectively the Heat Flow curves, were overlapped (Figure 2.A and B).

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Instrumental screening regarding the preformulation of prednisone in binary systems

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Keywords: prednisone, preformulation, compatibility

Prednisone is a prodrug-type active pharmaceutical ingredient belonging to the class of corticosteroids which is mainly used in the treatment of immune system disorders. It acts by decreasing the immune system's response to various factors and by reducing symptoms like swelling and allergic reactions, being also used in the treatment of skin diseases, arthritis, blood disorders as well as cancer [1–3]. The structural formula of prednisone (abbreviated PSONE) is shown in Figure 1.

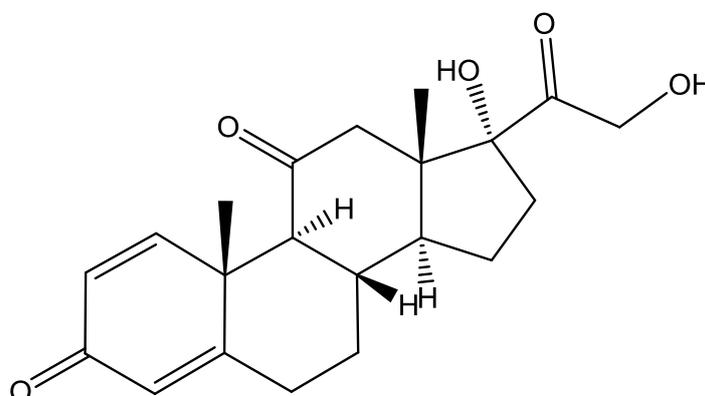


Figure 1. Structural formula of PSONE

In this study, we set our goal in extending a previous analysis that was performed by our research group regarding the solid-state compatibility study between prednisone and pharmaceutical excipients in dynamic inert atmosphere [3], by employing several instrumental techniques, such as thermal analysis in dynamic air atmosphere (Figure 2), UATR-FTIR spectroscopy and PXRD.

PSONE was used in binary mixtures along with sodium carboxymethylcellulose, tylose, methylcellulose, talc, magnesium citrate, mannitol, starch, calcium lactate, magnesium stearate, fumed silica and polyvinylpyrrolidone K30, while the working protocol for the evaluation of the compatibility is in agreement with our previous published studies [4–6].

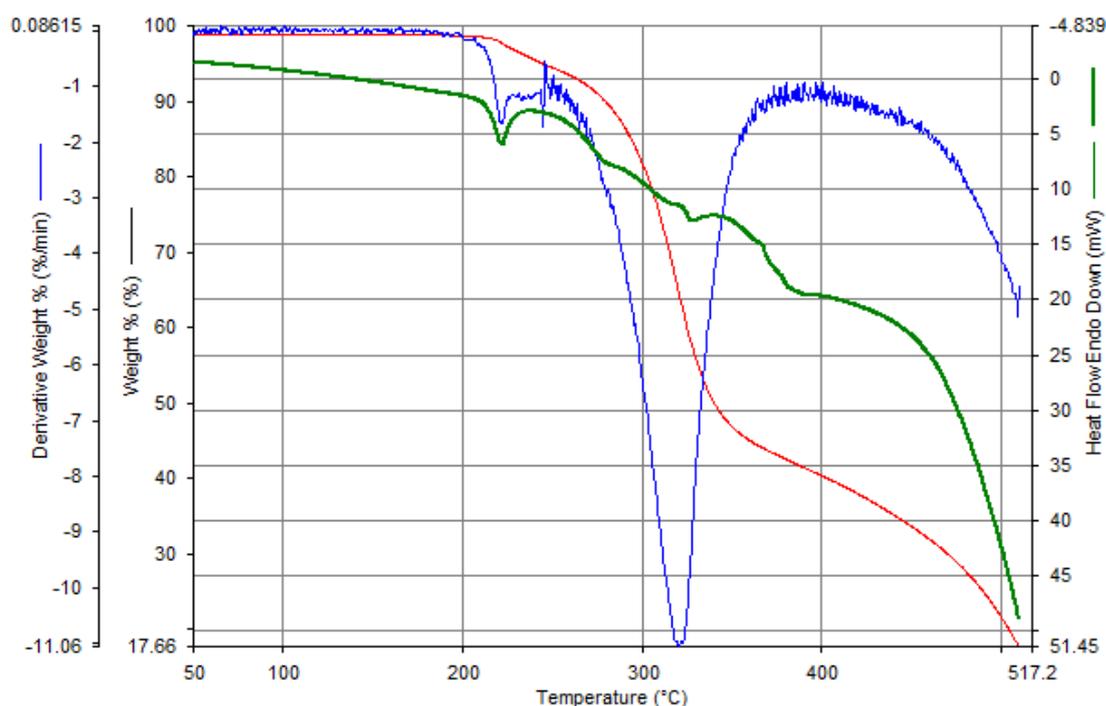


Figure 2. Thermoanalytical data (TG/DTG/HF) recorded for the binary mixture 1:1 m/m PSONE+methylcellulose in dynamic air atmosphere at $\beta = 10 \text{ }^{\circ}\text{C min}^{-1}$

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Thermal stability of antihypertensive drug moxonidine – an isoconversional kinetic study

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Keywords: moxonidine, solid-state stability, kinetic study

Moxonidine (abbreviated MOX, IUPAC name 4-chloro-N-(4,5-dihydro-1H-imidazol-2-yl)-6-methoxy-2-methyl-5-pyrimidinamine) is a new-generation active pharmaceutical ingredient used in the treatment of mild to moderate essential hypertension, administered *per os* [1, 2]. The chemical structure of MOX is presented in Figure 1.

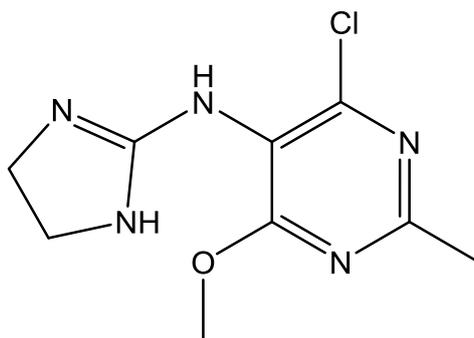


Figure 1. Chemical structure of MOX

MOX (mostly formulated as commercial drugs Physiotens®, Moxon® and Cynt®) reduces blood pressure similarly to the majority of first-line antihypertensive agents. It is used both in monotherapy and in combination with other active pharmaceutical ingredients. On the other hand, MOX is a reliable option mainly as a therapeutic alternative for patients with metabolic syndrome [2, 3].

This study presents the analysis of thermal stability of the antihypertensive drug moxonidine during thermal stress in oxidative atmosphere, study performed using five heating rates $\beta = 5, 7, 10, 12$ and $15 \text{ }^\circ\text{C min}^{-1}$. The obtained experimental data were processed using the isoconversional methods of Kissinger–Akahira–Sunose, Flynn–Wall–Ozawa, Friedman and the decomposition mechanism was evaluated using the modified NPK method [4, 5].

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Structural and thermal characterization of polymorphic system metilethanolammonium 2-chloro-4-nitrobenzoate

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Keywords: polymorph, crystal structure, thermal analysis, kinetic study

2-Chloro-4-nitrobenzoic acid (2Cl4NB) is an active pharmaceutical ingredient used as potential antiviral agent in the treatment of immunodeficiency diseases and the human immunodeficiency virus (HIV) infection [1, 2]. Our previous works [3, 4] provided several examples of multicomponent crystal forms of cloronitrobenzoic acid-alkanolamine systems, revealing the key role of components and solvent selection. This study discusses the interrelationship between crystal structures, thermal stability and thermal decomposition kinetics for two polymorphs (α and β) of metilethanolammonium 2-chloro-4-nitrobenzoate (HMMEA)(2Cl4NB), obtained in one-step synthesis under ambient conditions, using 2Cl4NB purchased from two different commercial companies.

Structural similarity and dissimilarity in polymorphic pair are revealed by infrared spectroscopy and single-crystal X-ray diffraction. The polymorph α crystallizes in triclinic $P-1$ (No2) centrosymmetric space group and consists of one cation and one anion, while the polymorph β crystallizes in orthorhombic $Pna2_1$ (No33) non-centrosymmetric space group and contains two crystallographically independent cations and anions in the asymmetric unit. In both polymorphic structures, components are held together in hydrogen-bonded supramolecular chains (Figure 1), obtained from $R^2_2(9)$ and $R^4_4(13)$ heterosynthons. The Hirshfeld surface analysis and 2D fingerprint plots show that the major contribution in crystals is made by O \cdots H/H \cdots O contacts (41.3 and 46.3%, respectively), followed by H \cdots H interactions (25.3 and 23.9%, respectively).

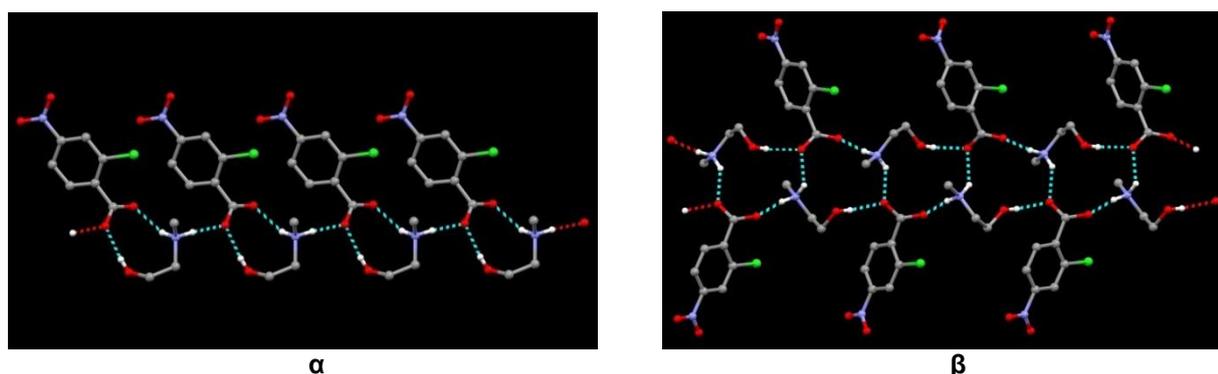


Figure 1. Fragments of hydrogen-bonded supramolecular chains in polymorphs pair

The thermal behavior of two crystalline forms was studied by TG/DTG/DSC analyses (Figure 2). Particular attention was focused on the thermodynamic stability relationship of polymorphic pair. DSC experiments clearly show that α is the thermodynamically stable polymorph, having the melting point (105.8 °C) higher than β (79.7 °C).

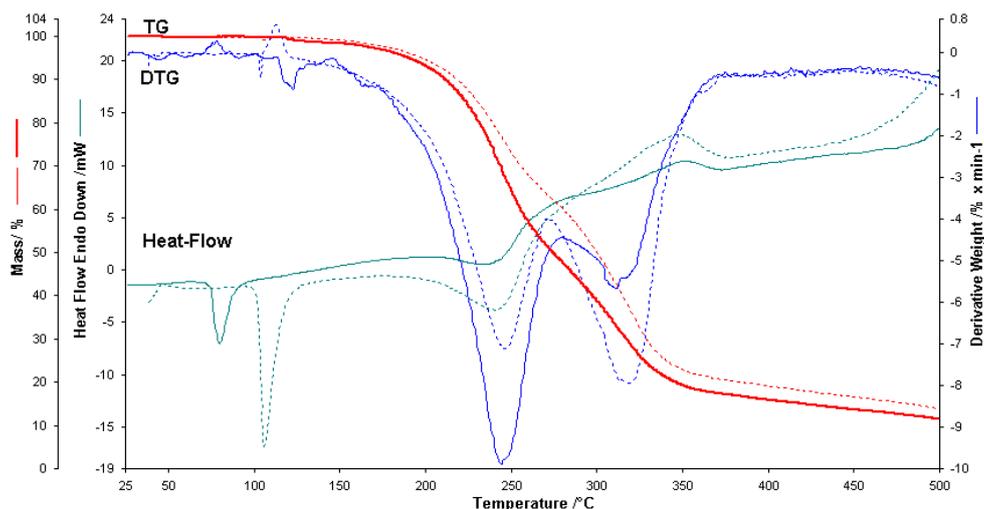


Figure 2. Thermoanalytical curves of polymorph α (dotted line) and β (solid line) obtained in air atmosphere with $10\text{ }^{\circ}\text{C min}^{-1}$, in temperature range 25–500 $^{\circ}\text{C}$.

The thermal decomposition kinetics of the polymorphs were studied by four kinetic methods: Kissinger-Akahira-Sunose and Flynn-Wall-Ozawa (isoconversional integral methods), Friedman (isoconversional differential methods) and the non-parametric kinetic method (NPK).

Acknowledgements

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Substituent effect on crystal structure and thermal stability of iminophosphoranes

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Keywords: iminophosphorane, crystal structure, thermal analysis, kinetic study

Two new iminophosphoranes ($R_3P=NR'$) have been successfully obtained by Staudinger reaction of diphenylphosphorylazide with different substituted phosphines. The nature of substituent is one of the main factors that affect the thermal stability. In this study, we present the synthesis, structural characterization and thermal behavior of crystalline iminophosphoranes **2** and **3** containing the substituents anisole, as well as phenyl (Ph) and *p*-tolyl (*p*Tol), respectively (Table 1). The thermal and kinetic studies for the new compounds were compared with recently published compound **1** which has three *p*Tol substituents [1]. The thermal behavior of compounds was investigated by TG/DTG/DSC analyses under air atmosphere (Figure 1). The highest stability is observed for compound **3** (melting point 158.5 °C) with two Ph and one *p*Tol groups.

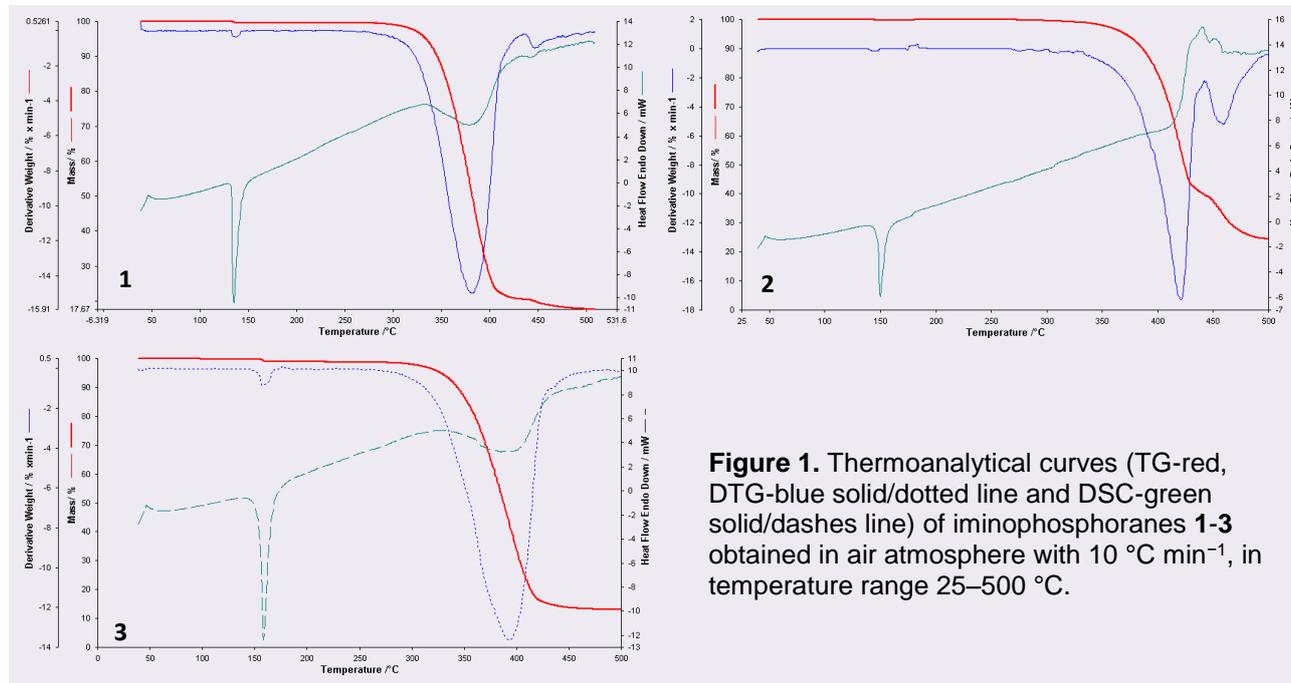
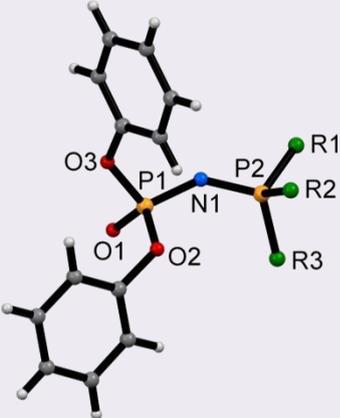


Figure 1. Thermoanalytical curves (TG-red, DTG-blue solid/dotted line and DSC-green solid/dashes line) of iminophosphoranes **1-3** obtained in air atmosphere with 10 °C min⁻¹, in temperature range 25–500 °C.

Four kinetic methods such as Friedman (FR), Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and modified nonparametric kinetic method (NPK) were used to determine the apparent activation energy (E_a) and other kinetic parameters of the thermal decomposition process. In order to establish the impact of different substituents on intermolecular interactions and on the crystal packing, the iminophosphoranes were characterized by single-crystal X-ray crystallography. The compounds **1** and **3** crystallize in orthorhombic space groups, while **2** in monoclinic space groups (Table 1).

Table 1. General representation of compounds **1-3** with their selected structural parameters

General representation	Substituents	Compound	Space group and unit cell parameters
	R1=R2=R3= <i>p</i> Tol 	1	<i>Pbca</i> $a=11.131(8)$, $b=19.182(15)$, $c=27.57(2)$ Å
	R1=R2=R3=anisole 	2	<i>I2/c</i> $a=19.8082(13)$, $b=9.8060(6)$, $c=32.915(3)$ Å $\beta=107.073(8)^\circ$
	R1=R2=Ph R3= <i>p</i> Tol  	3	<i>P2₁2₁2₁</i> $a=11.1954(7)$, $b=13.1346(6)$, $c=18.1011(12)$ Å

The study revealed that the nature of the substituents dictates the stability of iminophosphoranes, **1** < **2** < **3**, which means that substitution with three *p*Tol groups provides low stability compared to three anisole groups or combination of Ph and *p*Tol substituents. All three compounds are of interest as important reagents in synthetic organic chemistry and have been obtained as part of our research project focused on the development of new biological and pharmacological active iminophosphoranes derivatives.

Acknowledgements

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Solid-state stability of valsartan – an isoconversional kinetic study for drug and pharmaceutical formulation

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Keywords: valsartan, pharmaceutical formulation, isoconversional kinetic, degradation study

Valsartan (abbreviated VAL, chemical structure presented in Figure 1) is an antihypertensive drug which selectively inhibits the angiotensin receptor type II. It is mainly incorporated in solid dosage forms as film-coated tablets [1]. Regarding this drug's characterization, up to date, a monography has been published that presents data like thermal stability, spectroscopic characteristics (such as UV, IR, MS, and NMR data), solid-state organization and polymorphism [2].

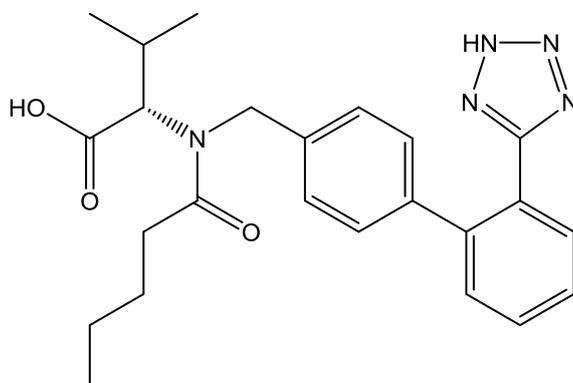


Figure 1. Chemical structure of VAL

VAL is used in the treatment of high blood pressure, heart failure and diabetic kidney disease [1, 3], formulated as such (single active ingredient) or in combination with hydrochlorothiazide [4], amlodipine [5] or more recently, sacubitril [6].

So far, thermal analysis in dynamic inert atmosphere [7] and compatibility studies with several pharmaceutical excipients [8] were reported for VAL. More recently, the kinetics of degradation in water matrices by heat and heat/ultrasound activated persulfate has also been presented [9]. According to our knowledge, no in-depth kinetic study was carried out presenting the comparative stability analysis of pure VAL vs. VAL incorporated in a solid dosage form (API content of 160 mg), this being the goal set for the present paper. Consequently, samples of VAL pure drug and VAL pharmaceutical formulation were subjected to thermal stress in controlled conditions at five heating rates $\beta = 5, 7, 10, 12$ and $15 \text{ }^\circ\text{C min}^{-1}$, and the resulted data were processed using the isoconversional methods of Kissinger–Akahira–Sunose, Flynn-Wall-Ozawa, Friedman and modified NPK method [10, 11].

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Preformulation studies for aripiprazole and risperidone – an instrumental approach

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Keywords: aripiprazole, risperidone, preformulation study, compatibility with excipients

Aripiprazole (abbreviated ARP, structural formula presented in Figure 1a) is an atypical antipsychotic active pharmaceutical ingredient (API) used for the treatment of schizophrenia and mania in type I bipolar disorder [1, 2]. Risperidone (abbreviated RSP, structural formula presented in Figure 1b) is also an atypical antipsychotic API, used in the treatment of schizophrenia, behavioral and psychological symptoms of dementia and irritability associated with autism [3].

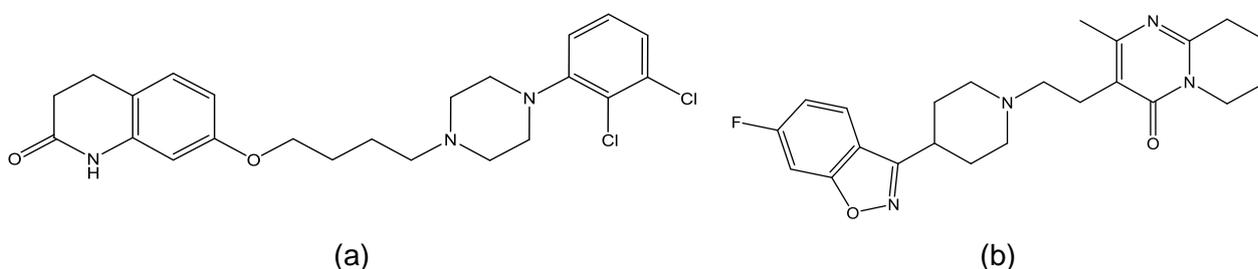


Figure 1. Structural formulas of active pharmaceutical ingredients: (a) ARP; and (b) RSP.

This study deals with the preformulation of ARP and RSP in binary mixtures prepared with different pharmaceutical excipients currently used in the development of solid dosage forms. Binary mixtures were obtained by triturating each pure drug with each excipient, in a mass ratio of 1:1. All the samples were investigated employing thermal analysis in dynamic air atmosphere at a heating rate $\beta = 10 \text{ }^\circ\text{C min}^{-1}$ in open aluminum crucibles. The thermal protocol was set to take place from ambient temperature up to $500 \text{ }^\circ\text{C}$ (Figure 2 presents the thermoanalytical data TG/DTG/HF recorded for ARP and RSP, respectively, in the mentioned conditions), and the results were corroborated with the compatibility evaluation performed using UATR-FTIR spectroscopy for the samples stored in sealed vials at $25 \text{ }^\circ\text{C}$ [4, 5].

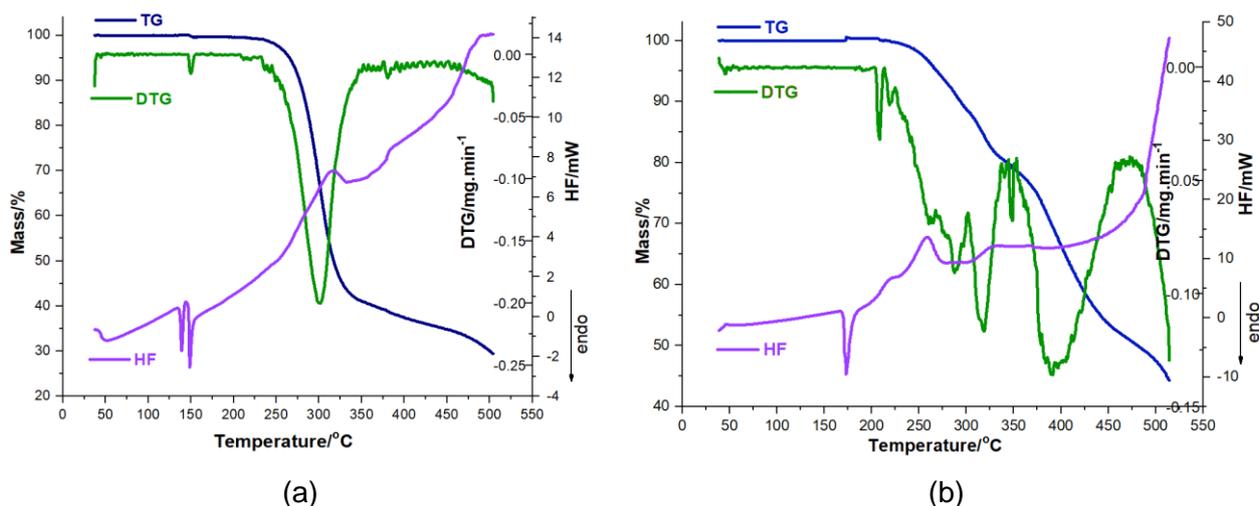


Figure 2. Thermoanalytical data (TG/DTG/HF) recorded for (a) ARP; and (b) RSP in dynamic air atmosphere at $\beta = 10 \text{ }^\circ\text{C min}^{-1}$

A discussion for the compatibility/incompatibility of these two atypical antipsychotic agents was carried out and the results can be used in the development of new generic solid dosage forms.

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Preliminary study for preparation of buccal patch with lidocaine and acyclovir

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Keywords: Lidocaine, Acyclovir. Buccal patch, Thermal Analysis, Drug delivery

The aim of the present study was to prepare and evaluate patches for the controlled release of lidocaine/acyclovir and of binary mixture between lidocaine: acyclovir in the oral cavity. For the current study, we consider important to study the interactions between, lidocaine and acyclovir and also between each material used in patches formulation.

Lidocaine (2-(diethylamino)-N-(2,6-dimethyl phenyl)-ace amide) (Lid) is used generally in many clinical applications and at the same time is the most used local anesthetic with an intermediate duration of action [1, 2] and class Ib antiarrhythmic agent. [3]

Acyclovir (Acv) or 9-[(2-hydroxyethoxy) methyl] guanine is an acyclic nucleoside analog, it is being used in the treatment of infections as herpes simplex virus[4], cutaneous herpes, genital herpes, varicella, zoster infections, etc. [5, 6].

Mucoadhesive buccal patches, containing 12.5 mg/cm² lidocaine/acyclovir or binary mixture base, were formulated and developed by solvent casting method technique, using sodium alginate, polyvinylpyrrolidone, glycerol, polyvinyl alcohol and Span 80;

Thermal induces interaction for all materials used in this study for patch preparation was studied using a TG/DTG/HF and FTIR analysis (see Figure 1 and 2 for obtained medicated patches, where AS: membrane with alginate 1% and Span 80, AS-Acv.: membrane with alginate 1%, Span 80 and Acv.; AS-Lid.: membrane with alginate 1%, Span 80 and Lid.; AS-Lid.-Acv.: membrane with alginate 1%, Span 80, Acv. and Lid.).

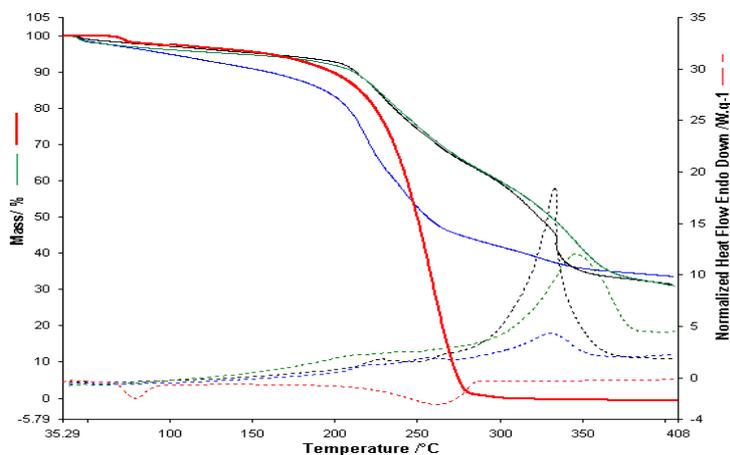


Figure 1. TG/ HF curves for Lidocaine (Lid), AS, AS-Lid, AS-Lid-Av.

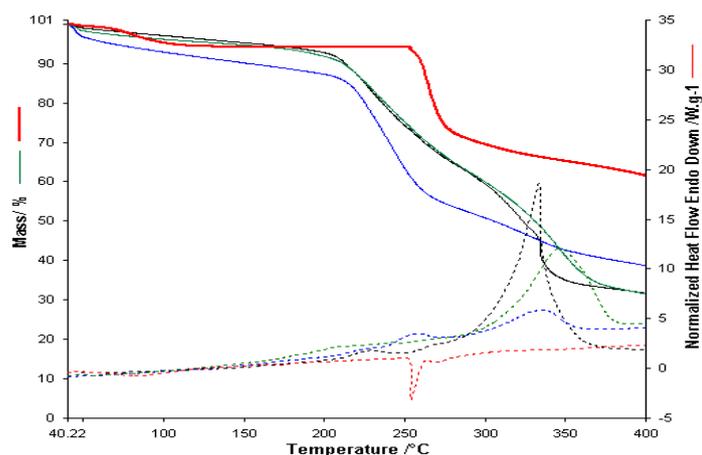


Figure 2. TG/ HF curves for Acyclovir (Acv), AS, AS-Acv, AS-Lid-Acv.

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Preliminary study for mediated jelly based on Ambroxol or Ibuprofen

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Keywords: Ibuprofen, Ambroxol, Medicated jelly, Thermal Analysis, Drug delivery

The aim of this study is to provide information regarding biocompatibility between various materials used in medicated jelly preparation (gelatin, pectin, alginate), ambroxol and ibuprofen. Last decades provide on the market many types of medicated jelly, those using different active substances like diflunisal, fenopfen, etc[1].

Ambroxol (Trans-4- [(2-amino-3, 5-dibromobenzyl) amino] -cyclohexanolis) is recognized as a metabolite of bromhexine and present similar actions and uses [2]. Ambroxol has been used for this purpose since 1987, the mechanism of actions is not really understood but it is known that the mechanism involves stimulation of surfactant synthesis [3].

Ibuprofen is recognized as a nonsteroidal anti-inflammatory drug and can be used in administration for different kind of problems (relieve pain, fever), this can be administrated to children older than three months. Ibuprofen is a non-selective balanced inhibitor of both the constitutive COX-1 and the inducible COX-2 enzymes [4].

Thermal induces interaction for all materials used in this study for preparation of medicated jelly with ibuprofen or ambroxol was studied using a TG/DTG/HF and FTIR analysis (see Figure 1 and 2 for obtained medicated jelly).

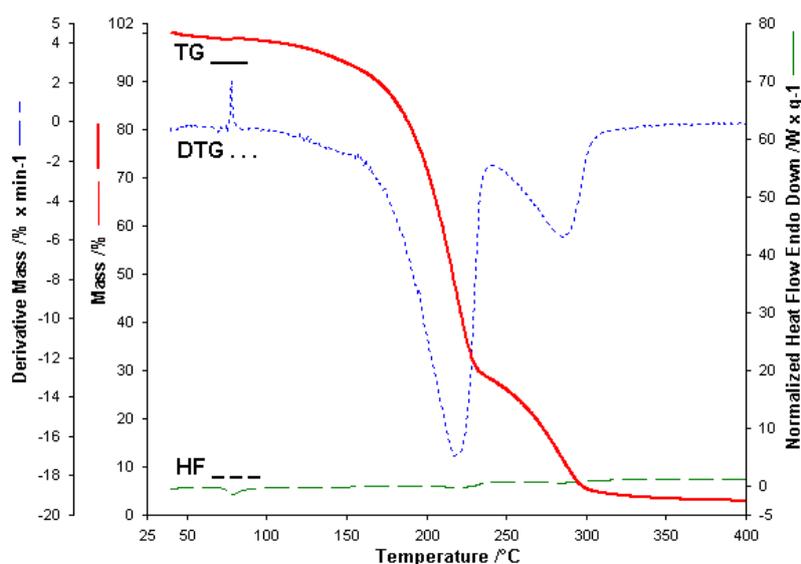


Figure 1. TG/DTG/HF curves for obtained medicated jelly with ibuprofen based on pectine.

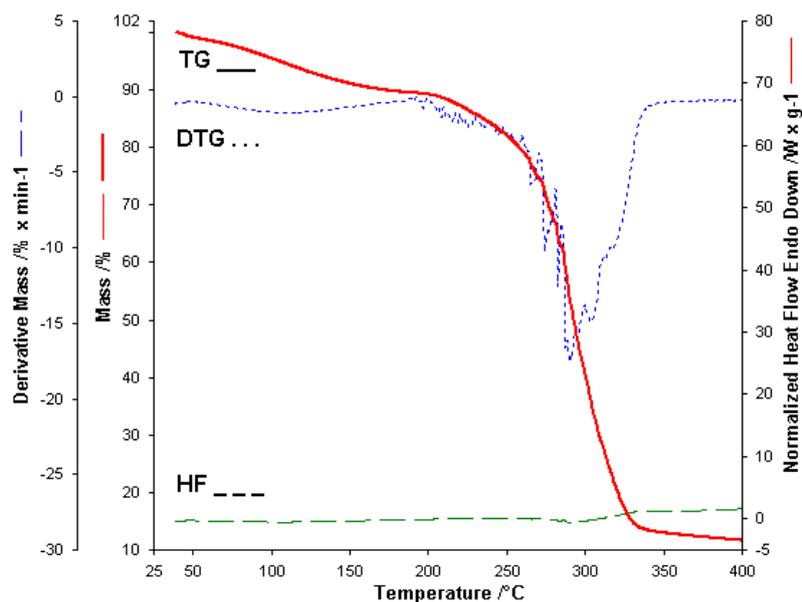


Figure 2. TG/DTG/HF curves obtained for medicated jelly with ambroxol based on pectine.

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A safety and efficacy Itraconazole loaded Diatomite encapsulation for drug delivery system.

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Keywords: Itraconazole, Drug delivery, Diatomite, Encapsulation process.

Drugs that are poorly soluble in water present a big problem of dissolution in the gastrointestinal tract and therefore their bioavailability is low. Since many years several techniques that lead to an increase of drug solubility characteristics have been discovered. So, formulating compounds for oral administration remain the most common challenge for scientists in the pharmaceutical industry. Itraconazole (ITZ) is a potent triazole antifungal drug which has low solubility at physiological pH conditions [1]. It has been used as a model compound for poorly soluble drugs because of its hydrophobic structure. It is also known as one of the best typical azole wide-spectrum antifungal agent, with fairly low side effects [2]. According to the US Food and Drug Administration Diatomite (DTM) which is a mineral natural compound of silica hydrates is generally recognized to be safe as oral delivery ingredient [3]. This prospective study aimed to encapsulate ITZ into DTM. Three binary systems were prepared using different proportions of the two components and the ability of DTM to improve the solubility of ITZ in aqueous and organic medium was tested. The effectiveness of encapsulation has been demonstrated by standard methods such as extraction and UV analysis. FTIR, MEB, AFM and optical microscopy were then used to investigate the morphology and the interaction between ITZ and DTM. Moreover, dissolution kinetics studies and mechanism of drug release in simulated gastric medium (pH=1.2) showed an improved dissolution compared with the commercial form of SPORANOX. In addition, a prolonged release profile of the different formulations was obtained for a period of two hours.

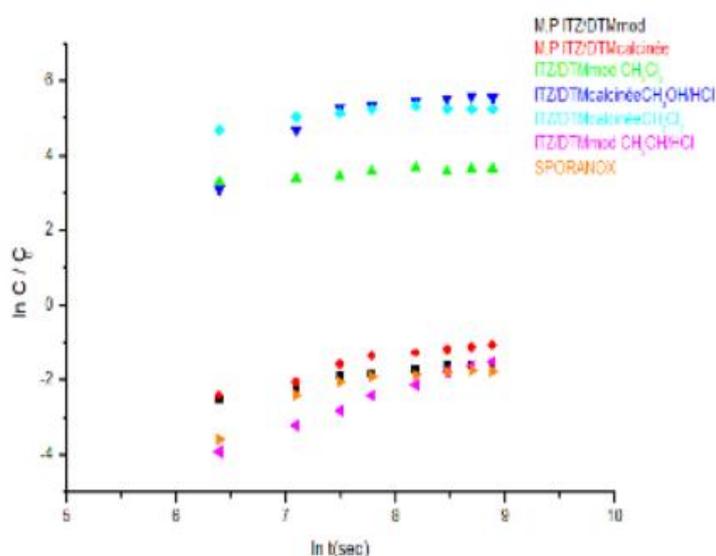


Figure 1. Comparative ITZ release study between the prepared systems and the commercial form SPORANOX

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Improved biological performance of ketoprofen using β -cyclodextrin multi-decorated diatomaceous earth as a novel drug delivery system

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Keywords: diatomaceous earth, β -cyclodextrin, ketoprofen, *in vivo* studies

Inexpensive and naturally available diatomaceous earth (DE) microparticles are good candidates for drug delivery because of their excellent features such as biocompatibility, non-toxicity, porosity, high surface area and ease of surface modification. On the other hand, they have some limitations such as poor drug loading capacity and a very high initial burst release [1]. In the present work, we describe the synthesis of a novel bio-composite obtained by polymerization of β -cyclodextrin using citric acid crosslinker on the surface of DE (DE-CD) as new drug carrier for tune drug loading and its release.

To validate this novel bio-composite as drug carrier, ketoprofen (KET), a non-steroidal anti-inflammatory agent, was used as drug model. KET is well-known to have a low solubility (0.05 mg mL⁻¹ at 25 °C in water) and a short half-life (1-4 h) which may cause its low bioavailability [2]. By embedding KET in this novel bio-composite, its bioavailability could be then optimized.

DE, CD, DE-CD and their corresponding formulations were characterized in detail by chemical analysis, powder X-ray diffraction (PXRD), thermal analysis (TGA-DTG), vibrational spectroscopy (FT-IR), scanning electron microscopy (SEM), particle size and zeta potential measurements. The release of the drug from the diverse formulations was also investigated by means of UV-VIS spectroscopy. In order to assess this novel bio-composite as drug carrier, hemolytic, anti-inflammatory and anti-nociceptive activities were performed [3,4]. And finally, the ulcerogenic activity and histopathological effects of all formulations were compared to that of pure KET. The results of this study suggest that this novel bio-composite can be considered as a promising tool for future pharmaceutical formulations.

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Investigation of thermal and thermophysical properties of ezetimibe

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Keywords: ezetimibe, thermal analysis, polymorphism

Ezetimibe ($C_{24}H_{21}F_2NO_3$, $M = 409.422$ g/mol, CAS No. 163222-33-1, systematic name: 1-(4-fluorophenyl)-(3*R*)-[3-(4-fluorophenyl)-(3*S*)-hydroxypropyl]-(4*S*)-(4-hydroxyphenyl)-2-azetidinone) is a lipid lowering agent that selectively inhibits the intestinal absorption of cholesterol (Fig. 1). This compound used in the treatment and/or prevention of atherosclerosis was first described in 1995 as an active pharmaceutical ingredient. Ezetimibe is a highly lipophilic molecule. Due to its high hydrophobic character, it exhibits very low bioavailability (35–65%). Ezetimibe is a weak acid having poor aqueous solubility characteristics but shows good intestinal permeability [1, 2].

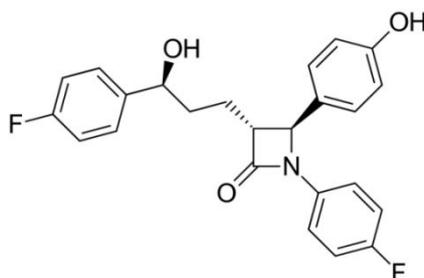


Figure 1. Molecular structure of ezetimibe $C_{24}H_{21}F_2NO_3$

Polymorphism may be defined as the ability of a compound to crystallize in two or more crystalline phases with different arrangements and/or conformations of the molecules in the crystal lattice. A single molecule, like ezetimibe, may give rise to a variety of crystalline forms having distinct crystal structures and physical properties. Thermal methods, and in particular differential scanning calorimetry (DSC), have been one of the mainstay methods for the study of polymorphs, providing a means of both identification and characterization [3].

In light of the above, the aim of this work was to study the thermal properties ezetimibe (three samples were supplied by various pharmaceutical companies from India and China). The thermal stability of ezetimibe was investigated by thermogravimetric (TG) analysis in the temperature interval 25–350 °C (Fig. 2). The thermophysical properties of ezetimibe were studied by differential scanning calorimetry (DSC) in the temperature range 25–200 °C (Fig. 3). As a result, the polymorphic transition of ezetimibe (form A \rightleftharpoons form B) was revealed. The anhydrous form A of ezetimibe was found to be more stable at a room temperature and to retain its crystallinity upon heating, even at high temperatures (up to 160 °C). This thermal behaviour of ezetimibe is in good agreement with the literature [4].

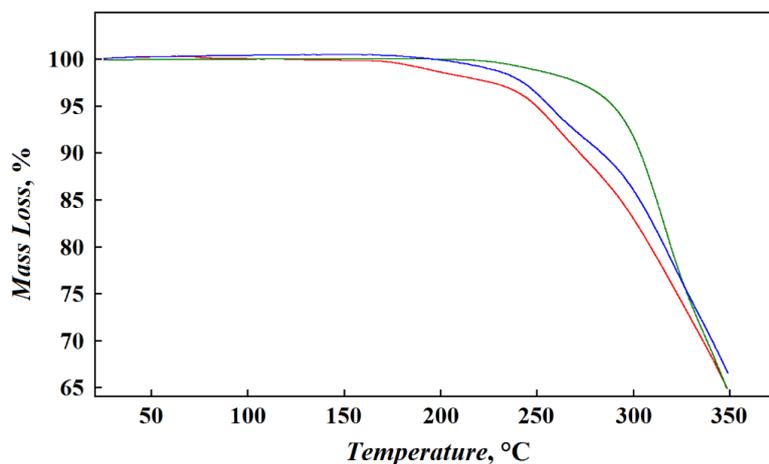


Figure 2. TG curves of ezetimibe

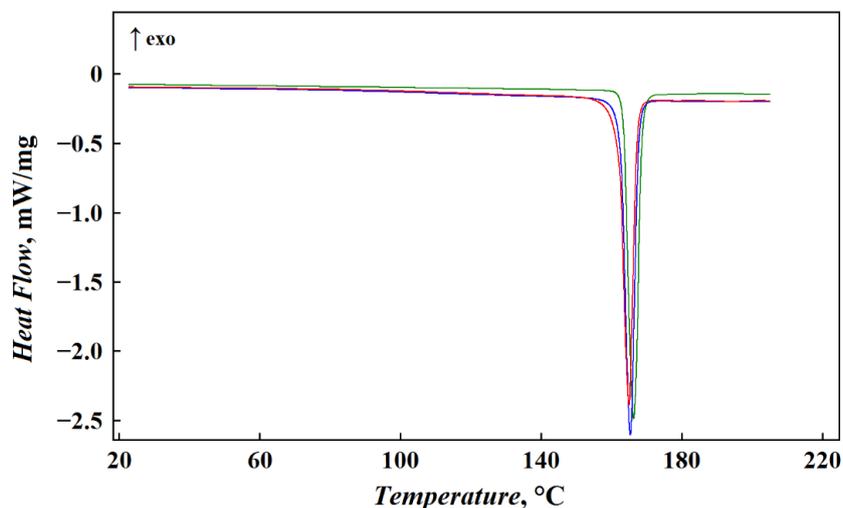


Figure 3. DSC curves of ezetimibe

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Calorimetric study of carbosilane core/phenylene shell hybrid dendrimer of the first generation

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Keywords: dendrimers, heat capacity, glass transition, thermodynamic functions

Dendrimers are nanoscaled well-defined globular macromolecules with a low polydispersity (in comparison with traditional polymers) and a highly branched three-dimensional architecture constituted of three main structural elements: a core (a multifunctional atomic group), an inner sphere (tree-like branches emanating from the core, consisted of the repeating units), and an outer layer (many terminal functional groups, increased exponentially as a function of generation and located on the macromolecule surface, which play a key role in the properties of dendrimers). In light of their unique molecular architecture, dendrimers have attracted increasing attention in the past few years. Due to the versatile physical and chemical properties of dendrimers, arising from the structural features, they are potential candidates for biomedical fields, nanoengineering, electronics, and catalysis [1-3].

Among the numerous dendritic macromolecules, carbosilane (Si–C) and siloxane (Si–O) dendrimers have emerged as one of the most important and promising classes of silicon-containing dendrimers [4, 5]. At the same time, hybrid dendrimers combining two chemically different dendritic segments with a perfectly branched molecular structure are quite rare. There was found that thermal behaviour of hybrid dendrimers was dramatically different from that of entirely rigid phenylene dendrimers or flexible carbosilane dendrimers. The presence of rigid phenylene blocks as a periphery layer in carbosilane dendrimers leads to a significant increase in the glass transition temperature, indicating increased rigidity of the whole macromolecule [6].

As a continuation of our previous calorimetric investigations of carbosilane and siloxane dendrimers, the aim of this work was to study the thermodynamic properties of carbosilane core/phenylene shell hybrid dendrimer of the first generation G1Si₁₃Ar₃₂ (Figure). This included the following tasks:

- the evaluation of thermal stability of hybrid dendrimer by thermogravimetric (TG) analysis;
- the determination of the molar heat capacity of dendrimer by methods of precise adiabatic calorimetry in the range of $T = (6–350)$ K and differential scanning calorimetry (DSC) in the interval of $T = (350–600)$ K;
- the detection of possible physical transformations of dendrimer, and the evaluation of its thermodynamic characteristics;
- the calculation of the standard thermodynamic functions of dendrimer for the range from $T \rightarrow 0$ to 600 K, as well as the standard entropy of its formation at $T = 298.15$ K;
- the comparative analysis of thermodynamic properties of the investigated hybrid dendrimer with those of the studied carbosilane and siloxane dendrimers.

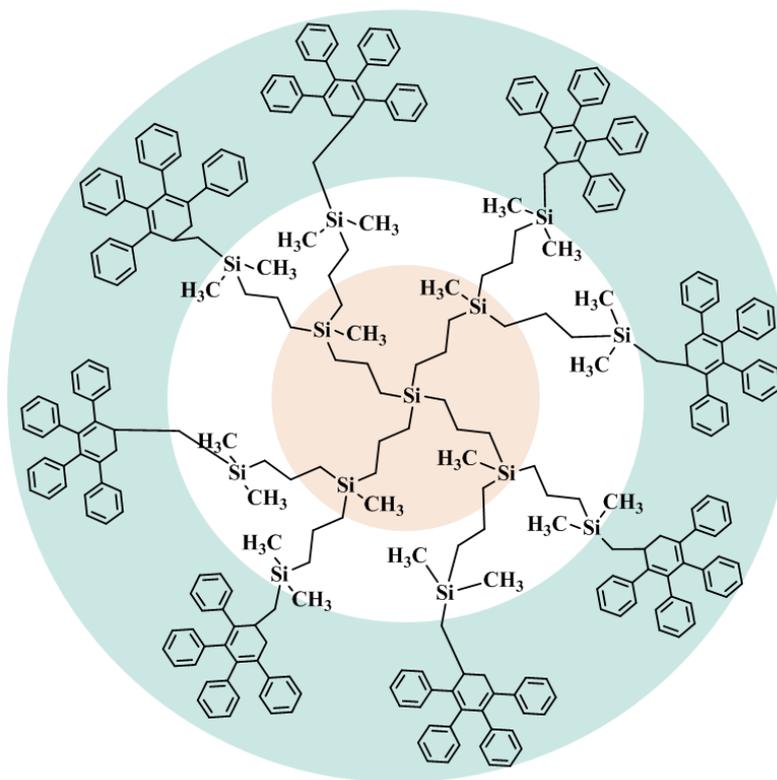


Figure 1. Molecular structure of carbosilane core/phenylene shell hybrid dendrimer of the first generation $G1Si_{13}Ar_{32}$ (brutto formula $C_{304}H_{332}Si_{13}$)

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Preliminary study for the preparation of the antibiotic medicated vehicle with stomatological applicability

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Keywords: Gelatin sponge, Clarithromycin, Oxacillin, Ampicillin, Thermal Analysis, Drug delivery

The aim of the present study was to obtain a medicated vehicle for delivering the most used antibiotics in stomatology. This vehicle is designed to deliver the active ingredient directly at the site of action, thereby improving the healing process of patients with various associated diseases.

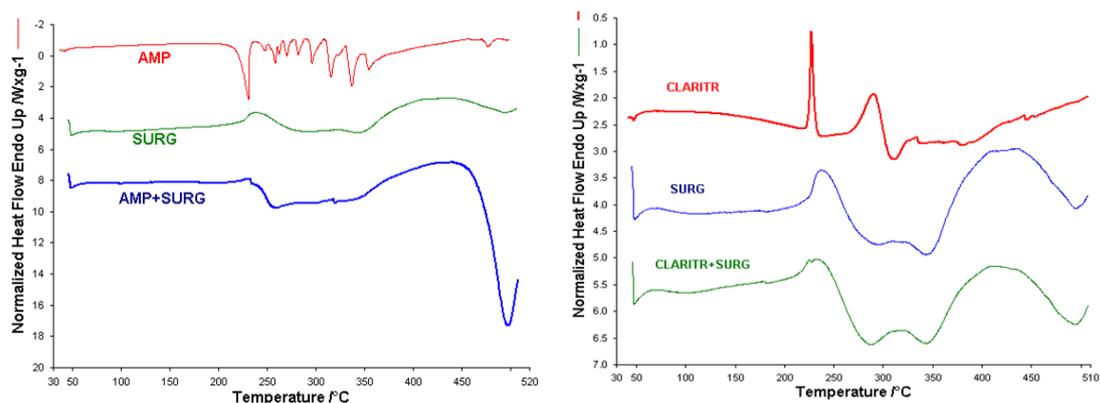
In order to observe the usability of the Gelatin sponge material following criteria was applied: antibiotics should have different dental application and should have also different molar masses. Materials considered for this study were Gelatin Sponge (Surgispon) and antibiotics: Ampicillin sodium salt ($C_{16}H_{18}N_3NaO_4S$), Oxacillin ($C_{19}H_{19}N_3O_5S$) and Clarithromycin ($C_{38}H_{69}NO_{13}$). Medicated vehicle was obtained by impregnation with active substances.

Absorbable gelatin sponge is recognized between dentists as a fast-hemostatic agent that performs effective hemostasis, it is used usually after dental extraction due to the fact that is a non-toxic, non-allergenic, non-immunogenic and non-pyrogenic.

Ampicillin and Oxacillin are the most used penicillin in dental industry. Those are used for the inhibition of the wall bacteria cell synthesis [1]. Penicillin antibiotics are prescribed for infections caused by penicillinase-producing Staphylococcus spp. or those involving gram-negative bacteria [2].

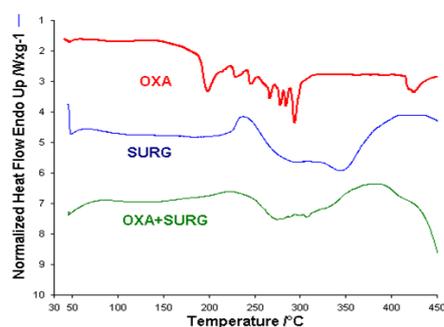
Clarithromycin is a macrolide with a large spectrum [3, 4], present favorable tissue distribution and a low incidence of adverse side effects. Its mechanism of action takes place by binding to the 23S ribosomal RNA in the 50S subunit of the bacterial ribosome, inhibiting in this way protein synthesis[5]. Clarithromycin is usually administrated to the patients with allergy at antibiotics form ampicillin class.

Thermal induces interaction for all materials used in this study for patch preparation was studied using a TG/DTG/HF and FTIR analysis.



A. HF curves for Ampicillin, surgispon and medicated vehicle

B. HF curves for Clarithromycin, surgispon and medicated vehicle



C. HF curves for Oxacillin, surgispon and medicated vehicle

Figure 1. HF curves for antibiotics, surgispon and medicated vehicles.

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Thermal stability of antihypertensive drugs from sartans class

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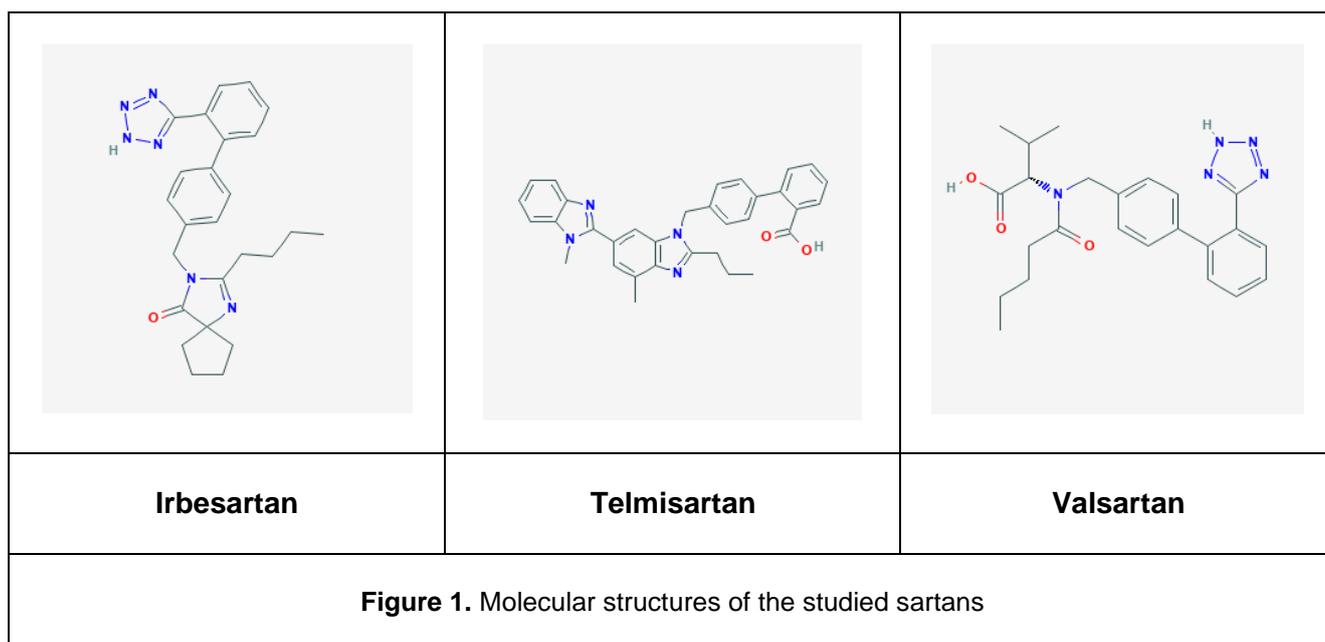
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Keywords: Sartans, Thermal Analysis, Drug delivery, Hypertension

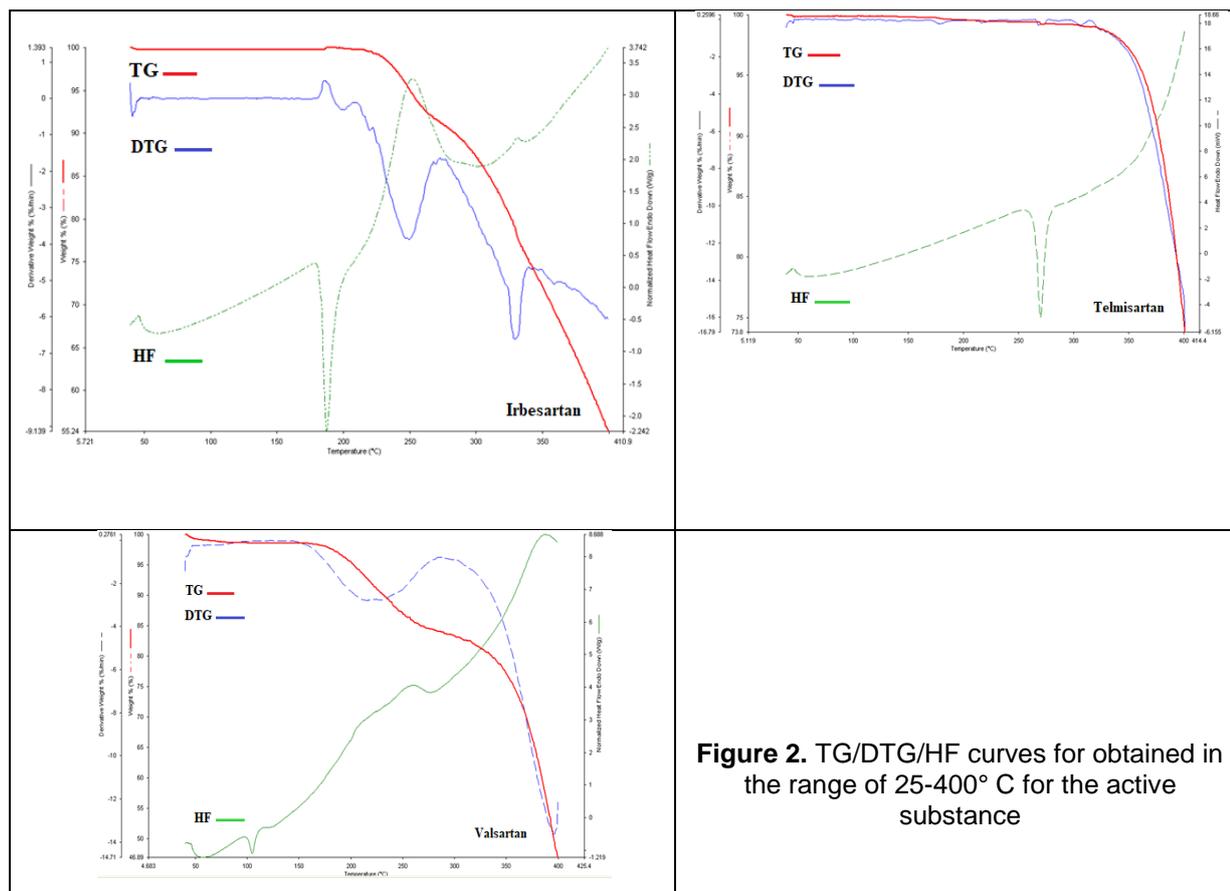
The purpose of this study is to compare the thermal stability of the studied active substances (Irbesartan, Valsartan and Telmisartan) according to their molecular structure, in order to synthesize new materials that will be used for the controlled release of the active principles.

Sartans (Figure 1) (angiotensin receptor blockers - ARBs) are a group of antihypertensive drugs that functions by blocking the effects of the hormone angiotensin II (Ang II) in the body, thus lowering the blood pressure. [1] [2] These are a class of compounds derived from 2- (1-benzyl-1H-imidazol-5-yl) acetic acid, though the class firstly consisted of an imidazole core, which was substituted differently at certain positions of the heterocyclic nucleus. [3]



In order to compare the stability of the analyzed substances, all compounds were analyzed at temperatures in a range from 25 up to 400°C, with a heating rate of 10°C/min in a synthetic air atmosphere environment. All samples were analyzed on a Perkin-Elmer Diamond thermo-balance in open aluminum crucibles.

According to a thermogravimetric study (Figure 2), the variation of the stability of the analyzed compounds can be established in the following pattern: Valsartan<Irbesartan<Telmisartan.



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Design and Thermal and Spectroscopic Characterization of novel architecture's POSS nanoparticles

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Keywords: Polyhedral Oligomeric Silsesquioxanes, Thermal properties, Thermogravimetric Analysis, Nanoparticles

Polyhedral oligomeric silsesquioxanes (POSSs), with Si vertices interconnected by –O– linkages, form three-dimensional nanometer size cage structures with substituents attached to silicon atoms. These substituents may contain reactive groups, such as hydroxyl or isocyanate. A combination of a rigid inorganic nanocore with organic vertex groups makes POSS molecules useful hybrid building blocks that can be chemically incorporated in the polymer matrix by copolymerization, grafting or reactive blending, or physically mixed by solvent casting or polymer processing by using, for example, the extrusion technique [1]. The use of POSSs for making polymer composites has grown exponentially since the last few years of the 20th century. In comparison with the other most commonly used fillers, POSSs possess the advantage of being molecules. Thus, this allows us to combine their nano-sized cage structures, which have dimensions that are similar to those of most polymer segments and produce a particular and exclusive chemical composition. These characteristics linked with their hybrid (inorganic–organic) nature allow researchers to modify POSS according to particular needs or original ideas, before incorporating them into polymers [2].

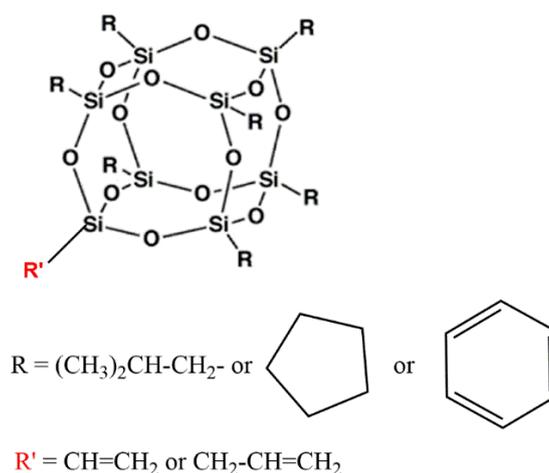


Figure 1. Molecular structure of the prepared and investigated POSSs

In this context, our research group at the University of Catania, in collaboration with eminent researchers in the field, tested the stabilization of different polymers, synthetics or naturals, such as polyethersulfone (PES), ethylene propylene diene monomer (EPDM), polyethylene oxide (PEO), and chitosan by the incorporation of polyhedral oligomeric silsesquioxanes (POSS) molecules [3-6]. Represented in their most common form by the symbol T_8 and having a diameter usually falling in

the range of 1.5–3 nm, POSS molecules comprise a silicon and oxygen cage completed by organic groups that are covalently bonded with silicon atoms. Novel architectures of POSS with various organic groups were synthesized by using corner capping reaction in order to verify their polymerizability in the presence of monomer. In this work, after a spectroscopic investigation aiming at verify that the obtained molecules have the structure for which they were designed, their thermal behavior in terms of resistance to thermal degradation were evaluated by means of thermogravimetric analysis (TGA). The obtained temperatures at 5% mass loss ($T_{5\%}$) were compared with each other and with those of the POSSs previously designed and studied by us.

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Thermal investigation of supramolecular self-healing nanocomposite for structural applications

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Keywords: self-healing nano-composites, structural materials, thermal properties

The interest for the use of composite materials in the production of primary structures is strongly related to the ability of conferring to the polymers important functionalities, such as improved impact damage resistance and high electrical conductivity, allowing to overcome the structural limits of the same composites and extending their use for structural applications. Many studies have been carried out in this direction, obtaining important results, among which those related to the formulation of new nano-charged thermosetting resins with auto-repair functionality based on the supramolecular chemistry [1-2]. For these materials, the self-healing activity is due to the presence, inside the epoxy matrix, of non-covalent interactions able to generate a supramolecular network which can heal the damaged sites [3-6]. Different types of non-covalent interactions such as ionic, π - π stacking or hydrogen-bonding interactions, can be established. In particular, in this work, supramolecular hydrogen-bonding self-healing systems have been analyzed. For these systems, the hosting matrix has been toughened, through the addition of a rubber phase, to increase the chains mobility and to favor the activation of auto-repair mechanisms. Furthermore, in order to simultaneously impart electrical conductivity and auto-repair ability to the material, covalently functionalized Multi-Wall Carbon Nanotubes (MWCNTs) have been embedded in the polymer to transfer to it electrical conductivity and self-healing ability. The chemical groups chosen to functionalize the carbon nanofillers are Barbiturate and Thymine based ligands and are shown in Figure 1A. The generation of the supramolecular network is based on the hydrogen bonds formed between the functional groups of the functionalized carbon nanofillers and those of the hosting matrix (Figure 1B). The epoxy resin has been loaded with two different percentages of functionalized MWCNTs (0.5 and 2% by weight) and the obtained samples have shown good values of healing efficiency and electrical conductivity [2].

The target of this investigation is to evaluate the thermal properties of the formulated self-healing carbon-based nanocomposites, by means of Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) analysis. The formulated materials manifest thermal properties capable to fulfill the requirements of those applicable for structural applications, as they show thermal degradation temperatures higher than 350°C and high values of the Cure Degrees (higher than 90%).

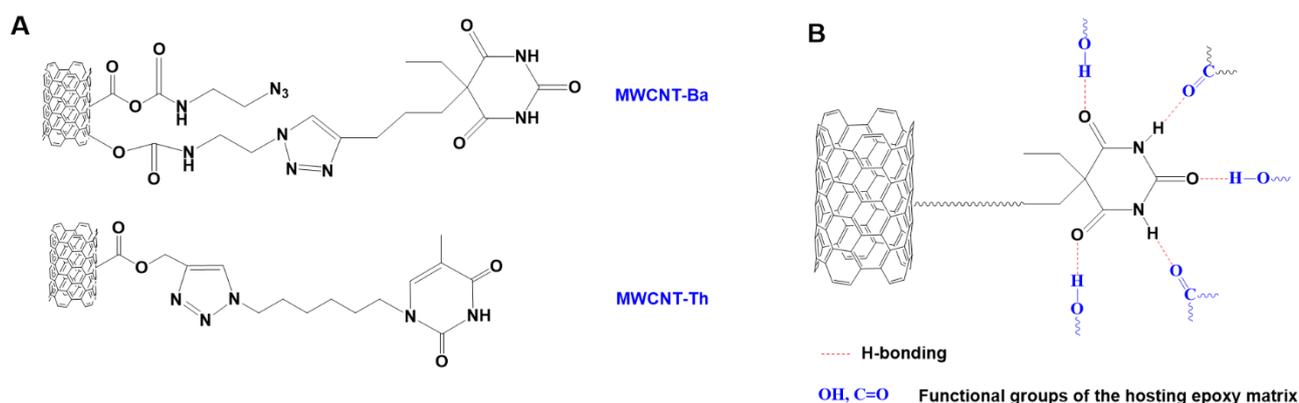


Figure 1. A) Chemical structures of MWCNTs functionalized with Barbiturate (MWCNT-Ba) and with Thymine (MWCNT-Th) based ligands; B) Schematic representation of H-bonding formation between the barbiturate ligand and the functional groups of the cured epoxy matrix

Acknowledgments

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Understanding the relationship between thermal analysis and geopolymer composition containing waste glass

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Keywords: Geopolymer, Waste glass, FTIR, Thermal Analysis

The use of waste glass in geopolymer matrices represents a very important resource for recycling of inorganic materials [1]. The aim of this study is the investigation of the thermal and mechanical modification of the metakaolin-based geopolymer network due to the presence of a different amount of waste glass.

The paste was prepared by mixing two homogenous powders, metakaolin and waste glass. No phase separation was observed since high viscosity was assured by a correct geopolymer formulation. The paste was poured into plastic molds and the setting phase carried out at 50 °C for 1 day, while the hardening phase was carried out at room temperature for 7, 14 and 28 days [2].

The chemical structure of the synthesized materials was investigated by Fourier Transform Infrared (FT-IR) spectroscopy, which showed the formation of bonds between the two components.

We adopted FT-IR spectroscopy to highlight the reticulation degree of the final amorphous solid product, as accurately reported in a previous study [3]. The bands at 3462 and 1640 cm⁻¹ were attributed to the -OH stretching and bending vibrations of water's hydration, respectively [4]. The band at 1640 cm⁻¹ was preserved in waste glass containing geopolymers. Furthermore, in all the spectra the typical signals of the silica matrix are found. The asymmetrical Si-O-Si stretching vibrations were detectable in the spectral region 1080–1050 cm⁻¹. Aluminosilicate's typical signals, assigned to internal vibrations of Si-O-Si and Si-O-Al bonds, are found in the spectra of waste glass based geopolymers, whereas the frequency of the absorption bands seems to be approximately related to the Si/Al ratio in the aluminosilicate framework. In the present case of waste glass powder addition to MK-based geopolymer the peak at 1080 cm⁻¹ shift to lower wavenumber (1008 cm⁻¹), accompanied by an increased contribution of the Si-O-Al bond (950–960 cm⁻¹), indicating the formation of a more efficient 3D geopolymer network. The spectrum of metakaolin also revealed sharp peaks ascribed to the stretching of hydroxyl groups and to Al(VI)-OH bonds in the kaolinite residues [4], whereas the Al(IV) absorption band at around 800 cm⁻¹, characteristic of metakaolin, seems to be not found in the spectra of the corresponding geopolymers. Indeed, a band at around 690 cm⁻¹, whose intensity decreases with the increase of waste glass content, is evident in geopolymers' spectra.

The thermal behavior of the geopolymer samples was studied using a simultaneous Thermogravimetry/Differential Thermal Analysis (TG/DTA). The TG/DTA experiments were carried out from ambient temperature to 1500 K at a heating rate of 10 K/min under both argon and air atmosphere at 50 ml/min. The thermal characterization of the three mixtures (GPMK1, GPMK2 and GPMK3, respectively with 30, 40 and 50wt% of waste glass) revealed that the oxidizing atmosphere does not affect the thermal behavior of all the samples tested. The TG and DTA curves of GPMK and of the three waste glass-containing formulations under flowing Ar are reported in Fig. 1.

Furthermore, they retained about 20 wt% of water, with lower amount for glass-rich geopolymers (GPMK2 and GPMK3 with 40 and 50 wt% of glass, respectively). Lower amounts of water were removed by dehydroxylation (in the range 573–973 K) in GPMK2 and GPMK3, since they have the lower content of geopolymer and, consequently, a lower number of hydroxyl groups to undergo condensation.

The mechanical stability of the 3D geopolymeric network has been measured in terms of the compressive strength. After 28 days at room temperature, the samples synthesized using different percentages of waste glass showed a good geopolymerization, reaching the highest mechanical performance at 40 wt% of glass incorporated into MK.

Preliminary biological data highlighted that cytotoxic and antimicrobial effects are significantly affected by the content of waste glass in the geopolymer matrix, due to the fact that the higher is the waste glass content the higher is the production of reactive oxygen species (ROS), responsible of both cytotoxic and antimicrobial effects.

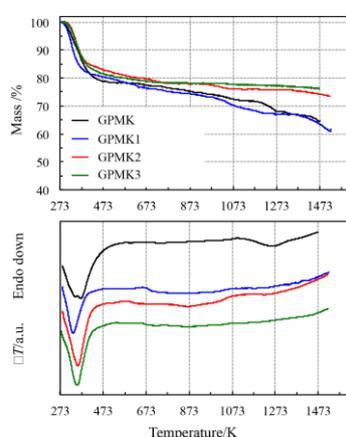


Figure 1. TG (up) and DTA (down) curves of GPMK and of the three mixtures at 10 K/min under Ar flowing atmosphere.

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Effect of nanoparticle aspect ratio on Joule heating of graphite-based bucky-paper

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Keywords: Conductive Nanomaterials; Expanded Graphite; Self-heating; Joule's effect; Thermal analysis

In the field of civil infrastructures, ice formation on bridges and roofs represents a problem that hinders the practicability and the lightning of load-bearing structures. In this paper, the manufacturing of graphite-based bucky-paper infiltrated with a very low amount of thermoplastic polymer is proposed. The bucky-paper is able to act as heating element to prevent the ice formation since 2D nanostructures, like bucky-paper, or graphene-based films, can satisfy requirements such as structural compatibility, flexibility, mechanical reinforcement, and adaptability in multilayered composite structures [1-5].

In this work, expanded graphite (EG) based film heaters infiltrated with PVA are produced by a green solvent casting process, using a biodegradable polymer. The resulting film heater offers an excellent combination of mechanical electrical and thermal performance. In particular, the effect of aspect ratio of two 2D fillers on the film properties has been investigated. Structural and morphological analysis (not reported here) showed that EG2 filler is characterized by an aspect ratio of about 1 order of magnitude higher than EG1 (see fig. 1c).

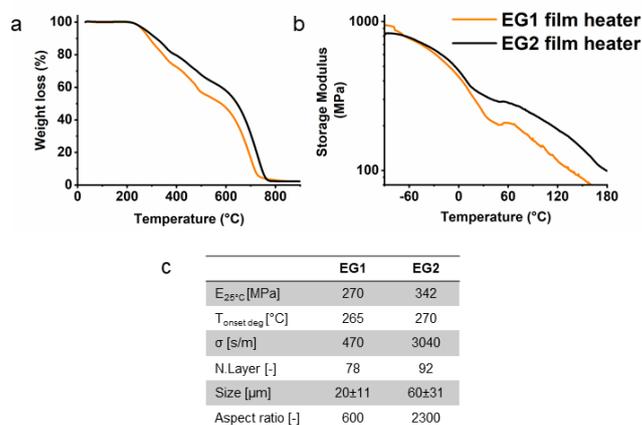


Figure 1. DMA (a) and TGA (b) of the film heaters; structural parameters of the fillers, electrical and mechanical parameters of the film heaters (c).

Thermal analysis performed by DMA, TGA analysis highlights that the film heater filled with the nanoparticles with a higher aspect ratio (EG2) manifests higher thermal stability and mechanical properties compared to EG1 system (see Figs. 1a,b,d). Moreover, the higher electrical conductivity of the EG2 based system (see Fig. 1c) results in a best heating performance. In fact, for the same applied voltage values, EG2 system achieves higher temperature values (see figure 2a).

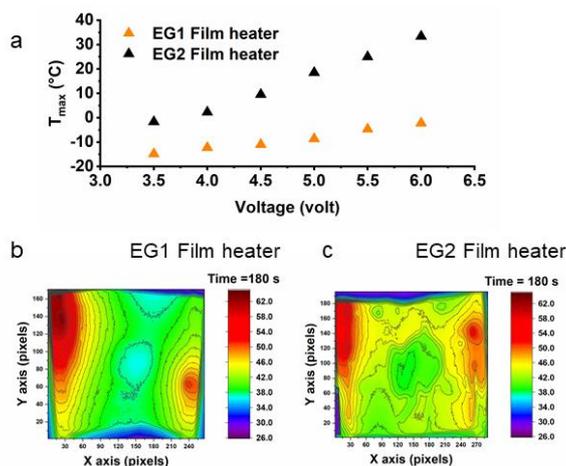


Figure 2. (a) T_{max} vs. applied voltage of the film heaters at $-20\text{ }^{\circ}\text{C}$; Thermal images on the film surface of the EG1 (b) and EG2 (c) film heaters after 180 s at the power of 2 W.

The thermal images, obtained by infrared camera, shown in Fig. 2b, show that, for the same applied power, the EG2 based system is characterized by a more homogeneous surface temperature distribution compared with the EG1 system. The uniformity is visible in the central area of the film, which presents the same color tone. An increase in the aspect ratio of the filler allows obtaining an increase in the de-icing performance of the heater film. It generates higher temperature values, using lower applied voltages. This result is crucial when considering the applicability of the heating system in the sector of civil engineering, like de-icing of roofs, bridges and repairs of buildings belonging to the artistic heritage, where it is not possible to massively intervene on the supporting structures.

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Knudsen Thermogravimetry for the Evaluation of Halloysite loading mechanism under vacuum pumping

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Keywords: Halloysite, Knudsen Thermogravimetry, water activity.

Halloysite nanotubes are effective nanocarriers for the loading and controlled release of functional molecules. Here, we investigated the influence of the vacuum pumping on the filling mechanism of halloysite cavity for several drugs (salicylic acid, sodium diclofenac, malonic acid and metoprolol tartrate) solubilized in two different solvents (water and ethanol). According to the Knudsen thermogravimetric data, we proved that the solvent confinement within the nanotubes' cavity is crucial to properly describe the driving process of halloysite loading. Both morphological investigations and thermogravimetric experiments evidenced that the amounts of the drugs encapsulated inside the halloysite cavity can be enhanced by the vacuum pumping in/out procedure. In addition, we detected that the the release kinetics of the drugs can be controlled by the pressure conditions used in the loading protocol. As a general result, we observed that the halloysite/drugs hybrids prepared under vacuum exhibited slower release profiles with respect to the corresponding composites obtained at ambient pressure. In conclusion, this study describes the physico-chemical aspects of the halloysite filling, which is controlled by solvent confinement within the nanotubes' cavity. The attained knowledge represents a fundamental step for the development of loading protocols into confined spaces of tubular nanoparticles.

Prediction of residual lifetimes for HDPE pipes using OIT measurements by DSC method: a mini-review

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Keywords: oxidation induction time, lifetime prediction, HDPE, thermo-oxidative degradation

Lifetime predictions of polymeric materials like HDPE has been the subject of numerous studies. Typical requirements for gas and water pipes are roughly 50 years. The traditional method to assess the lifetime of PE pipes materials is based on internal pressure tests according to EN ISO 9080. [1] This method can be very expensive and time consuming. For this reason, different approaches based on antioxidant consumption and thermo-oxidative degradation are proposed by some authors. [2-6] Basically, the resistance against the brittle failure is controlled by the stabilizers systems and the oxidative induction time OIT is widely used for the determination of the thermal oxidative resistance of PE materials. In PE materials a linear relationship exists between the concentration of phenolic/phosphites mixtures of antioxidants and the observed OIT. [7] The kinetic of the thermo-oxidative process can be described by the Arrhenius equation and the lifetime at a specific temperature can be estimated from the plot of $\ln OIT$ vs $1/T$ for temperature above or near the melting point. [2, 4, 5] For PE materials some authors have observed a discontinuity in the Arrhenius plot around the melting point. [8, 9, 10] Long term OIT experiments up to several 100-1000 hours show an Arrhenius plot with a knee around the melting point. The knee indicate that different degradation process and different activation energy are occurring above and below this temperature. This curvature shows that straight line extrapolation from short term experiments at high temperature at temperature below the melting may give wrong results. Another problem is the scattering of the OIT data. The data obtained from round robin tests shows a substantial variation in the measured values, the high value for repeatability and reproducibility standard deviations shows that the OIT data with regard to lifetime prediction must be considered as rather critically. [11, 12] In order to overcome the above-described difficulties to predict the residual lifetime at relatively low temperature, new approaches combining fractur mechanics and thermic analysis concepts, such as OIT, are proposed. Even if these techniques depend on the specific problem under investigation and dedicated mechanical tests are generally used, they appear to be the most promising approach. [3, 13, 14,15].

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Energetic characterization of phenolpiperazine derivatives

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Keywords: Phenolpiperazine derivatives; Energy of combustion; Enthalpy of formation, Enthalpy of sublimation

Piperazine and its derivatives are a well-known class of heterocycle organic compounds that are present in a large range of medicines and are used as key structures in the design and synthesis of new drugs with high biological potential [1,2]. So, for all chemical, industrial or pharmacological processes involving these compounds, the knowledge of their thermochemical and thermophysical properties, as well as the understanding of their correlation with molecular structure, has a critical importance.

In this context, the present work aims to contribute to the knowledge of the energetics and structure of two of the piperazine derivatives. The standard molar enthalpies of formation, in gaseous phase, at $T = 298.15$ K, of 3-(1-piperazinyl)phenol and 4-(1-piperazinyl)phenol were derived from the experimental values for the standard molar enthalpy of formation in the condensed phase, at $T = 298.15$ K, obtained from static bomb combustion calorimetry measurements, and from the values of the standard molar enthalpy of phase transition, at $T = 298.15$ K, determined by the Calvet microcalorimetry technique.

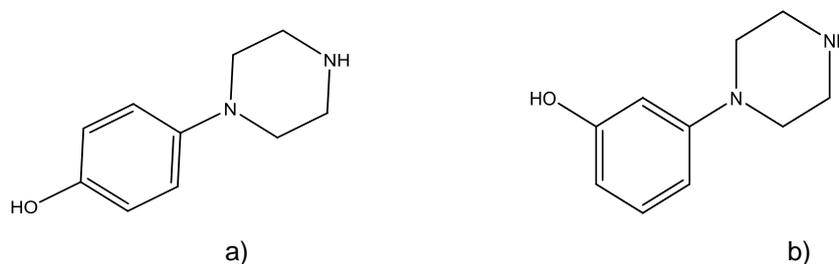


Figure 1. Molecular structure of the two phenolpiperazine derivatives studied: a) 3-(1-piperazinyl)phenol and b) 4-(1-piperazinyl)phenol

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Curing kinetic analysis of epoxy formulations

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Keywords: Thermosetting resins, Thermal properties, Cure kinetics, Kamal's model

Epoxy resins are widely used for carbon fiber-reinforced composites (CFRCs), due to their excellent processability and properties [1]. In the manufacturing of CFRCs based epoxy resins, the curing reactions are responsible not only of the mechanical properties, but also affect the adhesion between matrix and fibers, and play a crucial role in determining the mechanical properties of the finished composite products. Generally, epoxy resins obtained by solidifying the only epoxy precursor with hardeners for structural materials, are brittle and have poor resistance to crack propagation [2]. To overcome this drawback, the epoxy resins are mixed with modifying agents, such as low molecular weight polymers, reactive oligomeric compounds, plasticizers, reactive diluents, etc., which modify the viscosity of the resin so that the processability of the system is not impaired [3]. On the other hand, these components can strongly modify the curing kinetic. Generally, after the selection of promising industrial formulations, the knowledge of aspects related to their curing kinetic is a fundamental requirement to optimize the manufacturing processes and therefore the properties of the final materials. The cure kinetic of an epoxy resin based on the tetrafunctional epoxy precursor N,N'-tetraglycidyl methylene dianiline-(TGMDA) hardened with 4,4-diaminodiphenyl sulfone (DDS) was investigated. In particular has been investigated the effect of introduction of a reactive diluent (diglycidylether of 1,4 butane diol) on the curing kinetic of the epoxy system at a concentration of 80 % / 20 % (by wt) epoxide to diluent. From viscosity measurements, not shown here, the inclusion of the reactive diluent significantly reduces the viscosity value of about two orders of magnitude, allowing a best processability of the resin. An advanced iso-conversional method, under isothermal condition, the Kamal's model-diffusion controlled [4], has been applied to simulate the systems in the whole curing process

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n f_d(\alpha) \quad (1)$$

where m and n are the reaction orders, k_1 , k_2 are the rate parameters which are functions of temperature and f_d , has the form[4] of

$$f_d(\alpha) = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (2)$$

with C and α_c are temperature-dependent fitting parameters. When α is much lower than the critical conversion α_c , $f_d(\alpha)$ approaches unity and the effects of diffusion are negligible. However, when α approaches α_c , $f_d(\alpha)$ decreases and eventually vanishes with further increase in conversion. The temperature dependence of the rate constants is given by the Arrhenius expressions in Equation (3), where i indicates the primary or secondary amine-epoxy reaction (see Figure 1c), A_i is the pre-exponential factor, E_i the activation energy, R is the universal gas constant and T the reaction temperature.

$$k_i = A_i \exp \frac{-E_i}{RT} \quad i = 1,2 \quad (3)$$

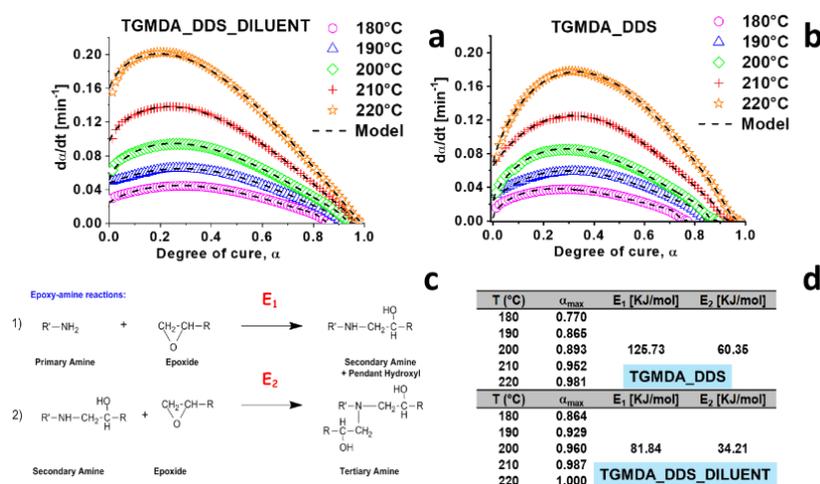


Figure 1. Comparison of fitting model (dash line) with experimental data (symbols) for a) the system TGMDA_DDS and b) TGMDA_DDS_DILUENT; c) Scheme of cross-linking reactions between epoxy pre-polymers and amine hardeners; Values of the kinetic parameters for obtained systems.

Figure 1a and b clearly shows that Eq. (1) leads to a very good description of the experimental data in the whole range of the conversion α . Some kinetic parameters determined for the amine-cured TGMDA resin system are listed in the Table of Figure 1d. The maximum degree of cure α_{max} increased with higher temperatures. The activation energy E_1 and E_2 decreased significantly compared to the system without the reactive diluent. This means that the new epoxy system needs a lower amount of heat for the curing. In particular, E_2 decreases by about approximately 50 %, compared to the value obtained with the system TGMDA-DDS. The decrease of the viscosity, obtained by the introduction of reactive diluent, allows the upper local mobility of the chain segments. This is reflected on the activation energy at later curing stages. The effect of the reactive diluent is remarkable for the secondary amine-epoxy reaction. This result leads to consider the possibility of being able to cure the resin at lower temperatures.

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Geopolymers for Cultural Heritage: morphometry and thermal characterization

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Keywords: TGA-FTIR, micro-CT, geopolymer, porosity

Geopolymers are ceramic-like inorganic polymers produced at low temperature, consisting of chains or 3D networks of aluminosilicate linked with covalent bonds. These materials are attracting increasing interest in research and development due to their technical properties, accessibility and cost-effectiveness of the raw materials [1].

Geopolymerization mechanism starts with the dissolution of a solid precursor, source of reactive Si and Al by an alkaline solution, followed by polycondensation of oligomers into small ribbon-like aluminosilicates that develops 3D structures where Si and Al atoms are in the center of tetrahedra. The nature of the hardened geopolymer is amorphous to semi-crystalline [2]. The microstructure, strength and durability of the products depend on the degree of dissolution and tridimensionality of the consolidated structure. An important role is played by the composition of the starting mixture as well as the curing process (t and T) [3].

Recently, metakaolin (Mk)-based geopolymers have been proposed in built heritage conservation interventions as substitutes for conventional materials due to their adaptability to the substrate, good breathability, mechanical behavior, fire and acid attack resistance [4]. In this framework, the AGM for CuHe (Advanced Green Materials for Cultural Heritage) project aims to enhance the knowledge on these new generation materials to be effectively used for conservation purposes. As part of the project, new geopolymer formulations with low amount of commercial Mk were designed by using low-cost iron rich local raw materials [5] that would ensure the most cost-effective and best integrated restoration practices in terms of aesthetic appearance and textural character, solving the conflict between the use of traditional and modern materials.

This paper will present the results from the thermal and morphometrical characterization of a set of geopolymers designed by employing 5 Fe-rich types of precursors (clay, volcanic ash, pumice, gravel and recycled industrial tiles). Among the formulations studied, different weight percentages of commercial metakaolin (from 0 to 25%) have been added in order to study its effect on the mechanical and thermal properties of the geopolymers establishing the extent of modification while controlling the costs of the product. The analytical approach (Figure 1) combined Thermogravimetric analysis (TGA), coupled to the Evolved gas Analysis (EGA) through Fourier transform infrared spectroscopy (FTIR), X-ray crystallography (XRD), calcimetry and micro-Computerized Tomography (micro-CT).

Results will discuss the composition and thermal properties of the raw materials and geopolymers highlighting the differences in their thermal behavior. The role played by the raw material used as a precursor, the percentual of metakaolin added, the activator used and its ratio as well as the thermal treatment of the mixture will be discussed in terms of physical morphometry of the geopolymers and their thermal characteristics.

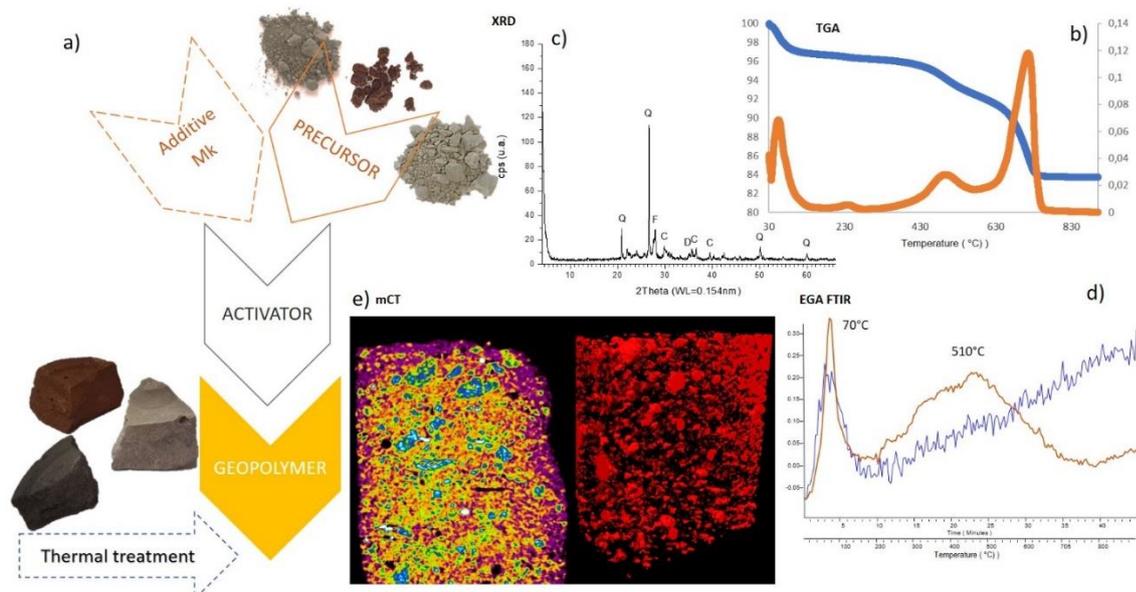


Figure 1. a) Synthesis scheme of the formulation of geopolymers followed by the AGM for CuHe project; Results from the analysis of raw materials b) TGA and c) XRD and final products; d) profiles of the evolved gas CO_2 and H_2O (EGA-FTIR coupled with TGA) from the TGA and e) 2D slice and 3D rendering from micro-CT.

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Electro-Curing: an efficient strategy for the curing of epoxy-nanocomposites

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Keywords: nanocomposites; cure behavior; joule effect; electro-curing

Nanostructured forms of carbon can be incorporated in epoxy resin to confer self-sensing properties, heating ability, auto-repair function, damage monitoring function, etc.[1-3]. The curing process of epoxy composites is currently based almost exclusively on thermal curing cycles, for which an oven or an autoclave is used [4]. Alternative curing methods for composite manufactures are of great industrial interest and can help save energy. Methods as the irradiation hardening process, heating with infrared and laser radiation [5] have drawbacks because they present high costs and manifest poor application flexibility. In this paper, an alternative curing strategy, based on the application of an electric field, is proposed. The resin is obtained through the dispersion of carbon nanotubes (3% by weight), which act as nanometric heater elements in the epoxy matrix. The electro-curing is activated by applying an external electric power, which allows tunable cross-linking within the epoxy matrix entrapped between the nanotubes. The initiation and propagation of the crosslinking reaction result to be power/time-dependent. The electro-curing method allows reaching higher Curing Degrees (C.D.) with respect to the conventional process in oven and consequently higher glass transition temperatures (see Figure 1c).

Table 1. Comparison of Curing Degree (C.D.) for the filled sample subjected to different curing approaches.

Sample	Method	Curing cycle	Curing Degree (C.D.) (%)
O	Oven	(1h@80°C+20min@120°C+1h@180°C)	91
EC	Electro-Curing	(5min@10W+15min@5W)	100
EC*	Electro-Curing	(2min@5W+58min@2W) + (5min@10W+15min@5W)	100

The values of the curing degree displayed in Table 1, for the different curing conditions and strategies were obtained from Differential Scanning Calorimetry (DSC) not shown here. The polymerization in oven allows a C.D. of 91%. A C.D. higher than 95% has been obtained after an oven curing cycle of 3 hours at 180°C. The flow of an electric current through the material produces heat, due to the resistive nature of the epoxy/CNT nanocomposites, and therefore the temperature increase of the nanocomposite

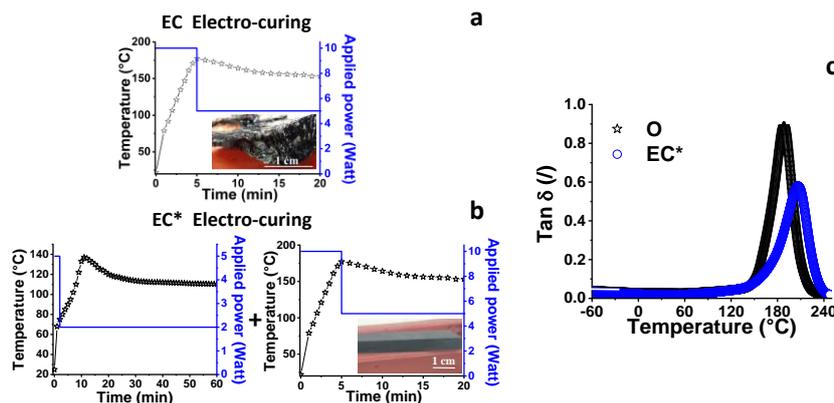


Figure 1. a) Electro-curing cycles carried out for obtaining sample EC (Inset: Optical images of the sample EC); b) sample EC* (Inset Optical images of the sample EC*); c) $\tan \delta$, obtained by Dynamic Mechanical Analysis, relating to the composite after the different curing approaches: O (solidification through thermal treatment); EC* (solidification through electrocuring)

The increase of the temperature must be accurately controlled by adjusting the applied power and choosing electro-curing cycles suitable to obtain a good compromise between the material performance and the energy employed. Table 1 shows two different approaches. In the first, a single electro-curing cycle is used (see sample EC of Table 1) and, although the C.D. is 100%, the sample evidences numerous trapped bubbles (see the inset image of Figure 1a). The poor temperature control during the fast curing process also affects the final dimensions, and shape of the sample, which results completely compromised. The second approach (EC*) uses a double electro-curing cycle (see Figure 1b) where, in first stage, lower values in the temperature are reached, followed by a second stage where higher applied powers determine higher value of temperature values. The double curing cycle limits the autocatalytic nature of the cross-linking reactions, avoiding the formation of bubbles and locally degraded regions as shown in inset image of Figure 1b. The electro-curing process results in a higher curing degree and glass transition temperature (see Figure 1c) of the filled material, it result a less energy-intensive thermal process; in fact, the cycle in oven requires about 5 MJ for the curing of the sample, whereas the electro-curing process requires about 12.4 kJ for the complete curing of the same sample.

Acknowledgments

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The application of isothermal titration calorimetry to thermodynamic control of interactions in solutions of polyelectrolytes used as textile auxiliaries

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Keywords: isothermal titration calorimetry, textile materials, microcapsules, polyelectrolytes

The application of microencapsulated preparations to textile materials is one of the promising methods of functional finishing. The substance contained in the capsule can have an unlimited range of practical functions. It is proposed to use the isothermal titration calorimetry (ITC) to identify the optimal conditions for obtaining stable microcapsules with specified characteristics. One of the fields of application of ITC can be thermodynamic control of micelle formation in solutions of polyelectrolytes used as textile auxiliaries.

In this work the interactions in solutions of surface-active substance (surfactants, carboxypav) and polyelectrolytes used in the processing of textile fibers treatment was studied by the ITC. Thermochemical measurements were performed by using TAM III calorimetric system (TA Instruments) at $T = 298.15$ K equipped with a 20 ml titration cell. Two series of experiments were carried out. In the first series, a solution of carboxymethylcellulose was placed in the calorimetric cell, to which a solutions of cationic polyelectrolyte VPK-402 and then anionic polyelectrolyte of Acremon B were injected. In separate experiments, VPK-402 was added to a calorimetric cell containing water, and, similarly, the addition of Acremon B to water was made. The second series of experiments consisted in studying the interaction of the VPK-402 with Acremon B. In the main experiments, a solution of VPK-402 with an initial concentration of 10 g/l was loaded into the calorimetric cell. The titrant was a solution of Acremon B with a concentration of 20 g/l. The correction experiment consisted in adding Acremon B to the water contained in the cell. The heat effect of the interaction of polyelectrolytes was corrected for the corresponding heat effect of the blank experiment. It was found that the mixing of carboxypav with VPK-402 is endothermic, and the further addition of Acremon B to the mixtures of carboxypav with VPC-402 indicates exothermicity at the mixing process. However, the interaction of VPK-402 with Acremon B is accompanied by an endoeffect, and dilution of the solution of VPK-402 in water is exothermic. In the case of the addition of a solution of Acremon B to water, the initial additions of the titrant are accompanied by endoeffects, and then the sign of the heat effect changes to the opposite. As a result of mixing the VPK solution with Acremon B solution, turbidity of the solution was observed, which indicates the formation of the nonstoichiometric complex VPK-402- Acremon B, and it is also confirmed by the results of calorimetric titrations.

Acknowledgement

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Interaction of quercetin with human serum albumin in H₂O-DMSO solution: an isothermal calorimetric study

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Keywords: cyclodextrins, human serum albumin, intermolecular association, quercetin

The scientific selection of optimal conditions for the solubilization of biological active polyphenols-flavonoids that are of interest to the food and pharmaceutical industries is an urgent task. The solubility of many drugs based on flavonoids in water is low, that decreases their bioavailability and, thus, reduces the effectiveness of their use. In the presence of cyclodextrins, the solubility of hydrophobic biomolecules as well as their resistance towards hydrolysis, thermal and oxidative destruction increases due to formation of the «host-guest» inclusion complexes. The unique properties of cyclodextrines as solubilizers of hydrophobic molecules could be optimized due to the purposeful use of solvent and pH during solubilization process. Medium influence allows change the solvate state of the reagents and gives an opportunity for purposeful regulating the complex stability and the energy of complex formation reactions or processes of intermolecular associations.

Quercetin (QCT) is a flavonoid possessing many activities, such as neuro/cardioprotective, anti-inflammatory and anticancer, but its pharmacological application is severely curtailed by its low water solubility and *in vivo* bioavailability. The formation of a QCT-hydroxypropyl- β -cyclodextrin «host-guest» complex ([QCT HP β CD]) is promising to improve QCT therapeutic potential.

In this work the reaction of QCT and its inclusion complex [QCT HP β CD] with model transport protein human serum albumin (HSA) has been studied by isothermal titration calorimetry (ITC) in aqueous-dimethylsulfoxide mixed solvents (92 vol. % 0.05M PBS + 8 vol. % of DMSO). Thermodynamical binding parameters have been estimated with use of Independent binding model. ITC experiments has been provided by using PEAQ ITC (Malvern Pananalytical) and TAM III (TA Instruments) calorimetric equipments. PEAQ ITC experiments has been implemented under the following conditions: 0.015 mM of HSA was in the cell, and quercetin (0.330mM) was in a syringe. It was checked that the stability of HSA and QCT solutions was maintained for several hours at concentration of 5-8% of DMSO. The experimental conditions for TAM III measurements was: 0.016 mM of HSA in the cell, and QCT (0.119 mM) as well as QCT+HP β CD (0.331 mM + 2.75 mM) solutions in a syringe. Similar concentration conditions were used for a blank experiments.

Acknowledgement

The calorimetric measurements were carried out at the Institute of Thermodynamics and Kinetics of Chemical Processes of the Ivanovo State University of Chemistry and Technology (ISUCT) using the equipment of the Centre for Collective Use of ISUCT, and of the Center for Precision Genome Editing and Genetic Technologies for Biomedicine, Institute of Gene Biology, Russian Academy of Sciences. The work was carried out with the financial support of the RFBR and VANT [project No. 19-53-54004].

Determination of the thermodynamics of Iron(III) complexation with nicotinic acid in water-ethanol solutions from calorimetric results

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Keywords: nicotinic acid, complex formation, enthalpy, mixed solvent

Studies of equilibria in solutions containing nicotinic acid are of scientific and practical interest, since it is a vitamin B actively involved in many physiological processes. The determination of the solvent role in reagents solvation allows to receive the information for controlling the process of a complex formation.

The purpose of the study is the determination of water-ethanol solvent composition influence on thermodynamic parameters of complex formation in solutions of nicotinic acid and Fe^{3+} ions.

Stability constants of Iron (III) – nicotinic acid complex of FeHNic^{3+} composition were obtained by potentiometric method ($T = 298.15 \pm 0.10$ K, $I = 0.25$ (NaClO_4)) earlier [1].

The changes in enthalpy of complex formation ($\Delta_r H$) were obtained by calorimetry at temperature 298.15 ± 0.01 K and $I = 0.25$ (NaClO_4). The changes in Gibbs energy ($\Delta_r G$) and entropies of these reaction ($T\Delta_r S$) were calculated (Table 1).

X_2 , mol. fraction	0.0	0.1	0.3	0.5	0.70
$\Delta_r G \pm 0.3$ [1]	-18.7	-22.0	-26.5	-26.1	-22.8
$\Delta_r H \pm 0.9$	-10.4	-24.7	-6.6	1.1	0.5
$T\Delta_r S \pm 1.0$	8.4	-2.7	19.9	27.2	23.3

Table 1. Thermodynamic characteristics of the interaction between nicotinic acid and Iron(III) in water-ethanol solutions at 298.15 K

It was observed that the change in the stability of the complex is mainly determined by the predominance of the entropy component of the changes in Gibbs energy over the enthalpy component.

The experimental data are considered using the approach based on thermodynamic parameters of each participants of investigated processes. The changes in enthalpy of transfer $\Delta_{tr} H_r^0$ of complexation from water into the mixed solvent are calculated. The changes in enthalpy of Iron(III) transfer $\Delta_{tr} H^0(\text{Fe}^{3+})$ are adopted from [2].

In this work the changes in enthalpy of dissolution $\Delta_{dis} H^0(\text{HNic})$ of nicotinic acid in a mixed water-ethanol solvent (the mole fraction of the organic component ranging $0 < X_2 < 0.7$) at 298.15 K were determined by calorimetry. The changes in enthalpy of transfer of nicotinate $\Delta_{tr} H^0(\text{Nic}^-)$ and nicotinic acid $\Delta_{tr} H^0(\text{HNic})$ from water into the mixed solvent are calculated. The value of $\Delta_{dis} H^0$ of these compounds are to increase (for nicotinate to a greater extent).

The analysis of the contributions of reactants enthalpy of reaction into formation FeHNic^{3+} showed that the enthalpy change of the reaction when changing the solvent composition is caused by the changes in solvation state of nicotinic acid at X_2 from 0 to 0.1 m.f. and desolvation of the reaction product in more concentrated solutions ($X_2 > 0.1$ m.f.).

Acknowledgement

The study was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation (project FZZW-2020-0009).

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Molecular complexation of cyclodextrins with benzoic acid, quercetin and curcumin in mixed water-organic solvents

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Keywords: cyclodextrins, flavonoids, molecular complexation, thermodynamic

Information on the thermodynamic and structural characteristics of the inclusion complexes of benzoic acid (BA), quercetin (QCT) and curcumin (CURC) with cyclodextrins (CD) in mixed water-organic solvents is necessary for the development of innovative pharmaceutical compositions based on hydrophobic polyphenolic bioactive molecules. In the presence of CDs, the solubility of phenolic acids and flavonoids, as well as their resistance to hydrolysis, thermal and oxidative degradation, increases as a result of the formation of "guest – host" inclusion complexes. It is possible to optimize the unique properties of CD as solubilizers of hydrophobic organic molecules during the processes of inclusion complexation due to the targeted use of the solvent and pH. In addition, in non-aqueous media, the solubility of phenol derivatives is higher than in water, which may also favor the processes of inclusion complexation. The effect of the influence of the medium will change the solvated state of the reagents and purposefully regulates the stability of complexes and the energy of reactions of their formation.

The aim of this work is to generalize our results obtained earlier [1-4] and to establish regularities and identify the features of the effect of solvation of reagents on the stability of molecular complexes of β -cyclodextrin (β -CD) and hydroxypropyl- β -cyclodextrin (HP- β -CD) with BA, QCT, CURC and on the thermodynamic characteristics of their complexation reactions.

The following methods were used for the research: isothermal titration calorimetry, differential scanning calorimetry, ¹H NMR, UV spectroscopy, phase solubility method. The research methodology consists on the provisions of the solvation-thermodynamic approach based on the relationship between the thermodynamic characteristics of complexation reactions and solvation of reagents.

To achieve this goal, we had to solve the following tasks:

-to determine the thermodynamic parameters ($\lg K^0$, $\Delta_r H^0$, $\Delta_r G^0$, $T\Delta_r S^0$) of reactions of formation of inclusion complexes of BA, QCT and CURC with β -CD and HP- β -CD in water-ethanol (H₂O-EtOH) and water-dimethyl sulfoxide (H₂O-DMSO) of variable composition;

-to analyze the effect of reagent solvation on changes in the Gibbs energy, enthalpy, and entropy of molecular complex formation reactions during the transition from water to H₂O-EtOH and H₂O-DMSO solvents.

The main obtained results are listed below:

-An increase in the EtOH concentration in the H₂O-EtOH solvent leads to a decrease in the stability of the molecular complexes [BA β -CD] and [QCT HP- β -CD].

-In the H₂O-DMSO solvent, the stability of [BA β -CD] varies within the experimental error, while the

exothermicity of complexation decreases.

-Analysis of the solvation contributions of reagents has shown that changes in the solvation state of the "guest" molecules are a key factor in the change in the Gibbs energy of the reactions of the formation of molecular complexes involving crown esters and cyclodextrins. However, in the case of molecular complexes of amino acids with 18K6, desolvation of "guests" causes an increase in stability, and in complexes with CD, increased solvation of BA and QCT leads to a decrease in the stability of [BA β -CD] and [QCT HP- β -CD] during the transition from water to water-ethanol solvents.

-An increase in the EtOH concentration in the mixed solvent leads to an increase in the stability of the [CURC HP- β -CD] complex, which is different from the thermodynamics of the formation reactions of [BA β -CD] and [QCT HP- β -CD] in aqueous ethanol solutions and is probably due to the structural features of the [CURC HP- β -CD] complex.

The data obtained in this work will be useful for the development of a pharmaceutical composition based on cyclodextrins and hydrophobic bioactive molecules using a solvent as a means of controlling liquid-phase processes involving CD.

Acknowledgement

The work was carried out with the financial support of the RFBR and VANT [project No. 19-53-54004] and the Ministry of Foreign Affairs and International Cooperation of Italy [grants for foreign citizens not living in Italy and Italian citizens living abroad, no. 946-22/10/2018].

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Interaction Thermodynamics of Risedronic Acid and Metal Cations in Solution and in the Solid State

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Keywords: Risedronic acid, potentiometry, calorimetry, spectroscopy

Risedronic acid (see Figure 1) belongs to the class of biphosphonates (BP), widely used in the medical field to treat bone disorders. Bisphosphonates (BPs, e.g., alendronate, risedronate, and ibandronate) help to maintain bone mass, to inhibit osteoclast-mediated bone resorption, and to reduce the risk of both vertebral and non-vertebral fractures. The clinical efficacy of BPs is mainly based on two key properties: their capacity to strongly bind hydroxyapatite crystals of bone, and their inhibitory effects on osteoclast precursors and mature osteoclasts. Interaction of risedronate with metal cations is poorly investigated. Qualitatively, it is indicated that adsorption of risedronate is inhibited when the drug is taken with mineral water containing high levels of calcium or magnesium, but chemico-physical results are missing. In this work, the interaction of risedronate with Ca^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+} is investigated by means of potentiometric and calorimetric measurements to determine thermodynamic parameters (ΔG , ΔH and $T\Delta S$). The most important species resulted to be the M_2L and variously protonated MH_iL (with i from 0 to 2) depending on the specific metal cation considered. During all the measurements, the formation of a sparingly soluble species has been noted starting from very acidic pH values (~ 3.5). Thus, four solid samples have been properly prepared and characterized by means of a combination of spectroscopic techniques ($\mu\text{-XRF}$, XRD and Raman) and thermal analysis (TG-DTA). In addition, the solubility of these compounds has also been determined by the shake-flask method followed by differential pulse-anodic stripping voltammetry at different NaCl concentrations, to determine Setschenow and activity coefficients. Preliminary results show that the solubility of lead and copper risedronate increases with chloride concentration, probably due to the formation of chloro complexes with Pb^{2+} and Cu^{2+} .

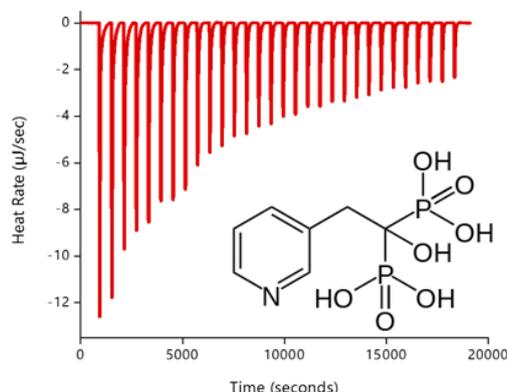


Figure 1. Calorimetric titration curve of Zn^{2+} (20.0 mmol L^{-1}) with Ris (2.0 mmol L^{-1}) in NaCl(aq) 0.1 mol L^{-1} at $T = 298.15 \text{ K}$.

Excess enthalpies of $[C_nMIM][NTf_2]$ ($n = 2$ or 10) + ethanol or + *N*-methyl-2-pyrrolidone mixtures at 298.15 K and 0.1 MPa

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Keywords: $[C_nMIM][NTf_2]$ ($n = 2$ or 10), mixtures, total and partial molar excess enthalpies, Isothermal Titration Calorimetry

The class of Ionic liquids, ILs, derived from an imidazolium cation and the anion bis(trifluoromethanesulfonyl)imide have proved to be very promising as lubricants in the industrial field. The modulation of the properties of this class of ILs can be increased by considering mixtures at different compositions with widely used solvents having suitable characteristics. Recently, different studies have been reported concerning the characterization of different kind of ILs in mixtures with *N*-methyl-2-pyrrolidone, NMP, [1] or ethanol, EtOH [2].

In this work, two protic ionic liquids, PILs; 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, $[C_nMIM][NTf_2]$ ($n = 2$ or 10) have been investigated with the purpose of ascertain their calorimetric properties in organic solvents as NMP and ethanol, known for their low toxicity and high solvent power over the whole concentration range.

ILs, obtained by IoLITec (Ionic Liquids Technologies) were pre-treated at 333 K and at reduced pressure in presence of P_2O_5 , to reduce their water content. Before using, ILs and organic solvents – obtained by Sigma-Aldrich – were kept in small bottles in presence of molecular sieves 3A.

The presence of both free and associated water in the studied ILs were revealed by characteristic bands in the spectra recorded, at 298.15 K, in a wavenumber range between (4000 and 400) cm^{-1} , by ATR-FTIR (Fourier-transform Infrared Spectroscopy in the Attenuated Total Reflectance mode).

The water mass fraction in the pre-treated ILs, determined by TGA (Thermal Gravimetric Analysis) by using an instrument STA 6000 (PerkinElmer), were 0.002 and 0.006 for $[C_2MIM][NTf_2]$ and $[C_{10}MIM][NTf_2]$, respectively.

Excess enthalpies of the mixtures and partial molar excess enthalpies of components have been determined adopting an ITC (Isothermal Titration Calorimetry) technique [3] by using a differential microcalorimeter produced by Thermometric (Thermal Activity Monitor - model 2277).

The correlated RK equations for partial molar excess enthalpies, H_i^E , and excess enthalpies, H^E , where ($H^E = x_1H_1^E + x_2H_2^E$) are expressed as:

$$\frac{H_i^E}{RT} = a_1x_j^2 + b_1x_j^3 + c_1x_j^4 + d_1x_j^5 + \dots \quad (1)$$

$$\frac{H^E}{RT} = x_1x_2 \sum_{i=1}^n A_i(x_1 - x_2)^{i-1} \quad (2)$$

The values of the experimental H^E and H_i^E data, of the binary mixtures containing $[C_n\text{MIM}][\text{NTf}_2]$ (1) + NMP or EtOH (2) are expressed by means of the coefficients of the RK equation.

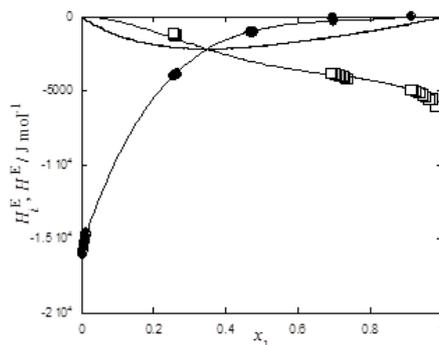


Figure 1. Experimental excess partial molar enthalpies, H_i^E , and molar excess enthalpies H^E , for the binary mixtures $[C_2\text{MIM}][\text{NTf}_2]$ (1) + NMP (2) as function of x_1 , at 298.15 K and 0.1 MPa. Points, experimental data; (●) H_1^E of $[C_2\text{MIM}][\text{NTf}_2]$; (□) H_2^E of NMP; lines, interpolated values calculated by means of the RK equation (—) for H^E , H_1^E and H_2^E .

Both mixtures in ethanol are endothermic and the H_i^E of the components are always positive while those in NMP are exothermic and the corresponding values of H_i^E are all negative. For each subclass of mixtures, at fixed x_1 values, H^E , decrease in absolute value as the alkyl chain of the ILs increase. The deviations from ideality are quite significant, being the H^E values at equimolar composition, $H_{\text{eq}}^E \pm u$; $(+1799 \pm 37$ and $+2112 \pm 13)$ J mol⁻¹ for ethanol-containing mixtures and $(-1409 \pm 10$ and $-1984 \pm 16)$ J mol⁻¹ for NMP-containing mixtures. u is the standard uncertainty.

H^E curves are asymmetric as a consequence of the non-specular shape of H_i^E curves. NMP-containing mixtures show a minimum at $x_1 \approx 0.33$, suggesting the existence of IL:NMP aggregates of the 1:2 type. The H^E curves of ethanol-containing mixtures are less similar to each other; those relating to $[C_2\text{MIM}][\text{NTf}_2]$ show a maximum around $x_1 = 0.5$ while that of $[C_{10}\text{MIM}][\text{NTf}_2]$ show a maximum around $x_1 = 0.4$.

In **Fig. 1** are represented the experimental values of H_i^E , and H^E for $[C_2\text{MIM}][\text{NTf}_2]$ (1) + NMP (2) vs x_1 .

The values of the partial molar enthalpies at infinite dilution of the components, $H_i^{E,\infty}$, show regular trends. The $H_1^{E,\infty}$ are always greater than the $H_2^{E,\infty}$; their ratio is about 1.8 for mixtures in EtOH and 2.5 for NMP-containing mixtures. The greatest thermal effects are found when the molecular compound acts as a solvent, in the dissolution of one mole of IL, at extreme dilution.

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Platinum compounds adsorption on modified silica for water treatment

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Keywords: Platinum compounds, silica, water treatment, isothermal titration calorimetry, ICP-MS

Concentrations up to $\mu\text{g/L}$ levels of cytostatic drugs (CD) have been detected in water bodies [1]: these CDs are characterized by environmental persistence. Several methods for their removal and degradation have been developed [2] which are often expensive and sometimes inefficient for CDs complete removal from the treated water.

Among them, platinum-based chemotherapy agents are widely used for the treatment of a variety of cancers and demonstrate a high toxicity and low biodegradability. Such drugs, after use, are excreted intact to hospital waste-water or as highly toxic derivatives in significant percentage [1]. The presence of rising Pt-based drugs in the $\mu\text{g/L}$ range in hospital effluents concerns about the long-term exposure of living organisms to low levels of such toxic compounds [3]. A potentially effective strategy to treat such low levels of Pt-containing contaminants is to pre-concentrate the sample to be treated by selective adsorption with specifically designed materials. Then, the adsorbed compounds can be desorbed and treated by advanced oxidation processes. Desorption can be realized by changing the temperature of the system which would make the process more sustainable as no chemicals (e.g. strong acids, organic solvents) would be needed.

In this contribution, the adsorption of cisplatin (A) and carboplatin (B) in the $\mu\text{g/L}$ range by cysteine (cys)- (C) and diethylenetriamine (dien)- (D) modified silica is evaluated.

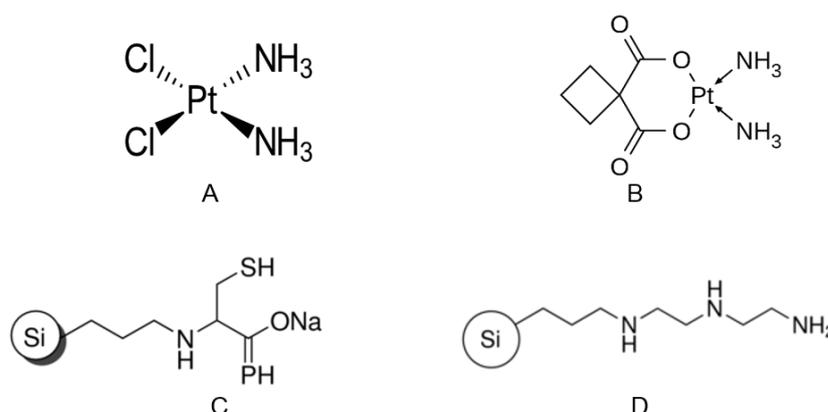


Figure 1. Cisplatin (A), carboplatin (B) and modified cys- and dien-silica (C and D) used in this work.

The choice of this material is based on the potential high affinity of cysteine and amine groups for Pt²⁺ [4]. Adsorption kinetics and isotherms have been built by analyzing the free concentration of Pt by using ICP-MS.

Isothermal titration calorimetry (ITC) has been then used to monitor the heat exchanged in the adsorption process. Early results show that the adsorption of the cisplatin and carboplatin in both functionalized silicas wasn't complete. Preliminary ITC evidences an exothermic reaction of cisplatin with dien-silica: further investigation are planned to quantify the obtained results.

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Water - Ethanol Liquid Binary: Microwave Heating reveals the faster temperature increase of the azeotropic composition.

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Keywords: Microwaves, azeotrope

Microwave (MW) heating promotes [1 - 4] aroma release from vegetal tissues and allows production of concentrated essential oils or MW aromatized products. Significant help in either R&D investigation comes from the possibility to predict the effects of the MW treatment.

The susceptibility of a system to the microwave action is reflected by the resulting heating rate, (dT/dt) . Since water is the main component of most products currently treated with MW, it is of help to compare the behavior of a MW susceptible compound, C, to the behavior of water [6] and to use the dimensionless ratio $R = [(dT/dt)_C / (dT/dt)_W]$,

For many MW susceptible compounds, R was experimentally determined [3, 4] and compared with the values reported in literature: as a rule, a poor agreement was often found. For this reason, the present investigation aimed to reexamine the experimental and formal approach to R , treating the simple case of water-ethanol liquid mixtures that can mimic the competition between different 2450-MHz-MW susceptible compounds within a given system. This paper is a readjustment of a 25-year old communication [7] that remained somehow hidden for most chemists and physicists.

The observed heating rate of the water-ethanol liquid mixture with the azeotropic composition (0.96% w/w) is the largest one even at temperatures below the respective boiling point (Figure 1).

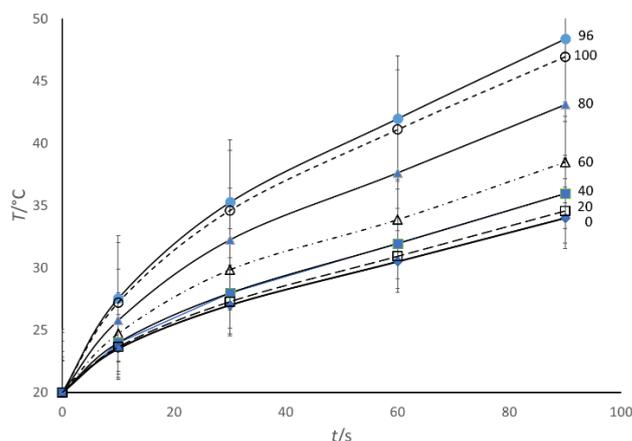


Figure 1. Temperature records at various MW exposure time for different water-ethanol mixtures. Each trace is sided by the relevant ethanol % (w/w) content. The bars correspond to the standard error determined through EXCEL software.

An empirical fit of these data allowed the evaluation of the relevant $(dT/dt) - vs - t$ trend and the corresponding $R - vs - T$ traces. The treatment of these data included the comparison with those predicted through the expression

$$R = \frac{\rho_W C p_W \exp(-2a_C z)}{\rho_C C p_W \exp(-2a_W z)} \quad (1)$$

where ρ , C_{pi} , a_i and z stand for density, heat capacity at constant pressure, MW attenuation parameter of the compound "i" and depth from the exposed surface, respectively. Density and MW attenuation factor of the water-ethanol mixtures were drawn from the literature [8, 9], whereas their heat capacity was experimentally determined with a Mettler DSC 20 calorimeter. The R trends predicted through Equation 1 are rather smooth and regular, not showing any peculiar behavior for the azeotropic composition. When one scales the "experimental" with "predicted" trends (at any T) the peculiarity of the azeotropic composition is clearly enhanced.

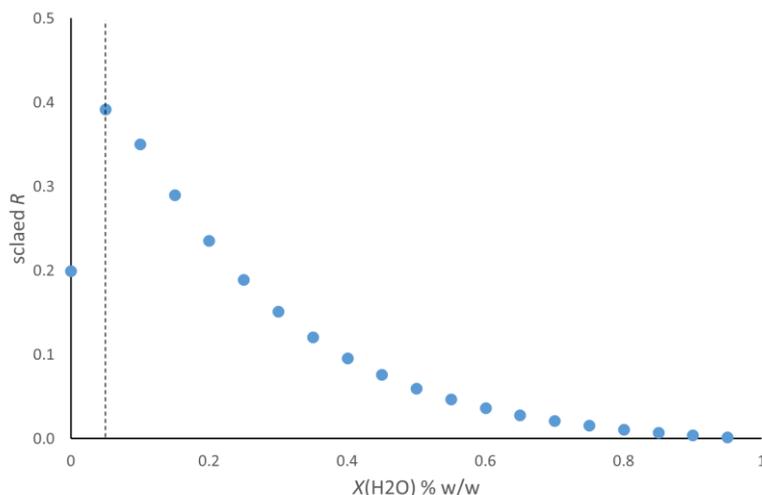


Figure 2. Scaled R trend (at 30°C) shows the peculiarity of the liquid mixture of azeotropic composition.

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Temperature and pH responsive supramolecular aggregates between cyclodextrin and multiresponsive surfactants: a Calorimetric analysis

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Cyclodextrins (CDs) are a class of cyclic oligosaccharides and play an important role in self-assembly systems of amphiphiles. The most common ones α , β and γ -cyclodextrins are formed, respectively, by six, seven and eight (1-4)-D-glucopyranoses units. The hollow shape structure of CDs provides unique physicochemical properties, including the ability to form host-guest complexes [1]. Surfactants are attractive host molecules due to their wide variety, availability, versatility, responsiveness to different stimuli, and high relevance in different fields [2]. The complexation affects the properties of guest molecules and can produce highly ordered aggregates with desirable characteristics for fundamental and practical applications [3]. Polyoxyethylene alkyl ether carboxylic acids ($C_nE_jCH_2COOH$) – a class of highly water-soluble and pH-responsive surfactants – and cyclodextrins are able to form well-defined structures spontaneously (Figure 1), which features are dependent on the physical-chemical characteristics of the systems [4]. Those structures can also present responsiveness to pH, due to the ionization degree of the terminal carboxylic acid, temperature, and other external stimuli. Additionally, the low toxicity and biocompatibility make the systems suitable for a large range of applications.

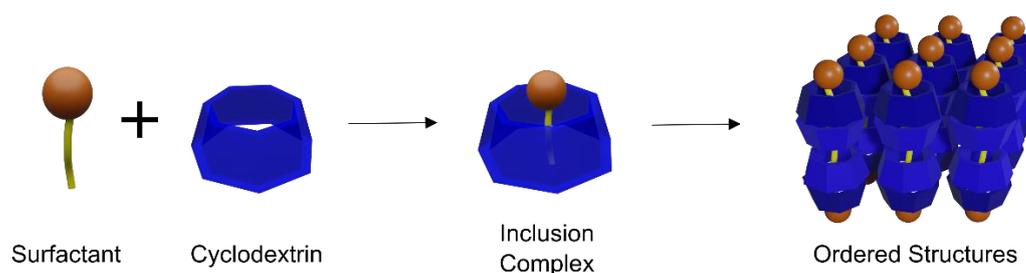


Figure 1. Schematic representation of inclusion complexation. The surfactant is inserted into the cyclodextrin forming the CD/Surfactant complex. Finally, the inclusion complexes can spontaneously assemble into highly ordered structures.

The size-match compatibility of host and guest is a simple concept able to anticipate possible interactions, but the quantitative analysis of the thermodynamic parameters obtained by calorimetric methods is important to understand the complexes properties and predict its behavior.

Then, several series of the systems of surfactants $C_{12}E_5CH_2COOH$ and $C_{12}E_{10}CH_2COOH$ with α and β CDs at various CD/S molar ratios and different pH were prepared. The thermodynamic parameters for the inclusion complexation were obtained from isothermal titration calorimetry and the crystallinity

of the structures probed by differential scanning calorimetry. Volumetric studies also provided additional information on the inclusion complexation process. As a result, the cavity size of cyclodextrins, the head group and ionization degree of the surfactant were shown to strongly affect the inclusion complexation.

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Silver(I)-Polyamine Complex Formation in Non-aqueous Solvents: a Thermodynamic and DFT Study

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The thermodynamics of metal complex formation with nitrogen-donor (N-donor) has been widely studied in water[1-3] as well as in non-aqueous or mixed solvents[3-6]. The main aim of these works has been to investigate the influence both of different basicity and steric properties of the ligands and of the solvents on the stability and nature of the complexes formed. Values of the complexation constants in organic solvents are of great help to design metal active centers for catalytic applications, to describe the behavior and speciation of metals in the environment, to design selective and efficient separation methods and could provide basic information on the effect of solvation on complex formation. When this last point is concerned, the knowledge of other thermodynamic quantities (enthalpy and entropy of complex formation) is desirable. This latter field is evidently very wide and rich of a number of data which should be rationalised in order to find useful correlation between thermodynamic parameters and, for example, steric, electronic and solvation effects of both the reagents and the complexes formed.

In particular, our group carried out many thermodynamic studies for the coordination of transition metals and block-*f* ions with a number of polydentate amines in organic solvents, mostly dimethylsulfoxide (DMSO) and acetonitrile (AN) [4-6]. Data in aprotic organic solvents provided in fact fundamental information on the effect of solvation on complex formation and on the strength of metal-ligand interactions, as these solvents are simplified systems with respect to water. The results obtained showed that the stability and nature of the complexes formed were largely influenced by ligands structures, donor-atom basicity and steric properties, in addition to solvent properties.

As an extension of previous works, we report here the results of a potentiometric and calorimetric study on the complexation reactions of neutral N-donors 1,4,7-triazaheptane (DIEN), 1,5,9-triazanonane (DPT) and 1,4,7,10-tetraazadecane (TRIEN) with Ag(I) ion in the solvent AN, which are compared with those available in DMSO, dimethylformamide (DMF) and propylenecarbonate (PC), solvents with quite different dielectric constants (ϵ) and donor number (Dn) with respect to AN.

The results show that a polynuclear $\text{Ag}_3\text{L}_2^{3+}$ species of high stability is formed by DPT, which inhibits the formation of AgL_2^+ . The species is hypothesized to be stabilized by the formation of two large, stable cyclic rings around the three metal centres: DFT studies are in advanced stage to clarify this point. The overall enthalpy terms associated to complex formation are strongly exothermic whereas entropy terms oppose the complex formation, in line with what found for complexation of several metals with neutral ligands in aprotic solvents[4-6]. The trend of stabilities of the Ag(I) complexes is discussed extending the comparison to the results obtained previously in DMSO and AN for other primary polyamines with different structures and donor strength.

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Intermolecular interactions of L-carnosine with isonicotinic acid in aqueous solutions studied by isothermal titration calorimetry

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Keywords: enthalpy, isonicotinic acid, L-carnosine, thermodynamics

One of the leading trends in modern chemistry, pharmacology and medicine is the creation of directional transport system for drugs, in which drugs are transferred in the body with the help of carrier molecules, which act as "protein vectors", nanoscale particles, capsules, etc. Peptides, hormones, enzymes, etc. that have selectivity for certain body cells can act as "vectors" for drug delivery. Therefore, a number of experimental and theoretical studies on model compounds are required to show the relationship between the active centers of the amino acid and peptide fragments that make up the carrier proteins and the physicochemical properties of the "protein vector - drug - water solution" system on changing solution conditions (acidity of the medium, temperature, etc.).

The aim of this study is to establish the nature and the driving forces of the interaction between the drug isonicotinic acid and the peptide L-carnosine, as model of polypeptide chains in proteins as albumin, to determine their selectivity and preferred types of bonding (hydrogen bonding, van der Waals or electrostatic interactions) in liquid media. The obtained results were compared with the interaction of isonicotinic acid and L-asparagine. The structures of the compounds are in Fig.1.

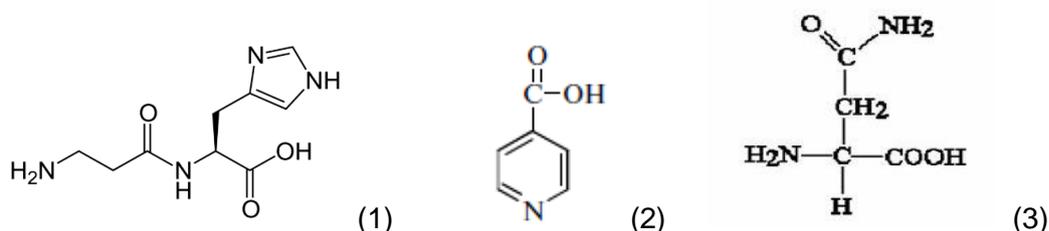


Figure 1. Structural formulas of L-carnosine (3-alanyl-L-histidine, C₉H₁₄O₃N₄, LC) (1), isonicotinic acid (4-pyridinecarboxylic acid, C₆H₅NO₂, ISO) (2) and L-asparagine (C₄H₈N₂O₃) (3).

The interaction of L-carnosine with isonicotinic acid was studied in aqueous solution at 298 K by ITC. The heats of mixing of aqueous solutions of L-carnosine with aqueous solutions of isonicotinic acid (Q_{com}) were determined on a TAM III microcalorimetric titration system (TA Instruments) equipped with a 20 ml titration cell. The thermal effect of dilution of L-carnosine in water (Q_{dil}) was taken into account by an additional blank experiment.

The ITC experimental trend of the data does not reflect the functional form that characterizes the formation of a complex. The curve diverges and it is not possible to determine the values of the standard enthalpy and constant of binding. Probably the constant is small and the concentration range experimentally accessible does not allow to reach a plateau. For this reason, the data were processed in order to derive the enthalpy coefficient of cross pair interaction, h_{xy} , which are the enthalpy contributions to the corresponding free energy coefficients, according to the McMillan-Mayer theory, which continues to be widely used in studies of intermolecular interactions in solutions. By processing the data, a value of the $h_{xy} = (-1.99 \pm 0.02) \cdot 10^6 \text{ J kg mol}^{-2}$ was found. This value is very large and suggests that the interaction is the limit between non-specific interaction and binding.

Previous studies found that the interaction of zwitterionic forms of isonicotinic acid with L-asparagine leads to the formation of complexes with a stoichiometry of 1:1 [19]. The thermodynamic parameters of this complexation process are characterized by the following values: $\log K_c = 3.514 \pm 0.033$, $\Delta_c G = -20.03 \pm 0.25$ kJ / mol, $\Delta_c H = -1.18 \pm 0.31$ kJ / mol, $T\Delta_c S = 18.85 \pm 0.61$ kJ / mol. In the case of L-asparagine - isonicotinic acid – H₂O system, the positive values of $T\Delta_c S$ show that the hydrophobic force was the main binding force to stabilize the complex and the small negative $\Delta_c H$ values observed can be indicated that hydrogen bonding and electrostatic interactions are also contributed to the stability of the complex.

When considering the L-carnosine-isonicotinic acid-water system, it was not possible to calculate the thermodynamic parameters of complexation. However, rather high values of the coefficients of intermolecular interactions indicate the formation of relatively strong association. The structures of L-asparagine and L-carnosine, in addition to identical functional groups within the hydrocarbon skeleton, are distinguished by the presence of an imidazole group in the L-carnosine molecule. In the light of the above considerations, it can be supposed that imidazole group sterically prevents the formation of L-carnosine-isonicotinic acid complex with a large stability constant. However, the strong association with the high h_{xy} , found in this study, could be derived from the interaction of positively charged groups of L-carnosine with negative charged carboxylic group of the zwitterionic form of the isonicotinic acid.

This work shows the importance of thermodynamic studies to obtain information on interactions between molecules of pharmacological interest. Our data could explain the synergistic effect of L-carnosine and isonicotinic acid through water-mediated interactions in the treatment of ocular cataracts. Furthermore, L-carnosine is a model peptide and its not-so strong interaction with the drug isonicotinic acid could suggest a better drug release from transport proteins.

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The calorimetric measurements was carried out at the Institute of Thermodynamics and Kinetics of Chemical Processes of the Ivanovo State University of Chemistry and Technology (ISUCT) using the equipment of the Centre for Collective Use of ISUCT. The study was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation (project FZZW-2020-0009).

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Binding of vitamin B6-derived hydrazones to bovine and human serum albumins: an ITC study

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Low molecular weight compounds binding to the transport proteins of blood is an important step of their delivery into living cells. For this reason, a study of newly synthesized compounds with potential biological activity often includes the investigation of its interaction with some model transport proteins (e.g. bovine or human serum albumin (**BSA** or **HSA**)).

3-Hydroxy-2-methyl-5-[(phosphonoxy)methyl]-4-pyridinecarboxaldehyde (pyridoxal-5'-phosphate, **PLP**) is the cofactor which exhibits a wide spectrum of enzymatic activity including, among others, decarboxylation, deamination and transamination processes [1]. Hydrazones derived from vitamin B₆ could also have biological activity. For example, several pyridoxal-containing hydrazones were tested as anti-mycobacterial agents in a recent paper [2]. Vitamin B₆-derived hydrazones possible influence on vital functions is also associated with their capability of binding metal ions into stable chelate complexes. For example, d-metal ion chelating pyridoxalisonicotinoyl hydrazone and its analogs have shown anti-proliferative action [3], prevent copper-mediated ascorbate oxidation [4] and might be used for the treatment of Wilson disease and thalassemia [5].

The study of bovine and human serum albumin interactions with proper **PLP**-based hydrazones might be of interest considering both their beneficial and adverse effects. Therefore, we aim to determine the influence of the structure of hydrazones derived from pyridoxal 5'-phosphate on the solutions thermodynamics of their interactions with **BSA** and **HSA**. Structural formulas of the investigated hydrazones are shown in Figure 1.

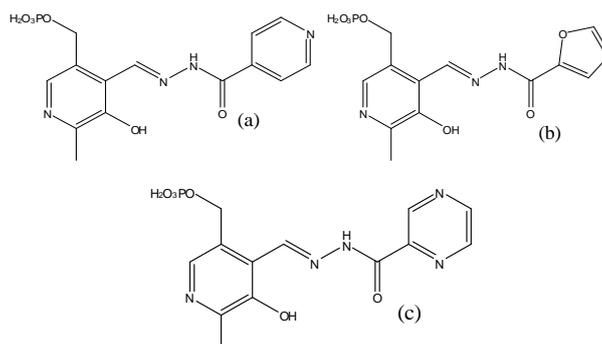


Figure 1. Structural formulas of pyridoxal-5'-phosphate isonicotinoyl hydrazone (**PLP-INH**) (a), pyridoxal-5'-phosphate 2-furoylcarbohydrazone (**PLP-2FH**) (b), pyridoxal-5-phosphate pyrazine-2-carbohydrazone (**PLP-PRZ**) (c).

The complex species, binding constants and thermodynamic parameters for the reactions of hydrazones derived from pyridoxal-5'-phosphate with bovine or human serum albumins were determined using nano-isothermal titration calorimetry. All measurements were carry out in phosphate buffer (pH = 7.4, I = 0.25) at 298 K. The concentration of **BSA** and **HSA** was controlled daily before each experiment by UV-Vis spectroscopy. The analysis of the calorimetric data was

carried out by HypCal program [6] and allowed for the determination of the driving forces of the molecular recognition processes occurring in solution.

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Vlase	Titus	P3 p.73, P4 p.75, P32 p.125, P33 p.127, P35 p.131, P36 p.133, P37 p.135, P38 p.137, P39 p.139, P40 p.141, P46 p.153, P47 p.155

