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Dear colleagues from Romania and abroad

It is our pleasure to welcome you to the 28th edition of the Progress in Organic and Macromolecular Compounds Conference, MACRO Iasi 2021, a traditional event organized by the Petru Poni Institute of Macromolecular Chemistry, Iasi (*Institutul de Chimie Macromoleculară Petru Poni* – ICMPP).

The Conference gives a broad overview of the hottest topics in organic and polymer synthesis, polymer physics, multifunctional polymeric architectures, engineering of polymeric materials, nanocomposites, hybrid materials, polymer networks, smart polymeric materials, polymeric membranes, polymer-based electronics, biologically-inspired nanostructures, drug carriers and biopolymers.

MACRO Iasi 2021 addresses professionals from academia, research institutes and industry, being intended as a dynamic platform for the presentation and sharing of their research and ideas. It brings together more than 60 participants from 25 top research institutions from 11 countries. The attendance of excellent researchers from the Polymer Science and Organic Chemistry fields provides the best environment to connect and share knowledge and professional experiences with the Romanian and European polymer research community and to assemble, network, collaborate, and further develop polymer science research

This meeting could not have been organized without the generous and tireless support and contribution of many individuals and groups within and outside the ICMPP. Therefore, we would like to acknowledge to all the invited lecturers, speakers, board and committee members, chairpersons, sponsors and all the people that have been involved in the organization and presentation of relevant results and perspectives.

Best wishes for a professionally rewarding conference!

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INVITED LECTURES

A. Dieter Schlüter is currently Professor Emeritus for polymer chemistry at the Materials Department of the ETH Zürich where he was active from 2004 to 2018. He studied chemistry and geophysics at the University of Munich (LMU) and received in 1984 his Ph.D. After post-doctoral stays with Prof. K. P. C. Vollhardt (UC Berkeley, USA) and Prof. W. J. Feast (University of Durham, UK) he was head of the polymer synthesis research group in Prof. G. Wegner's department at the MPI for Polymer Research (Mainz, Germany). 1991 he finished his habilitation, received a scholarship award of the Fonds der Chemischen Industrie (Dozentenstipendium) and started as Associate Professor for polymer chemistry at the Karlsruhe Institute of Technology. From 1992 to 2004 he was Full Professor at the Free University of Berlin. Since 2012 he is an elected member of the Swiss Academy of Engineering Sciences. In 2017 he was awarded the Society of Polymer Science, Japan, International Award for the discovery of 2D polymers. His research interests are in the area of synthetic polymer chemistry. Schlüter believes that organic chemistry is the fundament of innovative polymer synthesis. He has over 360 peer-reviewed publications with >14'000 citations and gave over 350 invited talks worldwide.

Ion Tiginyanu has completed his PhD in 1982 from Lebedev Institute of Physics, Moscow. He realized research projects at the Technical University Darmstadt (1995/96 and 1998/99) and at the University of Michigan in Ann Arbor (2000/2001). He serves as founding Director of the National Center for Materials Study and Testing, Technical University of Moldova. In 2019 he was elected president of the Academy of Sciences of Moldova. Professor Tiginyanu's research interests are related to nanotechnologies, multifunctional nanomaterials and fabrication of novel device structures. Among recent developments one can mention self-organized hybrid nanoarchitectures with dual hydrophilic/hydrophobic properties, light-driven nano- and micro-engines, self-propelled liquid marbles. He has more than 400 journal publications and 52 technological patents, his personal Hirsch index equals 43 (Scopus). He is member of the Academia Europaea, honorary member of the Romanian Academy, honorary doctor of the Joint Institute for Nuclear Research (Dubna, Russian Federation), Fellow of SPIE, member of AAAS, IEEE, OSA, MRS, the Electrochemical Society

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Andreas Fery is head of the institute for Physical Chemistry/Polymer Physics at the Leibniz Institut für Polymerforschung Dresden since 2015. He studied Physics at Konstanz University, where he received his Diplom in 1996. He did his PhD at the Max-Planck Institute for Colloids and Interfaces (MPIKG)/Potsdam University in 2000. After a post-doc at Institute Curie Paris in 2001, he became group leader at MPIKG and received his habilitation in 2006. In 2007 he joined Bayreuth University as associate professor and was promoted to full professor in 2008. He received the Richard Zsigmondy award of the German colloid society and an ERC starting grant. He has published more than 250 papers in peer-reviewed journals in the area of Polymer science and Colloid and interface science which have been cited more than 10000 times. His research interests are in development of novel approaches for Responsive/Bio-interactive Coatings and Nanophotonic/Plasmonic Surface Assemblies. Both research directions benefit from expertise in Characterizing Mechanics and Interactions of Colloidal Particles on the single particle level, using atomic force microscopy techniques. Deputy spokesperson of German Colloid Society, treasurer of European Colloid and Interface Society.

David Haddleton has been working in the area of controlled polymer synthesis for over 25 years since being employed at ICI. His PhD "Photochemistry of some organometallic ethene compounds" was under the supervision of Robin Perutz at the University of York in 1986. He spent one year at the University of Toronto as a PDRA. He joined ICI in 1988 and spent one year at the University of Southern Mississippi working with polymer liquid crystals. Moving back to the UK in 1988 he spent 5 years working on GTP and anionic polymerisation prior to moving to Warwick in 1993 and was promoted to full Professor in 1998. He has published over 500 papers and has a google h-index >85 with over 25000 citations. He has graduated over 75 PhD students from Warwick. Current work in the group is in different aspects of developing new polymerisation methodology and using this for novel polymers for industrial applications, polymers for personal care applications, (hair and skin care) and for biomedical and nano medicinal applications (new and targeted peptide and protein conjugation). Recent work includes new conjugation strategy, glycopolymers, monomer sequence control and polymerisation in biological media. He has formed two companies and is currently CSO of a transdermal drug delivery company Medherant Ltd.

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EXPANSION OF THE STAUDINGER 'MAKROMOLEKÜL'-CONCEPT TO TWO DIMENSIONS

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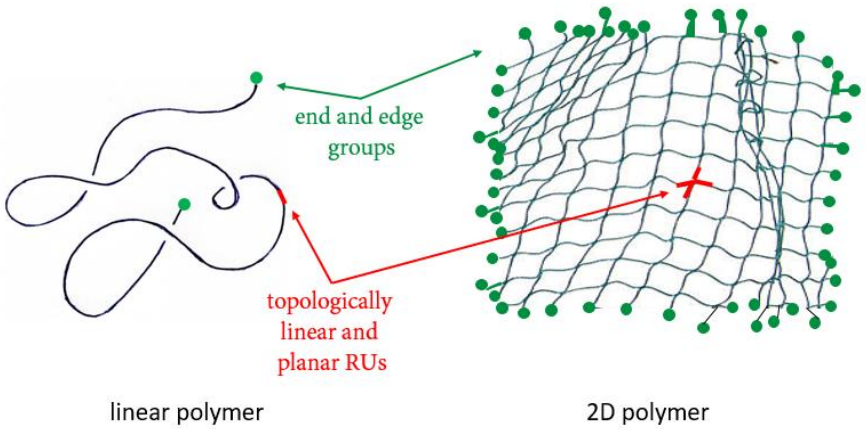
1. Introduction

Since Staudinger postulated the existence of 'Makromoleküle (English: macromolecules)' in the early 1920s[1], linear (and branched) macromolecules have been developed into an important materials class, somewhat loosely called 'plastics'. Linear synthetic macromolecules come into existence by binding low molar mass monomer molecules together to form chains. Nowadays these chains are commonly called polymer molecules or short: polymers as this term (Greek: polý 'many' and méros 'part') refers to their repetitive molecular structure consisting of a string of repeat units (RU) terminated by end groups on each side (Figure 1a). Although the usage of the terms polymer and macromolecule is not carved into stone, many contemporaries would agree that repetitiveness of the structure is a condition for polymers rather than for macromolecules. The latter term instead is often understood generically, thus representing synthetic and natural high molar mass covalently bonded molecules irrespective of their molecular structure. Consequently, macromolecules not only encompass polymers but also, for example, the naturally occurring cross-linked phenolic resin Lignin and the branched carbohydrate Amylopectin as well as the rubber of car tires or cross-linked polyurethane foams of matrices. In common practice the term polymer is not only used when referring to individual macromolecules but also to polymeric materials as a whole. This article restricts the use of polymer-to-polymer molecules. Thus, 2D polymer, for example, stands for 2D polymer molecule.

***Figure 1**. Sketches of a linear and a 2D polymer the molecular structures of both of which can be fully described by repeat units (RU) and end groups. For linear polymers the RUs are topologically linear, while for 2D polymers they are topologically planar. The end groups of 2D polymers should better be referred to as edge groups, as the entire circumference of their monolayer sheet-like structure presents the end groups*



In terms of topology, linear polymers are one-dimensional (1D) structures. Given their triumph, the question arose whether two-dimensional (2D) polymers can be made as well[2]. According to the above, that would concern macromolecules, whose entire structure consists of two-dimensional RUs and, of course, end groups wherever the structure terminates (Figure 1)[3]. For 2D polymers, it was suggested to refer to these end groups as edge groups[4]. In the same realm of thinking, 3D polymers could be in principle envisioned as well. Here however, aspects come into consideration, which are beyond the scope of this presentation and such polymers will therefore not be mentioned.

3. Results and discussion

This abstract article is a condensed form of Ref.[5] and the associated lecture presents all the features characteristic of a 2D polymer to show that these sheet-like macromolecules are polymers very much like linear chain macromolecules. As will be seen, 2D polymers have a molecular structure consisting of RUs and end (edge) groups, and are isolable and usable as individual molecular entities. Their average molar mass and the molar mass distribution can be determined although, given the dimensional differences to linear polymers, this may require other methods and/or may involve unprecedented aspects. The most important such aspect refers to structure. While to determine the molar mass of linear polymers requires to measure chain length, in the case of 2D polymers it requires to measure sheet area. This is quite a different story.

The lecture will also touch upon growth mechanism. The mechanisms according to which linear chains grow were investigated in detail and can be considered understood for the vast majority of cases. Mechanistic investigations are underway for 2D polymers, but the level of insight gained for 1D polymers has not yet been reached. The current state-of-the art in this important matter will be presented. Again, dimensionality will change things here too. While for linear polymers, growth is a one-dimensional process, for 2D polymers growth is two-dimensional, which requires different methods to look at it. To this end, a small warning may be appropriate: 2D polymers have orders of magnitude higher molar masses than linear polymers. Structural elucidation and mechanistic investigations are therefore in a different ballpark in terms of complexity, and many analytical methods reach their limits. Given this complexity and the only eight years that have passed since the first announcement of a 2D polymer comprised of topologically planar RUs, the reader will understand that the current article is more a progress report rather than a deep and thorough scientific discourse on a mature field.

4. Conclusions

2D polymers, very much as their linear chain counter parts, are ‘polymers’ or more precisely ‘polymer molecules’. They come as covalent sheets with a regular array of nanometer-sized pores. Thus, there are two categories of polymers, the one-dimensional and the two-dimensional ones. 2D polymers are ‘polymers’ because all the characteristic features that apply to linear polymers apply to these novel macromolecules as well. These features include (*i*) topological repetitiveness of the molecular structure, (*ii*) presence of defined and addressable end groups, and (*iii*) the fact that both the molar mass and the molar mass distribution can in principle be determined on the single molecule level. Furthermore, the mechanism according to which 2D polymers form has been elucidated unequivocally for the first case and suggested for other cases. While applying SCXRD for such purpose is demanding, the very fact that a mechanism has been deciphered for growth in two dimensions confirms that monomers suited for 2D polymers behave exactly alike monomers for linear polymers. They connect at predetermined positions following clear-cut kinetic protocols.

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TUBULAR NANOMATERIALS FOR MULTIFUNCTIONAL APPLICATIONS

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1. Introduction

There are two types of tubular nanomaterials, one type consisting of nanotubes and their networks, and the second one consisting of microtubes with nanometer scale thickness. Carbon and titania nanotubes are examples of tubular nanostructures where the properties depend on both chemical composition and dimensions. Over the last decade, a class of novel microtubular nanomaterials with extremely high degrees of porosity has been developed, the so called aero-nanomaterials: aerographite, aerogalnite, aerogallox, aero-ZnS etc. The diameter of microtubes may vary from a few to tens of micrometers, while the thickness of the walls is in the sub-100 nm range, thus assuring formation of extremely light-weight networks with very high degrees of porosity. In this paper, we will review the efforts related to the development and characterization of aero-nanomaterials based on wide-band-gap semiconductor compounds GaN and Ga_2O_3. Besides, we will discuss prospects of practical applications of aero-nanomaterials in various fields, including electronics, sensorics, microfluidics, microrobotics, biomedicine. The possibility to fabricate a new nanocomposite material based on aerogalnite architecture embedded in polymer matrix will be addressed.

2. Experimental

Aero-GaN represents an interconnected network of hollow microtetrapods which are obtained by direct growth of GaN on the sacrificial network of ZnO microtetrapods[1]. Ultrathin layers of GaN have been grown by hydride vapor phase epitaxy on sacrificial ZnO microtetrapods with diameter of arms ranging from 2 to10 μm and lengths from 20 to 100 μm. Note that at the growth temperature, GaN deposition is accompanied by simultaneous gradual decomposition and removal of the underneath ZnO template, which occurs due to harsh corrosive conditions. Aero-Ga_2O_3 or Aerogallox, represents an ultra-porous and ultra-lightweight three-dimensional architecture made from interconnected microtubes of gallium oxide with nanometer thin walls. The material is fabricated by annealing of aero-GaN template at temperatures as high as 950 °C in atmospheric conditions.

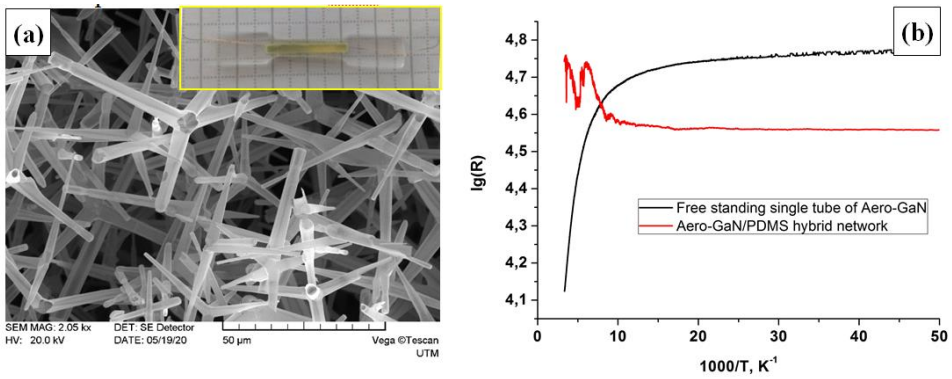
One of the most accessible materials for flexible pressure sensors is polydimethylsiloxane (PDMS), which exhibits excellent elastic properties, mechanical resistance and biocompatibility. The PDMS was prepared using a bi-component silicone elastomer kit - SYLGARD® 184, purchased from Sigma-Aldrich #761036. To synthesize PDMS, base and curing agents were mixed with the volume ratio of 10:1, respectively. The mixture was poured into a Teflon-made plate with known volume, where the Aero-GaN samples connected to Cu wires with silver paint were placed. Subsequently, the curing process occurred at 70 °C in the oven, for 4 h. The characterization of electrical properties of the network of Aero-GaN wired with silver paint and completely embedded into PDMS was realized using Keitheley 2400 instrument.

3. Results and discussion

Among the most fascinating properties of Aero-GaN one can mention the dual hydrophobic-hydrophilic properties. The interpenetrated GaN hollow micro-tetrapods have the inner surface of micro-tubular arms covered by an ultrathin film of zinc oxide, which is superhydrophilic, while the outer surface of tetrapod arms is superhydrophobic with the exception of their free ends which again exhibit superhydrophilicity due to the crystallographic polar planes, thus leading to the occurrence of dual hydrophobic/hydrophilic properties[1]. Using these dual properties, we encapsulated liquid droplets inside self-organized Aero-GaN membranes, thus fabricating Liquid Marbles (LM) with unique properties like self-propelled stationary rotation at record velocities or self-propelled pulsed rotation[1].

We demonstrated that Aero-GaN is an EMI shielding material with good performances in the X-band[2] and excellent shielding effectiveness in the terahertz region (frequency range from 0.1 to 1.3 THz), exceeding 40 dB in a huge frequency bandwidth. This finding places the aero-GaN among the best THz shielding materials known today[3]. To the contrary, Aerogallox exhibits extremely low reflectivity and high transmissivity in an ultrabroadband electromagnetic spectrum ranging from X-band (8–12 GHz) to several terahertz which opens possibilities for quite new applications of gallium oxide[4]. Besides, aero-Ga_2O_3 was found to be promising for photocatalytic applications. The functionalization of aero-Ga_2O_3 with noble metal nanodots proves to stimulate the photocatalytic degradation of methylene blue under UV or visible light illumination[5]. The electrical resistance of the Aero-GaN/PDMS composite was found to change when putting the sample into the vacuum. The dependence of the electrical resistance upon temperature in aero-GaN embedded in PDMS differs from that inherent to pure GaN semiconductor which is explained by different thermal expansion coefficients of the composite constituents.

Figure 1. *(a) SEM picture of initial Aero-GaN architecture. The inset in (a) shows the picture of a wired sample of Aero-GaN completely embedded in PDMS; (b) represents the dependence of the electrical resistance as a function of temperature for a single GaN microtube (black curve) and aero-GaN embedded in PDMS (red curve)*



4. Conclusions

Taking aero-GaN and aero-Ga_2O_3 as examples, we demonstrate that semiconductor-based aero-nanomaterials exhibit unique properties promising for multifunctional applications. The extremely low specific density and EMI shielding characteristics of aero-GaN open possibilities for space applications, while the excellent transparency in an extremely wide range of the electromagnetic spectrum, covering the X-band and THz region, makes aero-Ga_2O_3 perspective for internet-of-thinks applications. The dual hydrophobic/hydrophilic properties of aero-GaN are important for microfluidic applications. In particular, the demonstration of self-propelled rotating liquid marbles paves the way to the development of various mini-bioreactors for the study of living cells in specific confined conditions.

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RESPONSIVE COPOLYMERS BY RAFT POLYMERIZATION AS BUILDING BLOCKS FOR CONSTRUCTING SELF-ASSEMBLED BIO-HYBRID NANOSTRUCTURES

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1. Introduction

Polymer based bio-hybrid nanostructures, composed of synthetic or natural polymers and biomacromolecules or low molecular weight compounds of biological origin and medical interest, are attracting increasing attention due to their wide range of applications in the fields of nanomedicine (e.g. gene and therapeutic protein/peptide delivery, bio-imaging), bio-sensing, bio-catalysis, functional bio-interactive surfaces and agriculture[1,2]. They combine the properties of their biological and synthetic components and present nanoscale dimensions, bio-responsive properties and in many cases hierarchical internal structure. A convenient way to prepare them is the co-assembly of rationally chosen functional components, making possible their production in an easy and reproducible fashion, and allowing up-scaling of the formulation process. Functional synthetic copolymers, and especially block copolymers, are valuable building blocks for bio-hybrid nanostructures since they can be synthesized in a tailor-made manner. Controlled polymerization methodologies provide opportunities to precisely tune copolymer structure and introduce chemical and biophysical functionalities into the macromolecules that facilitate and determine structure formation and interactions at the supramolecular level. In this presentation some examples of novel bio-hybrid self-assembled nanostructures based on block copolymers, and developed in our group in the past five years, will be discussed, together with some proof-of-concept studies related to specific biomedical applications of the resulting nanoassemblies.

2. Experimental

Reversible addition-fragmentation chain transfer (RAFT) polymerization was employed for the synthesis of a series of diblock copolymers and triblock terpolymers, as well as mikto-arm star copolymers. The particular polymerization scheme allows for a good control over the macromolecular structure and chemical functionalities, giving copolymers with predetermined molecular weights, compositions and architectures, and narrow dispersity, through rational choice of monomers and chain transfer agents (CTAs) of appropriate reactivity. Further post-polymerization chemical modification i.e., *via* quaternization of ternary amine groups on the chains, provide copolymers of differentiated chemical and physical properties in respect to the precursor copolymers.

The block copolymers synthesized include amphiphilic poly((2-dimethylamino) ethyl methacrylate)-b-poly(lauryl methacrylate) diblock copolymers (PDMAEMA-PLMA), poly(N-isopropylacrylamide)-b-poly(oligoethylene glycol acrylate) (PNIPAM-POEGA) and poly(N-isopropyl acrylamide)-*b*-quaternized poly((2-dimethylamino) ethyl acrylate) (PNIPAM-QPDMAEA) thermoresponsive diblocks, quaternized poly((2-dimethylamino) ethyl methacrylate)-b-poly(lauryl methacrylate)-b-poly((oligoethylene glycol methacrylate) (QPDMAEMA-PLMA-POEGMA), poly(n-butyl acrylate)-*b*-poly(N-isopropyl acrylamide)-quaternized poly((2-dimethylamino)ethyl acrylate) (PnBA-PNIPAM-QPDMAEA) triblock terpolymers, and finally quaternized poly((2-dimethylamino) ethyl methacrylate)$_x$-poly(oligoethylene glycol methacrylate)$_y$ (QPDMAEMA$_x$-POEGMA$_y$) double hydrophilic mikto-arm star copolymers[3].

Bio-hybrid nanostructures were constructed by simple mixing of the components leading to electrostatic self-assembly, aided by hydrophobic and hydrogen bonding interactions between the components. The biological building blocks included DNAs of different lengths and insulin as a model therapeutic protein, but also low molecular weight hydrophobic drugs (e.g., indomethacin, curcumin).

Several analytical and physicochemical techniques were utilized for the molecular characterization of the copolymer synthesized, i.e., SEC, NMR, FTIR, and of the supramolecular bio-hybrid structures resulting from the co-assembly of the copolymers with nucleic acids, insulin and hydrophobic drugs, including light

scattering (SLS, DLS, ELS), spectroscopy (UV-Vis, FTIR, Fluorescence) and cryogenic transmission electron microscopy (cryo-TEM) techniques.

3. Results and discussion

Analytical data after polymer preparation support the successful synthesis of the designed copolymers which self-assemble in aqueous media, giving nano-assemblies of different internal structure, which respond to pH, temperature and ionic strength depending on the chemical nature and properties of the constituting monomers. Triblock terpolymers were found to assemble into smaller micelles**.**

Amphiphilic QPDMAEMA-PLMA diblock micelles complex effectively with DNA molecules. The morphology of the complexes (micelleplexes) depends on the structure of the micellar coronas. Shorter coronas give rise to worm like supramolecular micelleplexes. Micelle decorated fibers are formed after complexation of QPDMAEMA-PLMA-POEGMA triblock terpolymer micelles with long DNA, while complexes with short DNA are found to be globular containing a small number of terpolymer micelles. PNIPAM-(Q)PDMAEA copolymers form thermoresponsive polyplexes with DNAs which respond also to pH and ionic strength.

$QPDMAEMA_x$-$POEGMA_y$ mikto-arm stars form complexes with insulin that are pH and ionic strength responsive. Insulin structure remains unaltered after complexation indicating maintenance of it biological activity. Overall, the molecular structure of the synthetic copolymers influences greatly the structure, morphology and responsive properties of their nanoassemblies with DNAs and insulin.

Furthermore, it was possible to encapsulate indomethacin into PNIPAM-POEGA assemblies by mixing copolymer and drug solutions at temperature above LCST of the PNIPAM block, followed by cooling, due to hydrogen bonds developed between the components. Curcumin could be encapsulated into the hydrophobic domains of triblock terpolymer micelles showing increased intrinsic fluorescence.

4. Conclusions

Several novel bio-hybrid nanostructures have been constructed by co-assembly of rationally designed block copolymers, synthesized by RAFT polymerization, and nucleic acids, insulin and hydrophobic drugs. All structures showed nanoscale dimensions, intriguing morphologies and multi-responsive properties toward pH, temperature and ionic strength changes in aqueous media. These studies provide useful guidelines for the development of functional multicomponent nanostructures for biomedical applications.

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FROM RESPONSIVE SURFACE COATINGS TO SELF-REPORTING MATERIALS

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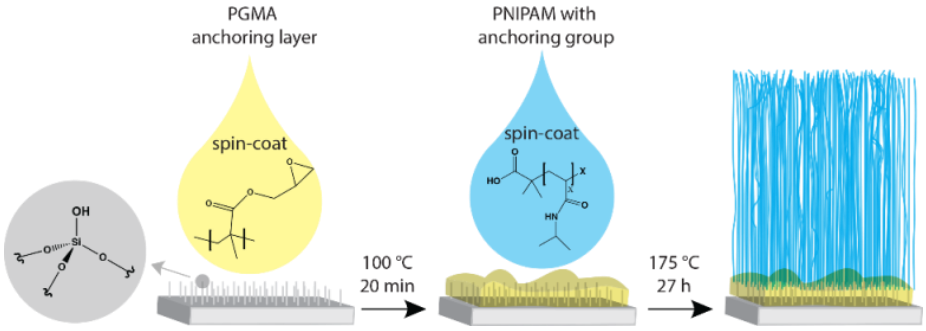
1. Introduction

Polymer brush surfaces, consisting of densely surface-grafted polymer chains, have the capacity to switch their surface properties in response to stimuli that cause conformational transitions between the polymer chains. Due to a coupling between polymer chains, such conformational changes tend to be rapid, and dramatic between the extremes of swollen and full collapsed. The conformational changes lead to, for example, different wettability, adhesion, lubrication, and exposed surface groups of the brushes. Developing new methods to transduce signals from polymer brush conformation, as well as investigating how the surfaces adapt after conformational transitions, may allow polymer brushes to be leveraged towards greater surface-based sensing materials. In our work, we investigate how poly(*N*-isopropylacrylamide) (PNIPAM) polymer brush surfaces adapt to surface solvation through specific orientation of the polymer chain ends[1], and how integration of Förster resonance energy transfer (FRET) fluorophores can lead to materials that self-report chain conformation across complex interfaces[2].

2. Experimental

We assemble dense polymer brush surfaces *via* a grafting-to process from a polymer melt onto a macromolecular anchoring layer of poly(glycidyl methacrylate) (PGMA) (Figure 1). This process typically yields polymer brushes that have a grafting density of greater than 0.13 chains/nm^2.

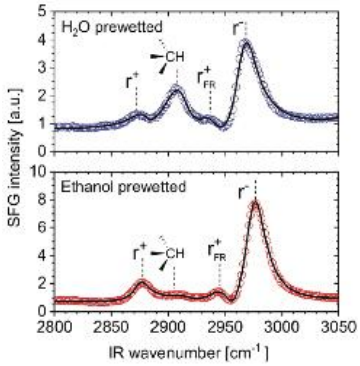
Figure 1. *Schematic of the assembly of PNIPAM brushes on PGMA-coated substrates*



3. Results and discussion

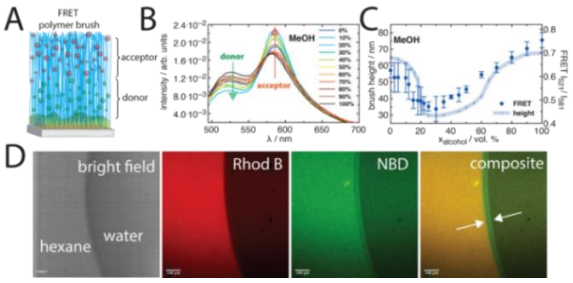
Co-nonsolvency effects arise when a mixture of two "good" solvents can then form a "bad" solvent, leading to polymer collapse/aggregation. For PNIPAM, this effect occurs in mixtures of water and alcohol. As a stimulus, this offers an intriguing possibility to tune polymer brush conformation *via* subtle changes in the composition of aqueous mixtures. We report on sum frequency generation (SFG) measurements of PNIPAM brush surfaces that have been prewetted with water, and then separately with ethanol. We found that when the polymer brush is prewetted with water, hydrophobic interactions drive a specific surface orientation of methyl groups from the PNIPAM, which is absent for samples prewetted with ethanol (Figure 2). This shows how the PNIPAM surfaces respond to the nature of the good solvent. Furthermore, we found that these specific orientations for the water-prewetted substrates leads to significant "memory" effects. A water droplet causes the surface polymer chains to adapt so strongly that a subsequent droplet can determine the position of the previous drop (even months later). This highlights a link between surface responses and memory in polymer chain conformation.

Figure 2. *Vibrational SFG spectra of PNIPAM brushes after prewetting. Figure adapted from reference*[1]



In other work, we have engineered FRET donor (green, NBD) and acceptor (red, Rhod B) fluorophores into separate blocks within the polymer brush (Figure 3A), where FRET pairing was used as a basis to report the conformation of the polymer brush. Co-nonsolvency effects were used to induce conformational changes and FRET (Figure 3B), which allowed for direct comparison between ellipsometry and FRET (Figure 3C), where high FRET was consistent with collapsed chains, and low FRET was consistent with fully swollen chains. This relationship was additionally confirmed by molecular dynamics simulations of polymer brushes impregnated with quasi-fluorophore molecules.

Figure 3. *(A) Schematic showing the integration of FRET pairs in the polymer brush; (B) fluorescence spectra of the surfaces in different water/methanol (MeOH) mixtures; (C) direct comparison of FRET to height as a function of MeOH concentration; (D) confocal microscopy images of the FRET relation across the hexane-water interface. Figure adapted from reference*[2]



Importantly, the use of FRET allowed spatial identification of chain conformation by use of confocal microscopy. This was used as a basis to spatially resolve conformation across complex interfaces, such as the hexane-water interface. It was found that at the interface of these immiscible liquids, there is a region of ~50 μm of low FRET (high donor fluorescence), indicating that the polymer brush is fully extended.

4. Conclusions

Through contact angle and SFG studies, we have shown how PNIPAM polymer brush surfaces adapt to being wet by liquid droplets, and remember this conformation of extended periods of time. By integrating FRET fluorophores within the PNIPAM brush layers, we have been able to spatially resolve chain conformation effects in bulk liquids, and across complex interfaces. Together, our works highlight how PNIPAM surfaces respond to solvation, and how this can be leveraged towards developing materials that spatially report conformational effects.

Acknowledgements

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CATALYTIC CHAIN TRANSFER (CCT) IN RADICAL POLYMERISATION TO GIVE CONTROLLED POLYMER STRUCTURES IN AN INDUSTRIAL USEFUL AND PRACTICAL WAY

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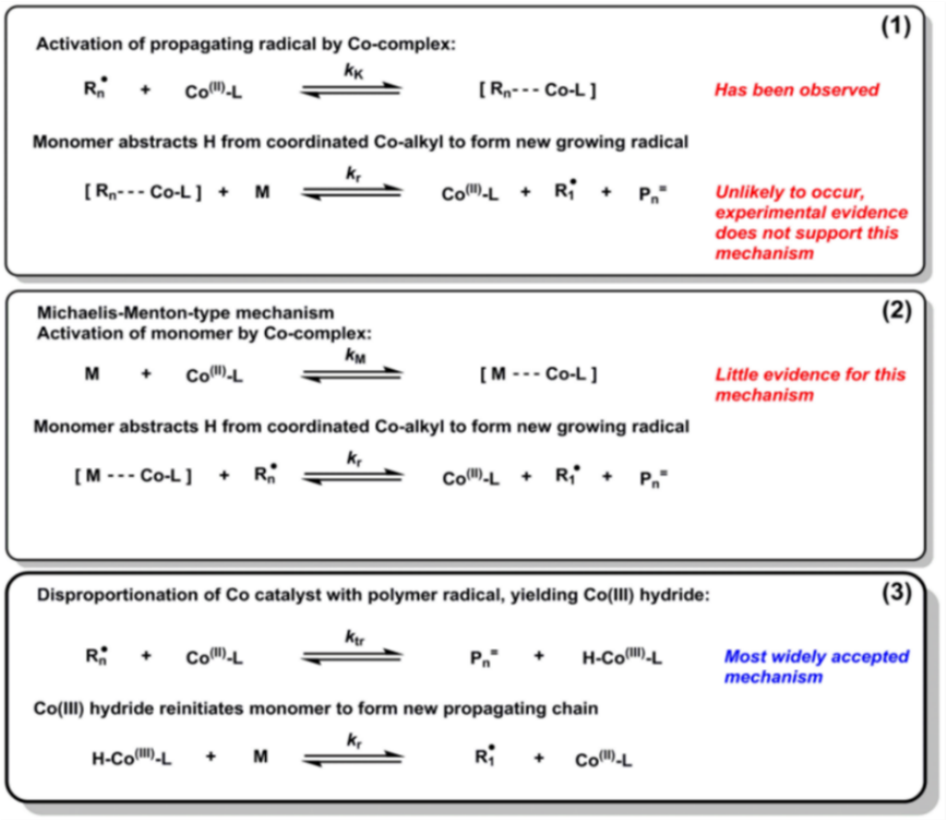
Catalytic chain transfer polymerization (CCTP) is an efficient and versatile technique for the synthesis of low molecular weight functional polymers/oligomers in free radical polymerization (FRP). The technique is based on the use of certain low spin Co(II) complexes which catalyze the chain transfer of hydrogen to monomer reaction and also provides a high level of vinyl ω-end group functionality. Due to their high chain transfer constants, Co(II) complexes are efficient in low concentrations (ppm to monomer). The effectiveness of the catalysts, and the fact that radical addition to the vinyl end group of CCTP macromonomers forms adducts that readily undergo β-scission, allow them to function as addition-fragmentation chain transfer agents (CTAs) and render CCTP extensively applicable in industry.

CCTP was discovered in the USSR in the mid-1970s, when Smirnov and Marchenko were investigating cobalt porphyrins (Figure 1-2, (1)) catalysts for the redox decomposition of peroxy initiators for radical polymerisation. The observation that some Co(II) complexes appeared to inhibit FRP of methyl methacrylate (MMA) lead to further investigation. Thus, further studies from Gridnev, DuPont O'Driscoll, the Glidden Paint company and ICI/Zeneca have led to a significant understanding of the catalytic process and to the very active cobaloxime catalysts being developed (Figure 1-2, (2, 3)).

In general, the most effective CCT agents are low-spin cobalt$^{(II)}$ complexes with octahedral geometry derived from a square planar ligand with two axial sites. Co(II) is a $3d^7$ electron system and can exist as either low- or high- spin (*i.e.* one or three unpaired electrons Figure 1-3**)**), so the choice of the correct ligand to give a low-spin complex becomes an important aspect of catalyst design for a CCT agent.

Figure 1. *Reaction scheme for a CCTP reaction*



Products from a CCTP reaction have a terminal vinyl group which are available for further reaction. Addition of a radical from a propagating polymer gives a relatively stable radical which is prone to fragmentation as a S-free RAFT agent or chain termination by abstraction of a hydrogen atom.

***Figure 2**. General structure of a product from CCTP*

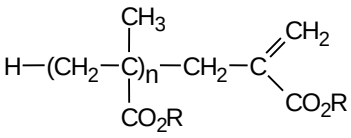
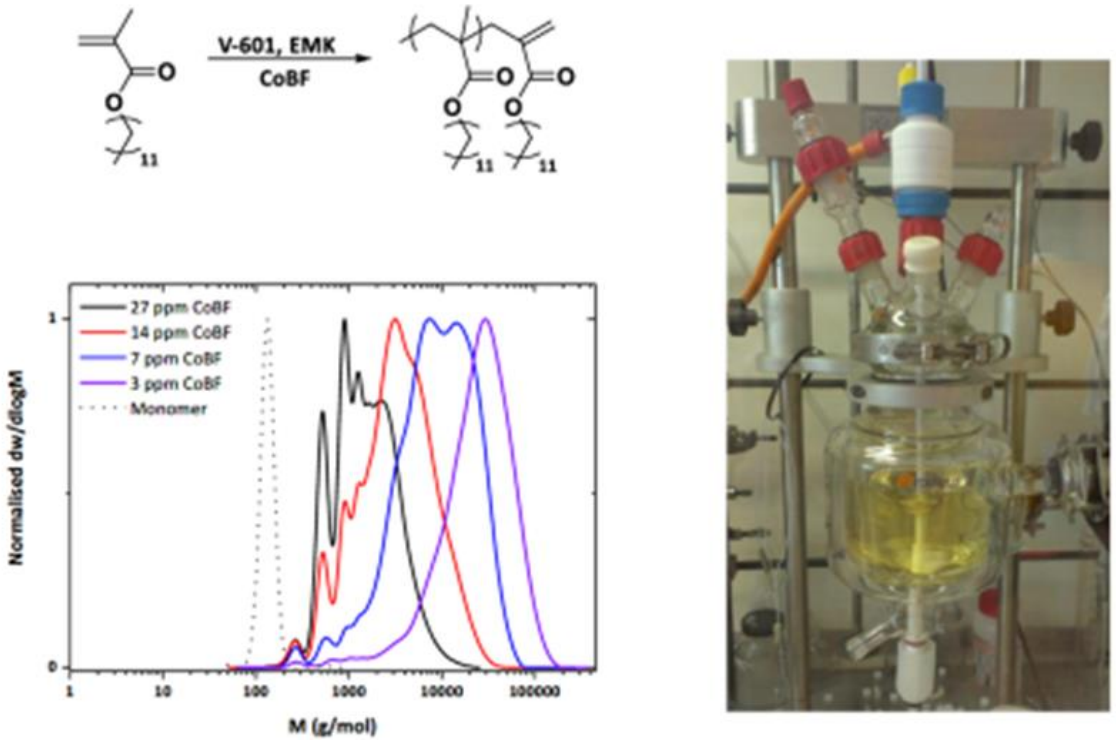


***Figure 3.** Reaction of lauryl methacrylate to give a series of low MW vinyl functional polymers for use as viscosity modifiers*



This talk will give examples of where we have been using this chemistry in the areas of

- ✓ Low molecular weight dispersants and viscosity modifiers
- ✓ Thiol-ene and hydroamination functionalization
- ✓ Addition fragmentation reagents for use in additive manufacturing and 3D printing
- ✓ Block copolymers of polyethene and polymethacrylates

EMERGING ROLE OF CARBONIC ANHYDRASE INHIBITORS

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Inhibition of carbonic anhydrase (CA, EC 4.2.1.1) was clinically exploited for decades, as most modern diuretics were obtained considering as lead molecule acetazolamide, the prototypical CA inhibitor (CAI).

The discovery and characterization of multiple human CA (hCA) isoforms, 15 of which being known today, led to new applications of their inhibitors. They include widely clinically used antiglaucoma, antiepileptic and antiobesity agents, antitumor drugs in clinical development, as well as drugs for the management of acute mountain sickness and idiopathic intracranial hypertension.

Emerging roles of several CA isoforms in areas not generally connected to these enzymes were recently documented, such as in neuropathic pain, cerebral ischemia, rheumatoid arthritis, oxidative stress and Alzheimer's disease.

Proof-of-concept studies thus emerged by using isoform-selective inhibitors, which may lead to new clinical applications in such areas.

Relevant preclinical models are available for these pathologies due to the availability of isoform-selective CAIs for all human isoforms, belonging to novel classes of compounds, such as coumarins, sulfocoumarins, dithiocarbamates, benzoxaboroles, apart the classical sulfonamide inhibitors.

The inhibition of CAs from pathogenic bacteria, fungi, protozoans or nematodes started recently to be considered for obtaining anti-infectives with a new mechanism of action[1-6].

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MACRO Iași 2021

HYBRID FIVE- AND SIX-MEMBER RING AZAHETEROCYCLES: SYNTHESIS AND APPLICATIONS

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1. Introduction

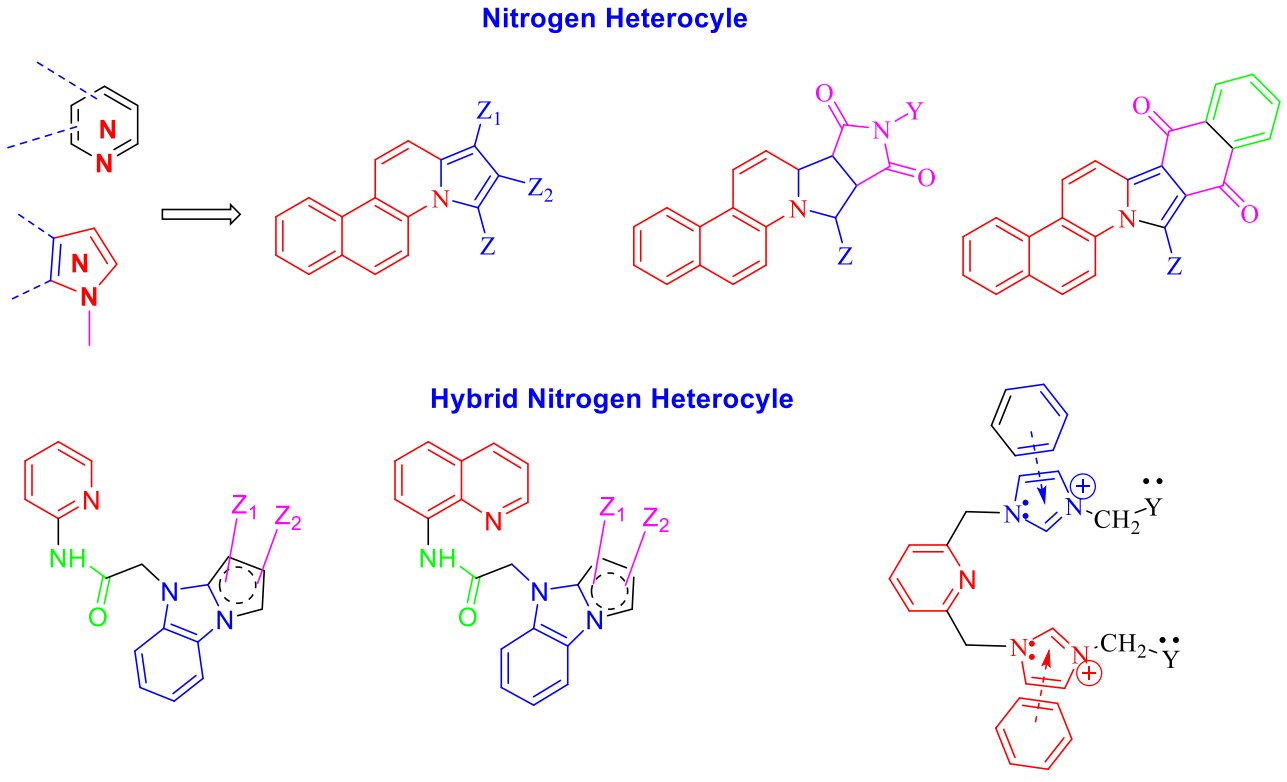
Five- and six-member ring azaheterocyclic and their hybrids compounds are reported as highly valuable materials in medicine and pharmacy (drugs, as antibacterial, antifungal, anti-inflammatory, anti-HIV, anticancer, antihypertensive, anticoagulants, diuretics, etc.), opto-electronics (fluorescent and electroluminescent materials, semiconductor devices, sensors and biosensors), agriculture (mainly herbicides and grow up factors), etc. This is why, obtaining of such derivatives continues to arouse a strong interest from academia and industry.

2. Experimental

The structures of newly hybrid sulfanylamide/benzimidazole quaternary salts were proved using Nuclear Magnetic Resonance (NMR) experiments (^{1}H, ^{13}C, 2D-correlations). The NMR apparatus (Bruker Advance III 500 spectrometer) is equipped with a 5 mm PABBO detection probe, operating at 500.1 MHz for ^{1}H and 125 MHz for ^{13}C. The chemical shifts (δ) are reported in ppm and the coupling constants (*J*) in Hertz.

3. Results and discussion. Conclusions

As part of our ongoing research in the field of azaheterocyclic derivatives, we present herein some representative results obtained by our group in the field of five- and six-member ring azaheterocyclic and their hybrid compounds.[1-5]



The chemistry involves straight and efficient organic chemistry reactions: alkylation, acylation, estherification, etherification, 3+n cycloadditions. Some of the new setup procedures were performed by using microwave and ultrasounds technology, as environmentally friendly methods.

The antibacterial, antifungal, antituberculosis and anticancer activity of compounds was determined, some of the compounds having an excellent biological activity. For the most active compounds, a complete ADMET studies have been performed with very good results.

The molecular docking experiments suggest important clues concerning the mechanism of actions of our nitrogen heterocyclic systems. Some of the obtained compounds are promising leading drug candidates.

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RECENT CONCEPTS IN ELECTROCHROMIC POLYMERS CONTAINING TRIARYLAMINE AS ELECTROACTIVE UNIT

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1. Introduction

Electrochromic (EC) polymers can be regarded as smart materials that reversibly change one of the optical characteristics, like absorbance, transmittance, or fluorescence in response to an applied voltage, either by an electron-transfer (redox) process or by a sufficient electrochemical potential[1,2]. EC devices attracted large applicative interest in many fields, such as optical storage, automotive rearview mirrors, smart windows in buildings, displays, electronic papers, eyewear, or energy storage devices.[3-7] Depending on the material used, EC devices can be classified into inorganic metal oxides, metal complexes, hybrid materials, metal plasmonics–metal/alloy, and organic molecules/polymers.[2] Nowadays, EC polymers are of particular interest due to their low cost, easy processing and facile control of perceived color. Since EC polymers display long lifetimes, high optical contrast, stable oxidation states, excellent switching reproducibility, and flexibility, they can be used in flexible electronics.

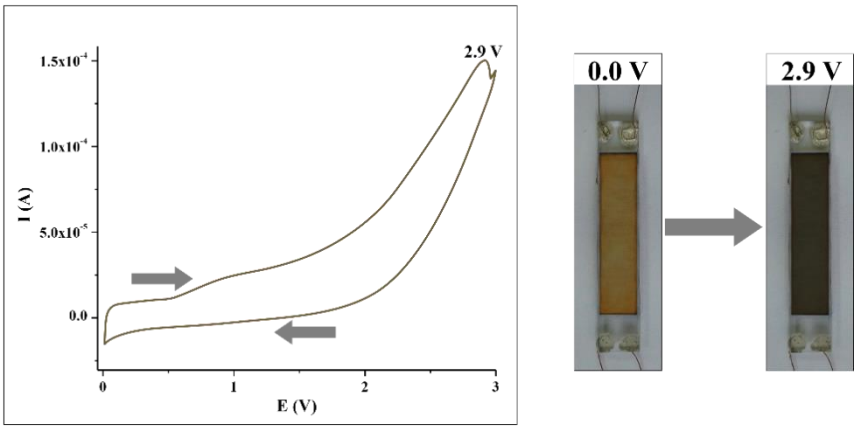
Several polymers are even more interesting since they can show more than two reduction/oxidation (redox) states and generate multiple colors.[8] On the other hand, triphenylamine (TPA) and its derivatives known as triarylamines form a class of versatile redox-active molecules widely investigated owing to their promising hole transporting ability.[9,10] Common applications of triarylamine derivatives include opto-electronic devices, like organic light emitting diodes (OLEDs),[11] electrochromic devices,[12] dye sensitized solar cells,[13,14] or organic solar cells (OSCs).[15,16] The electron-rich property of TPA has also been applied in electrochemical energy storage[17] and electrical memory devices.[18,19] The use of triarylamine derivatives in such applications is attractive due to a number of desirable properties, such as the synthetic versatility and the possibility of finely modulation of their redox and light absorption characteristics. Moreover, the introduction of bulky triarylamine into macromolecular compounds hampers the aggregation by reducing the crystallization propensity and improves the hole transporting ability. Until now, a large library of TPA-based electrochromic (EC) polymers have been investigated and recommended for use in practical applications.[20]Among them, high-performance polymers (aromatic polyimides or polyamides), conjugated polymers, epoxy resins, polysiloxane gels, metal complexes, and small molecules were successfully developed and nearly all these EC materials revealed specific and attractive EC features[21]. However, non-conjugated polymers such as polyimides, polyamides, or polyazomethines have not been so frequently studied as EC materials. The change of color can be adjusted with the change of the redox state of polymers. Due to their excellent thermal stability and film forming ability when adequately modified, these polymers are potential candidates in the EC field.

2. Results and discussion

Along these lines, here we summarize some of the newly developed triarylamine-based polymers, with emphasis on structural strategies and their performance as electrochromic materials. As well, the own structural approach in the design and synthesis of novel aromatic polyimides with donor-acceptor topology is presented. In this regard, the electro-optical features and performance of four polyimides containing in the same polymeric chain 1,3,4-oxadiazole substituted di-/triphenylamine and naphthalene or perylene units were investigated. Although the polyimides proved to be soluble only in polar aprotic solvents and at small concentrations, their processing into thin coatings with various morphologies proved to be feasible. These polyimides displayed excellent thermal stability, up to 400 °C, but no clear glass transition temperature up to 300 °C. Two of the investigated polyimides that exhibited electrochromic behavior during anodic scan in a classical electrochemical cell were tested in electrochromic devices, and their performance is discussed. The spectroelectrochemical measurements evidenced the evolution of some absorption bands upon potential increase, being associated with both polarons/bipolarons and radical cations formation. The

electrochromic devices rendered color variation between neutral and oxidized form of the polymers (Figure 1).

Figure 1. *The I–V curves of an EC device realized with a triarylamine-based polyimide and the color variation during potential sweep*



It was found that the response time to coloring and bleaching is low. The recovery of electrochromic devices was almost completed after tens of cycles. The obtained results demonstrated that efficient electrochromic properties in the anodic region can be obtained even with electrochemically active *n*-type polyimides by judicious material design.

Acknowledgements

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THERMAL ANALYSIS - VALUABLE TOOL FOR STUDYING POLYMER COMPOSITES

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1. Introduction

The result of a thermal analysis is a curve known as thermogram. A thermogram represents the mass change *vs* temperature or time of an analysed sample. It characterizes the sample and reveals the thermal and oxidative stability, as well as its composition.[1] There are a number of applications of thermal analysis regarding the composition of solid mixtures, developed to great extent during the last years.

One area is the analysis of the micro-plastics existent in the environment. The non-uniform distribution of these particles imposes complementary analyses beside FTIR and Raman.[2] The combination of thermo-analysis with chromatographic separation may identify and even quantify different polymers present in the organic sediments.[3] Application of thermal analysis for micro-plastics characterization increased lately. The method is based on the identification of the polymers by their degradation products, presenting a good selectivity and sensitivity due to the new automated procedures.[4] Thermo-gravimetric analyses (TGA) coupled with FTIR or MS were largely applied in the area.[5] TGA was also used for finding the composition of different geo-polymers,[6] or polylactic acid polymers reinforced with natural or synthetic fibers.[7] TGA profiles are efficient for a qualitative-quantitative determination of main components of mycelia from wood-decay fungi,[8] poplar wood,[9] or post-consumer plastic waste.[10]

This work presents the thermal analysis of two cryogel composites intended as carriers for immobilization of enzymes. The thermal properties of these polymers as well as those of a bio-composite with *laccase* are discussed.

2. Experimental

A potential carrier for enzyme immobilization was prepared according a previously described procedure, from a mixture of PVA and CMC.[11]

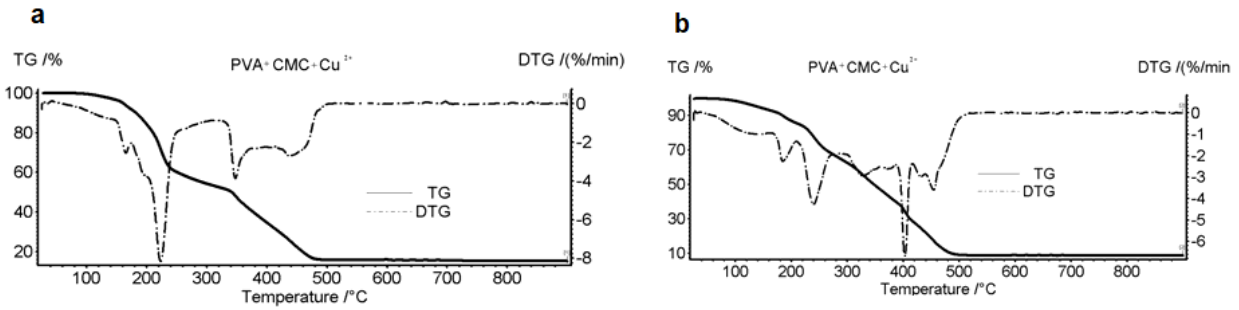
The PVA cryogel from the next study was prepared by cryotropic gelation, on moderate freezing, followed by storing in a frozen state and thawing of solutions containing the polymer precursors.[12] This polymer carrier was functionalized by treatment with glutaraldehyde and a commercial *lacase* was covalently linked, as described before (see procedure a).[13]

The thermal analyses have been performed with a Netzsch type 449C STA in the first case (PVA and CMC)[11] and Luxx STA Jupiter in the second case (PVA and enzyme).[14] The samples were placed in alumina crucible and heated with 5 or 10 K min^{-1}, respectively.[11,14]

3. Results and discussion

The first carrier was stabilized by cooper salt addition. A blue colored solid resulted. The thermal behavior of the composite compared with that of the component polymers confirmed its composition.

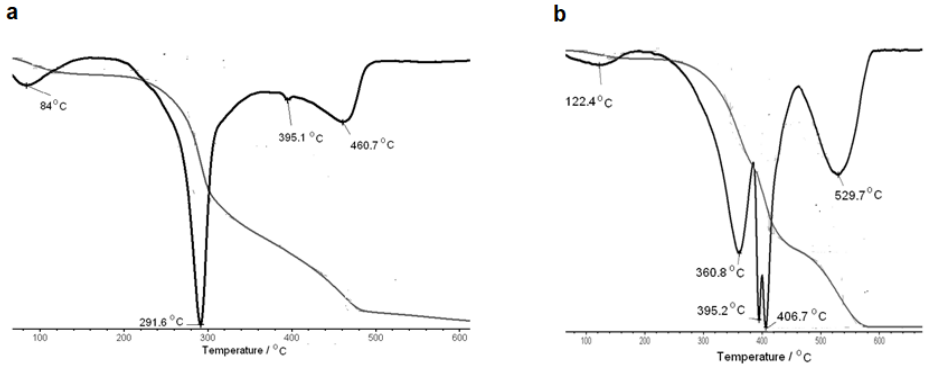
***Figure 1**. Thermal behavior of cryogel polymer composite PVA and CMC as cooper salt a) initial; b) after being kept in water*



The stability of the new carrier on water treatment was analyzed. Changed aspects of TG and DTG curves were observed (Figure 1). The partial water solubilization of the CMC cooper salt was evidenced by UV-Vis spectroscopy.[11] [11]

Information on the properties of the immobilized enzyme and the components of the catalyst have been obtained from the thermal analyses of the *laccase* PVA bio-composite. The higher stability of the commercial enzyme in comparison with an analytical sample was evidenced. An increase of the carrier stability by functionalization was also observed (Figure 2).[14] Other advantages of the immobilization process will be described.

***Figure 2**. Thermal behavior of cryogel PVA polymer a) initial; b) functionalized*



4. Conclusions

The thermal analysis proved to be a useful tool for the study of composite polymer materials, providing information about their composition and thermal stability.

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POLY(2-ISOPROPENYL-2-OXAZOLINE) - VERSATILE PLATFORM FOR ADVANCED MULTIFUNCTIONAL MATERIALS

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Multifunctional materials are designed to meet specific requirements through tailored properties. Nowadays, there is a high demand for "smart" materials with integrated functionalities that make them responsive to multiple stimuli, switchable and adaptive. "Smart" or stimuli-responsive materials can alter their chemical and/or physical properties upon exposure to external stimuli.[1]

The development of specialized stimuli-responsive polymers with potential applications in harvesting the photomechanical energy, healable hard coatings, self-repellent surfaces, detecting and sensing is witnessing exciting progress.[2] However, designing accessible stimuli-responsive polymers that can function as multi-signal processing sensors is of particular interest.

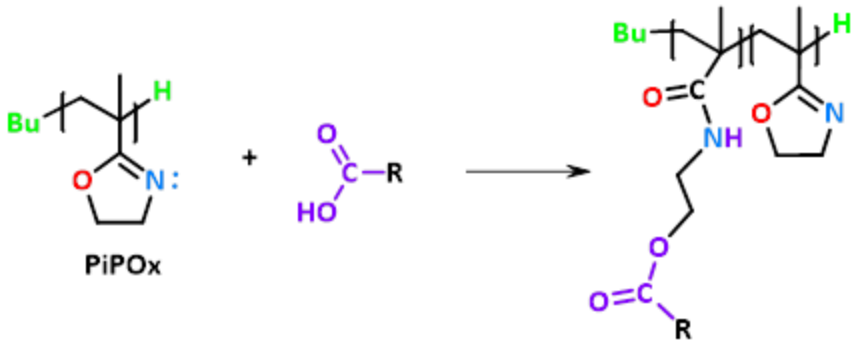
Inspired by this promising progress and current interest, we envisioned that poly(2-isopropenyl-2-oxazoline) (PiPOx) can stand as a reactive functional platform for the synthesis of well-defined stimuli-responsive materials.

2-Isopropenyl-2-oxazoline (iPOx) is a monomer belonging to the 2-oxazolines class, which via its 2-vinyl substituent, can be polymerized to poly(2-isopropenyl-2-oxazoline) (PiPOx), with the retention of the 2-oxazoline ring as reactive side-chain functionality providing a platform for a variety of post-polymerization functionalization methods.[3,4] iPOx was successfully polymerized via free radical polymerization[5], rare earth metal group transfer polymerization[6] and more recently living anionic polymerization[3] using commercially available n-butyllithium giving access to polymers with controlled molecular weight and narrow dispersity. PiPOx is a versatile polymer which is soluble in water and various organic solvents, exhibits high thermal and hydrolytic stability and is therefore storage stable at ambient conditions.

Additionally, PiPOx was shown to be biocompatible, rendering it suitable for medical and pharmaceutical applications.[7] The side chain 2-oxazoline rings in PiPOx are susceptible to quantitative polymer analogous reactions.[3,4] Statistical copolymers of iPOx and other vinyl monomers are attractive materials because of the synthetic simplicity of modification by polymer analogous reactions allowing the development of structure–property correlations.[3,5,8]

Compared to other polymeric scaffolds used for polymer analogous reactions, the ring opening addition reaction of iPOx functionalities does not generate any by-products and does not require any catalyst when reacted with carboxylic acids (Scheme 1).

Scheme 1. *The polymer analogous modification reaction of PiPOx with carboxylic acids leading to partially functionalized copolymers*

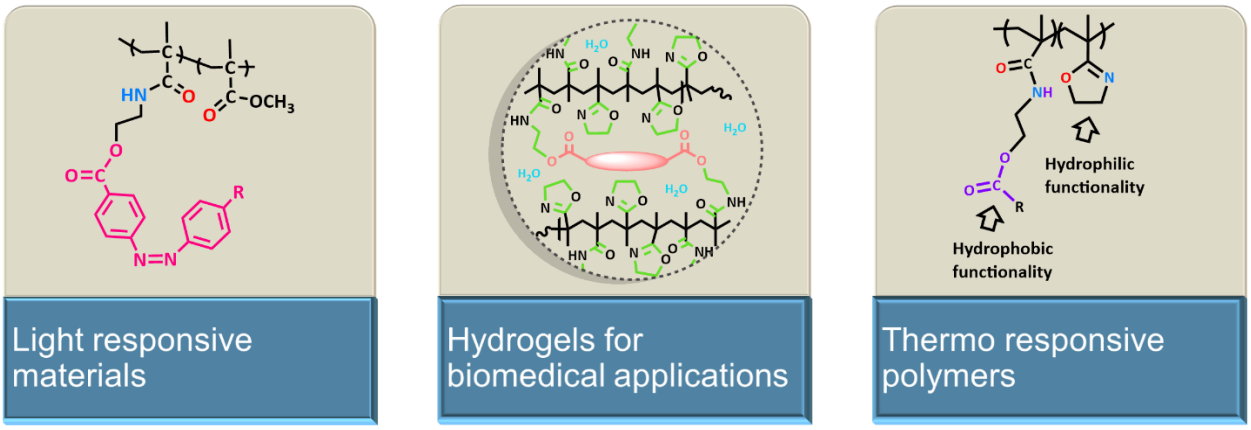


Post-polymerization modification reaction with (di)carboxylic acids is a versatile and robust reaction which enables the synthesis of soluble as well as 3D materials functional materials with a variety of applications (Figure 1). This versatile and functional platform was used for the preparation of thermoresponsive

copolymers with tunable lower critical solution temperature (LCST) behavior[3], hydrogels[9], molecular brushes[10] and materials for photonics.[11] Moreover, PiPOx hydrogel materials with properties that can easily be tuned from soft, to ultra-tough or elastic, simply by altering the nature of the crosslinker, were obtained.[12]

In this contribution we will outline the versatile one-pot multi-modification approach of PiPOx to synthesize stimuli-responsive materials with target properties. The emerging applications of these polymers as temperature sensors,[3] ophthalmologic biomaterials,[9] materials for detection and sensing applications, drug delivery[13], though hydrogels[12], and water purification materials[14] will be discussed.

Figure 1. *Applications of PiPOx based materials obtained by post-polymerization modification reaction with (di)carboxylic acids*



Acknowledgements

F.A.J. and V.V.J. acknowledge the Romanian Ministry of Research, Innovation and Digitalization, CNCS/CCCDI – UEFISCDI, project numbers PN-III-P1-1.1-TE-2019-0538 and PN-III-P1-1.1-TE-2019-1696 within PNCDI III, for financial support.

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POLYTRIAZOLE A NEW POLYMERIC PLATFORM FOR A WIDE RANGE OF MEMBRANE SEPARATIONS

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1. Introduction

Separation processes are essential in the chemical, pharmaceutical, and petrochemical industries. These industries used conventional separation techniques such as distillation, adsorption, evaporation, and extraction, which have high carbon footprints and are energy-intensive[1]. For example, processes like distillation used 10–15% of the world's energy consumption[2]. Additionally, conventional separation represents up to 40–70% of both capital and operating costs.

Therefore, membrane technology can totally or partially replace the traditional separation methods because it has better energy efficiency, low carbon footprint, and is relatively easy to scale up. However, there is still a lack of separation materials to handle the industries conditions and the complex mixtures. Therefore, more materials that are easy to process and are stable in a wide range of solvents and a wide range of pH are required to meet the industry demands. In addition to solvent and pH resistance, the membranes need to be stable at high temperatures since most of the separations are taking place in the range of 60-90 °C or even higher[3].

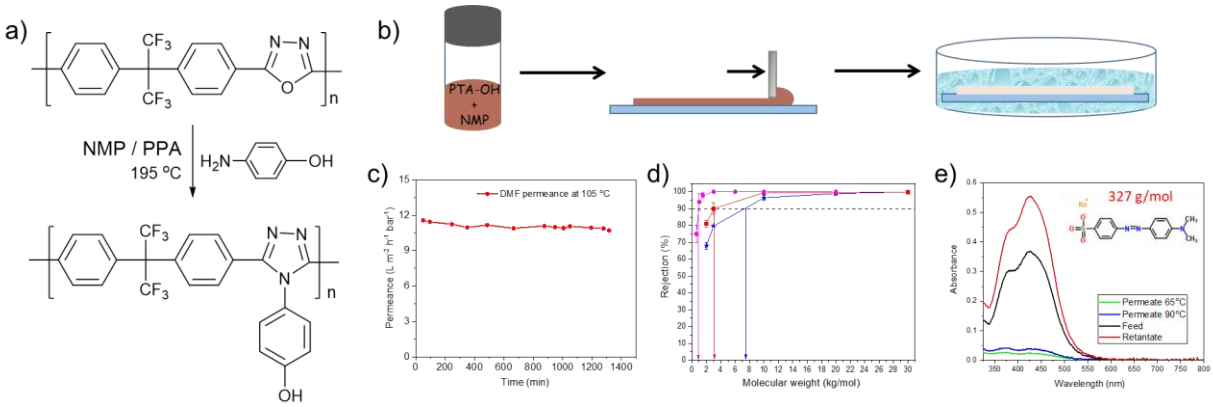
2. Results and discussion

In this paper, we report different strategies to prepare stable polytriazole membranes for organophilic filtration. We used the polytriazole with pendant hydroxyl (OH) groups because it can easily be synthesized in large amounts by reacting polyoxadiazole precursor with 4-aminophenol at high temperature (Figure 1a). The resulting polymer shows good mechanical properties and high thermal and thermal-oxidative stability[4,5]. Additionally, the presence of the pendant OH groups makes this polymer processable into membranes by phase inversion using a wide range of solvents (Figure 1b).

The resulting membranes were crosslinked by exposing them to aliphatic diepoxy crosslinkers. To demonstrate the robustness of the crosslinked polytriazole membranes, we permeated dimethylformamide (DMF) for 22h at 105 °C (Figure 1c). We obtained a constant permeance value, which indicates no significant physical aging and compaction during the experiment, demonstrating that the flexible crosslinker enhances mechanical membrane stability. Using different casting solutions in N-methyl-2-pyrrolidone and adjusting the length of diepoxy crosslinkers, it is possible to tailor the rejection of the polytriazole membranes to cover from the lower end ultrafiltration (7000 g/mol) to the upper end of nanofiltration (3000 g/mol). Moreover, due to the versatility of this polymer, we could tune the morphology of the membrane to obtain a rejection in the range of 1000 g/mol by using ionic liquids. The permeances were in the range of 4 - 10 L m^{-2} h^{-1} bar^{-1} (Figure 1d).

In addition, by direct crosslinking of the polytriazole membrane at high temperature, we obtained a rejection >95% for methyl orange (327 g/mol) in DMF, which is maintained at 60 °C or 90 °C filtration (Figure 1d).

Figure 1. *(a) Synthesis of the polytriazole with hydroxyl groups (PTA-OH); (b) Schematic illustration of the phase inversion method; (c) DMF permeance for 22 h through a crosslinked polytriazole membrane at 105 °C; (d) Rejection of different molecular weights of PEG during the filtration in DMF using different crosslinked polytriazole membranes; (e) UV-VIZ spectra for methyl orange separation in DMF at 30 °C, 60 °C and 90 °C*



3. Conclusion

In conclusion, using the right strategy to prepare crosslinked polytriazole membrane, we can cover all organic solvent nanofiltration ranges, making this polymer a starting platform for the chemical and petrochemical industry.

Acknowledgements

The authors thank King Abdullah University of Science and Technology (KAUST) for the financial support.

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DYNAMIC MECHANICAL ANALYSIS: WHERE WE ARE IN ICMPP AND WHAT CAN BE AHEAD

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1. Introduction

Dynamic mechanical analysis (DMA) is rheology applied to solid (polymeric) materials that have a well-defined shape. Namely, oscillatory tests in rheology are referred to DMA.[1] In the field of polymers investigators are interested in correlating the structure of the polymer with their properties in order to run the synthesis in the intended direction or to evaluate the usability of the polymeric material for a specific applicability. The response of polymers to oscillatory deformation is viscoelastic. The output characteristics depend not only on the structure, but also on time/temperature. The presentation will cover significant results obtained with polymers synthesized in Petru Poni Institute of Macromolecular Chemistry (ICMPP), Iasi, in the last years[2] and will outline few directions for the foreseeable future.

2. Experimental

Dynamic mechanical experiments were performed on a Perkin Elmer DMA analyzer in tension, bending and shear mode. Samples as films, bars and rectangular geometry were used. The isochronal experiments were run by increasing the temperature in ramp mode (2 °C/min, 1 Hz) until the temperature where on the elastic modulus value was too small to allow the experiment to be continued. Multifrequency experiments were conducted by raising the temperature in step-scan mode, with the step of 2 °C/min, the soak time 300 s and the working frequencies between 0.01 and 100 Hz. The changes of elastic modulus (E'), loss modulus (E'') and loss factor (tan δ) were recorded as a function of temperature and frequency.

3. Results and discussion

For a skilled user the DMA result represents the fingerprint of a polymer. A specific trend of the viscoelastic parameters with temperature and time for a specific polymer can be taken as the feature of it. Figures 1 and 2 displays the variation of the viscoelastic parameters for an amorphous glassy polymer – poly(methyl methacrylate) (PMMA), a high performance polymer (polyimide – PI), a polyurethane elastomer and a semicrystalline poly(lactic acid) - PLA.

Figure 1. *Viscoelastic behavior of PMMA and a polyimide in a single frequency DMA experiment*

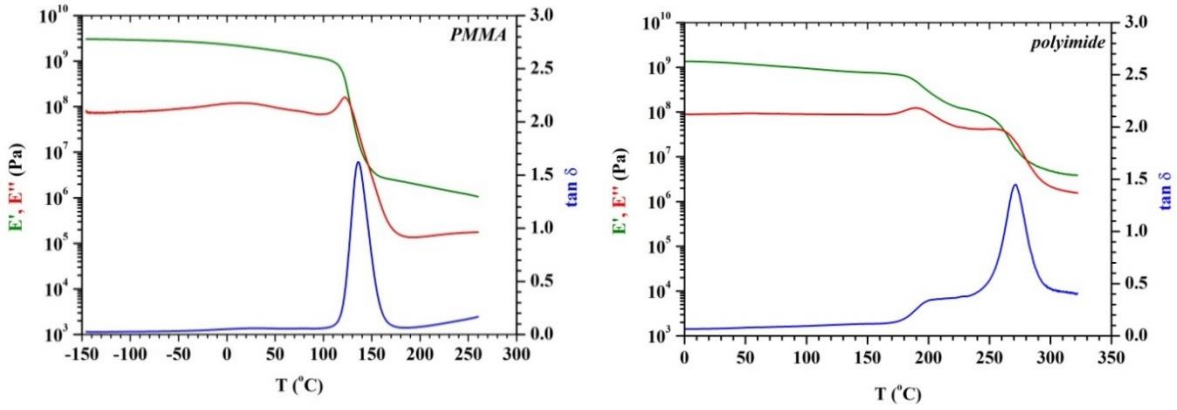
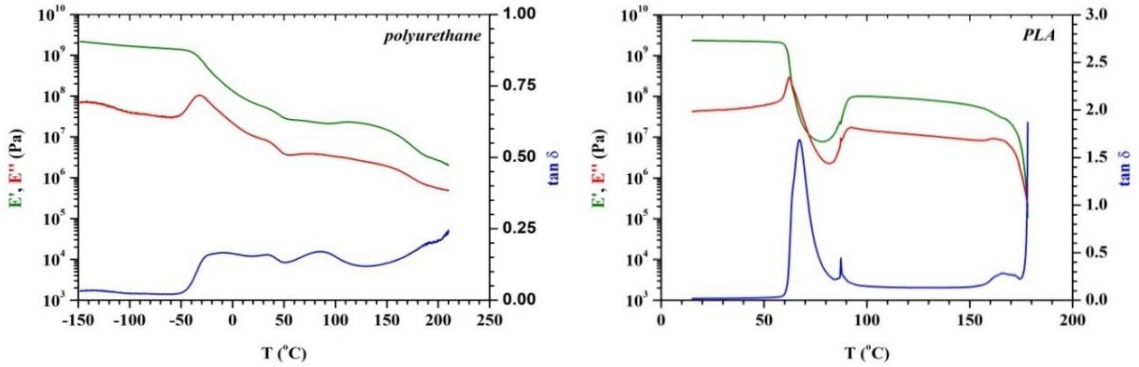


Figure 2. *Viscoelastic behavior of a polyurethane and a PLA in a single frequency DMA experiment*



The experiment captures the evolution of the polymer sample from the glassy state, through glass transition and rubbery plateau, until the mobility of polymer chains is so high that they slip past each other in the flowing region. Depending on the nature of the polymer (thermoplastic, thermosetting, elastomer), one of the two final steps can be absent. A polymer scientist is, by far, mostly interested in the temperature of α-relaxation, that is associated with the glass transition temperature (T_g). In contrast to other procedures (like DSC), DMA is to a considerable extent more sensitive in perceiving this temperature that practically dictates the boundaries for the applications. In general, any drop of E' and any peak of E'' and tan δ has a meaning; however, not any tan δ peak can be associated with a relaxation. Despite the fact that it is not that obvious as DSC in making a clear distinction between a glass transition (relaxation) and a melting/crystallization (kinetic process), there is the option to make the difference. A multifrequency experiment distinguishes the frequency-dependent phenomena (glass transition) from the frequency-independent phenomena (melting, crystallization). One striking particularity of the DMA behavior of each polymer included in Figures 1 and 2 are: PMMA (T_g~ 135 °C) – a classical viscoelastic behavior of an amorphous polymer; polyimide (T_g ~ 275 °C)– the very high value of the glass transition temperature and the presence of residual amic acid segments; polyurethane (T_g between -50 and 50 °C)– large glass transition region (hard and soft segments), network features (low tan δ value, E'>E'' all over the temperature investigated; PLA (Tg ~ 65 °C)– cold crystallization on the rubbery plateau. Time-temperature equivalence is typical for the viscoelastic behavior of polymeric materials and is used, under certain conditions, for the prediction of long-term properties[3]. In this sense, few examples will be included in the presentation. Also, a challenging issue is the utility of DMA in evaluating polymers with dynamic covalent bonds[4].

4. Conclusions

DMA represents a must-have analytical technique for the investigations of some unique properties of polymers. It is a sensitive mean to detect secondary and primary relaxation in polymers, while a temperature scan evaluates the E' and E'' moduli in a single experiment. Nevertheless, the experiment cannot be performed on shapeless samples and the correctness of the dimensions is crucial. Depending on the final purpose, DMA can be time-consuming and the insight of the experimenter in interpreting the results is crucial.

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ELECTROSPUN POLY(METHYL METHACRYLATE)/TiO_2 COMPOSITES FOR PHOTOCATALYTIC WATER TREATMENT

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1. Introduction

The creation of cost-effective and advanced materials for water treatment is one of the ongoing challenges of the century. Among the various new materials, electrospun membranes are considered to be the most versatile candidates for effective treatment of water, filtration and separation because of their high surface area, high porosity and lightweight.

Currently, a great attention has been paid on the photocatalysis as one of the most effective and ecofriendly technique for degradation of many organic pollutants. In this relation, one of the most reported and commonly used photocatalyst in the removal of organic pollutants is titanium oxide (TiO_2) because of its ability to generate hydroxyl radicals ($HO^{\bullet}$) and superoxide radical anions ($O^{2\bullet-}$) upon UV-light irradiation. Particularly, various studies revealed that poly(methyl methacrylate) (PMMA) is an appropriate host matrix for TiO_2 because of its excellent transparency for light, good environmental inertness, chemical and thermal stability, and relatively low cost.

Electrospinning has emerged as an appropriate technique to prepare polymer composites loaded with inorganic particles. Although electrospun PMMA/TiO_2 composites have been recently reported, to the best of our knowledge, there is no thorough study on the effect of TiO_2 nanoparticles as a filler in uniform defect-free fibers on the properties of electrospun PMMA/TiO_2 composites. In the past few years, we have demonstrated the possibility for fabrication of multifunctional hybrid materials by electrospinning.[1-3] Electrospun materials based on poly(3-hydroxybutyrate) and TiO_2 with tailored design, displayed excellent stability and preserved almost completely their photocatalytic activity.

2. Experimental

Solutions of PMMA (15% w/v) in DMF were prepared by heating at 50°C using a reflux condenser. In order to obtain PMMA/5TiO_2 and PMMA/10TiO_2 composites, TiO_2 nanopowder (5 and 10 wt. % with respect to PMMA) were added to the PMMA solutions. The obtained dispersions were homogenized by sonication for 1 h in an ultrasonic bath.

The experimental electrospinning setup was comprised of high voltage DC power supply, rotating collector, needle for syringe (i.d. 0,6 mm × o.d. 0,9 mm) and syringe pump for delivering the spinning dispersions. Electrospinning of PMMA solution and PMMA/TiO_2 dispersions was performed at 15 kV applied voltage, needle tip-to-collector distance of 10 cm, 2 ml/h flow rates and collector rotation speed of 1200 rpm. These optimal electrospinning conditions were found by testing of various combinations of processing parameters (applied voltage, flow rates and needle tip-to-collector distance).

3. Results and discussion

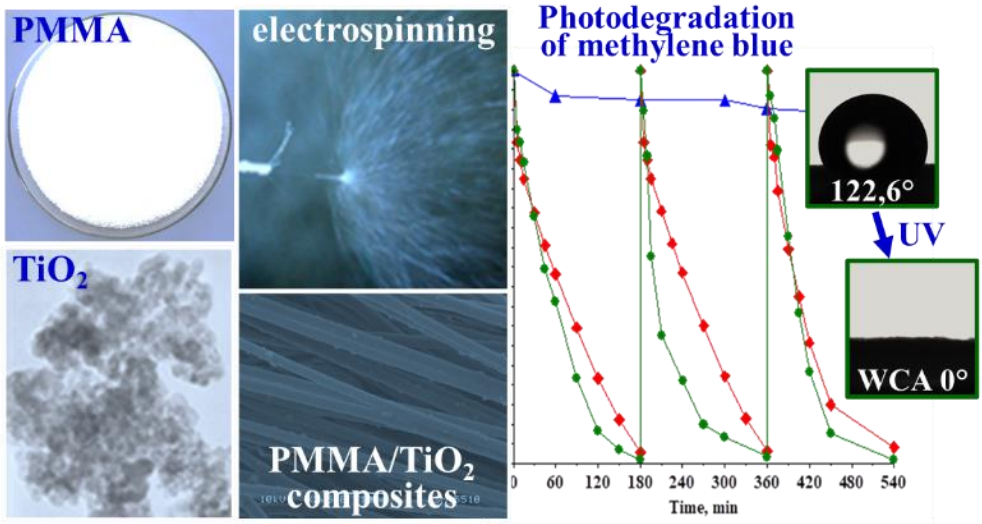
In the present study electrospinning was successfully used for one-step fabrication of poly(methyl methacrylate) (PMMA) fibers loaded with an inorganic photocatalyst – TiO_2. By tuning the PMMA/TiO_2 ratio and the electrospinning conditions (applied voltage, needle tip-to-collector distance and flow rates), PMMA/TiO_2 composites with selected organic/inorganic ratios, tailored design and targeted properties were obtained.

The morphology of the electrospun composites was affected by the amount of TiO_2 incorporated into PMMA fibers as shown by SEM analyses. The SEM micrographs clearly shows that the selected concentrations and electrospinning conditions lead to the fabrication of cylindrical, uniform and defect-free fibers with a certain fiber alignment in the direction of collector rotation. Interestingly, the surface of the composite fibers was decorated with TiO_2. Moreover, with increasing the TiO_2 concentration into PMMA

fibers, the number of the particles onto the fiber surface increase.

In addition, the inorganic photocatalyst had an impact on the wettability of the electrospun composites. Contact angle measurements revealed that the wettability of the composites might be easily changed from hydrophobic to superhydrophilic after 1 h UV-light irradiation. In particular, TiO_2 had slight impact on the thermal stability and optical properties of the composites.

It was found that incorporation of the inorganic component resulted in a significant increase in the modulus of elasticity and tensile strength, and a decrease in elongation at break. Furthermore, PMMA/TiO_2 composites preserve almost completely their photocatalytic activity and show excellent photocatalytic efficiency against model organic pollutant – methylene blue, even after threefold use. Thus, the proposed original and simple approach is very promising for the future development of highly efficient membranes for photocatalytic water treatment.



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ELECTRONIC STRUCTURE AND ISOMERIZATION MECHANISM OF AZOBENZENE DERIVATIVES DURING THE REACTION PATHWAYS FOLLOWING THE GROUND AND EXCITED-STATE LEVELS

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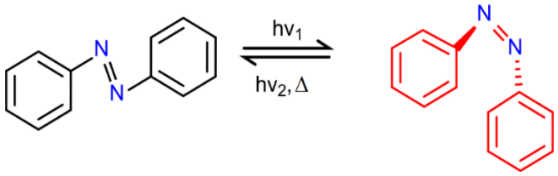
1. Introduction

Molecular photoswitches are known as light-responsive systems that are designed to enable to change the internal coordinates with high spatiotemporal resolution. These classes of compounds have found applications in nanomachines and smart materials, actuators, light-sensitive materials, design of light-modulated molecular devices, photoswitches for protein modulation.[1]

Azobenzene is a chemical compound that belongs to the class of photochromic molecular systems. Moreover, azobenzene compounds represent molecular systems that are capable to modify the intramolecular coordinates during the isomerization process, resulting distinct geometries with temporal and spatial precision. In the case of the azobenzene chemical system, two isomers have been proposed *trans* and *cis* isomers. The equilibrium geometry of *trans* isomer in ground state has an orientation to be a nearly planar or coplanar structure[2,3] and it is the most stable conformer by thermodynamic point of view. On the other hand, the *cis* isomer is a twisted molecular system with a non-coplanar geometry orientation being metastable due to the effect of distorted conformation having into account the sterically repulsion between aromatic moieties.[2,3] The isomerization reaction from the *trans* to *cis* isomer is activated with UV light ($h\nu_1$) (Figure 1). This reaction in case of azobenzene derivatives is a reversible process.

The *cis-trans* reverse isomerization can be realized by two procedures: thermodynamic path (Δ), when the temperature is the most important factor, and the second path, back conversion, which is a fast process, which can be driven by visible light ($h\nu_2$), Figure 1. These isomerization processes suggest that the azobenzene structure has distinct geometries due to the intramolecular conversion with different temporal and spatial precision.

Figure 1. *Trans ↔ cis isomerization reaction of unsubstituted azobenzene*



Theoretical and experimental determinations revealed that in the azobenzene derivatives two well-separated absorption bands in the UV-vis range appear. A strong absorption band in the UV region, where a $\pi \rightarrow \pi^*$ vertical transition ($S_o \rightarrow S_2$) occurred and an absorption band located in the visible range, much weaker in intensity, arising from an $n \rightarrow \pi^*$ forbidden excitation ($S_o \rightarrow S_1$).

The substitution of azobenzene unit with different substituents can introduce modifications in the electronic structure and into the isomerization mechanism. Unless specified the mechanism of isomerization reaction of azobenzene derivatives is unresolved. Four mechanism pathways have been proposed to occur during isomerization: rotation, inversion, concerted inversion, and inversion assisted by rotation. These mechanisms involve a modification of internal structural coordinates such as -N=N- bond length, C-N=N or N=N-C valence angles and C-N=N-C dihedral angles during the internal conversion. Nevertheless, the mechanism of isomerization in case of azobenzene derivatives is still unresolved and open for debate.

In this study the main idea was to investigate the electronic structure of some azobenzene derivatives having maleimide functional groups by a DFT, TD-DFT and *ab initio* computational determinations. The theoretical results were compared to the experimental data from UV-vis analysis.

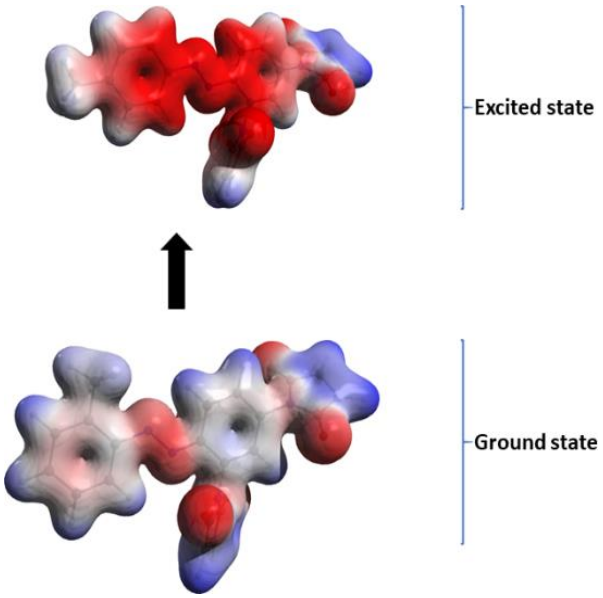
2. Computational details

All calculations were based on DFT and TD-DFT and ab initio theories and have been carried out with Gaussian G16 software.

3. Results and discussion

Theoretical calculations revealed that the electronic configuration was modified when the azobenzene core was substituted with maleimide groups. The maleimides units introduce a charge transfer (CT) along the excitation pathway. This CT effect appears because the maleimide moieties polarize the azobenzene core (Figure 2) and introduce the low-lying transitions.

Figure 2. *Polarization effect introduced by maleimide moieties on the azobenzene core*



The presence of maleimide fragments at the azobenzene core influences the *cis* - *trans* interconversion barrier by decreasing the activation energy by 7 kcal/mol as compared to unsubstituted azobenzene, thus favoring the inversion assisted by rotation isomerization mechanism.

4. Conclusions

Computational results showed that the maleimide moieties can introduce $n\pi^*$CT and $\pi\pi^*$CT low-lying transitions having a charge transfer effect. These transitions appear as effect of interaction (an intramolecular interaction) in excited state between azobenzene unit and maleimide groups and have implications on isomerization process.

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ENANTIOANALYSIS – A TOOL IN DIAGNOSTIC OF CANCER

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1. Introduction

Enantioanalysis became lately a very important tool in pharmaceutical and clinical analysis. Like chiral drugs with enantiomers having different pathways in the body, chiral biomarkers can indicate different diseases. Most of the chiral biomarkers were already studied by clinicians, and it was concluded that there is of high importance to perform enantioanalysis in order to have the correct diagnostic.

2. Results and discussion

For fast screening tests developed for cancer diagnosis, biomarkers like CEA, CA 19-9, cannot always conduct to the diagnosis. We did identify some enantiomers of amino acids that are found only in patients confirmed with cancer; screening tests based on the identification and quantification of these biomarkers may conduct to a faster diagnosis. The tools used for enantioanalysis as well as the results obtained will be shown.

Stochastic sensors were designed, characterized, and employed as alternative of amperometric and potentiometric sensors for enantioanalysis of specific enantiomers. Fast screening methods were performed with high reliability.

3. Conclusions

This study opened a new era for the enantioanalysis of biomarkers with chiral moiety in order to establish the role of the enantiomers in early diagnosis of cancers like gastric cancer, and can establish if the enantioanalysis of amino acids such as glutamine is a key factor in establishing the metabolomics process in gastric cancer. Ratios between L and D enantiomers may also indicate the stage of cancer faster than any other analysis; clinical studies in this regard were already started.

Acknowledgements

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MACRO Iași 2021

β-CYCLODEXTRIN HOST FOR THE SELECTIVE MOLECULAR RECOGNITION OF ISOMERS OF BISPHENOLS IN WATER

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1. Introduction

Bisphenols are a family of phenol-based building blocks widely used as additives for the synthesis of epoxy-resins and polycarbonates.[1] Many studies reported that bisphenol S (BPS) is frequently detected in the aqueous environment, and it also exhibits severe adverse effects on human health, such as estrogenic activity and carcinogenicity.[2] For this reason, over the last few years, many studies have been conducted on the removal of bisphenol as a pollutant.[3] In this context, cyclodextrins (CD) play a crucial role thanks to their molecular recognition abilities in aqueous solvent.[4]

During the synthesis of 4,4´-dihydroxydiphenyl sulphone (4,4´-BPS) large quantities of the isomeric 2,4´-dihydroxydiphenyl sulphone (2,4´-BPS) are formed as by-product. Consequently, the commercial product known as bisphenol S is in fact a mixture of both isomeric dihydroxy diphenyl sulphones, as the purification of the pure bisphenol S (4,4´) isomer from mixtures with the 2,4´-isomer cannot be easily achieved.[5] Unfortunately, the presence of the 2,4´-isomer complicates the issue of molecular control in the field of application of bisphenol S and increases the related pollution problems.

While many studies have been reported concerning the molecular recognition of 4,4´-dihydroxydiphenyl sulphone (4,4´-BPS) inside the hydrophobic cavity of β-CD in aqueous system, to date no information has been reported regarding the complexation abilities of β-CD toward the 2,4´-isomer in water. Prompted by these considerations we evaluated the complexation abilities of the β-CD toward the two isomeric dihydroxydiphenyl sulphones, in solution, solid state, and gas phase.

2. Results and discussion

The formation of the inclusion complexes 4,4´-BPS@β-CD and 2,4´-BPS@β-CD was proved by 1D and 2D NMR (NOESY and DOSY) experiments (Figure 1), while ITC investigation evidenced that the β-CD host shows a greater affinity for 4,4´-BPS with respect to its isomer 2,4´-BPS with a 4,4´-BPS/2,4´-BPS selectivity ratio of about 6.3. ITC shows clearly that the formation of the 1:1 species results enthalpically favored and driven but accompanied by an unfavorable entropic change. These results indicate that the formation of the inclusion complexes is driven by stabilizing secondary interactions between BPSs guests and β-CD.

The formation of the inclusion complexes between the β-CD and the two isomeric 4,4´-BPS and 2,4´-BPS was detected also in gas phase by FT ICR ESI MS studies. This result confirms that the presence of secondary interactions between BPSs guests and β-CD host plays a crucial role for the formation of 4,4´-BPS@β-CD and 2,4´-BPS@β-CD complexes. In gas phase, collision-induced dissociation (CID) experiments indicate that 4,4´-BPS has a higher kinetic barrier to escape from the β-CD cavity than the isomeric 2,4´-BPS. X-ray investigation (Figure 2), show that in the solid state, the 4,4´-BPS@β-CD complex forms a head-to-head dimer constituted by two β-CD macrocycles, which hosts two 4,4´-BPS guests. The dimer of β-CD is sealed by seven strong H-bonding interactions involving exclusively the secondary O3 hydroxyl groups. Analogously the 2,4´-BPS@β-CD complex forms a dimeric assembly in

the solid state in which two 2,4´-BPS guests were included into the cavity. In the solid state, the inclusion of 4,4´-BPS guest inside the β-CD cavity did not result in complete water-desolvation effect, in agreement with the results of the ITC study.

Figure 1. *Left- ^{1}H NMR spectra (600 MHz, 298K, D_2O) of: a) β-CD; b) equimolar mixture of β-CD and 4,4´-BPS; c) 4,4´-BPS; d-e) Expansion of the ^{1}H NMR spectrum (a) and (b); (f) Significant portion of the 2D NOESY spectrum of the 4,4´-BPS@β-CD complex. Right- ^{1}H NMR spectra (600 MHz, 298K, D_2O) of a) β-CD; b) equimolar mixture of β-CD and 2,4´-BPS; c) 2,4´-BPS; d-e) Expansion of the ^{1}H NMR spectrum (a) and (b); f) Significant portion of the 2D NOESY spectrum of the 2,4´-BPS@β-CD complex.*

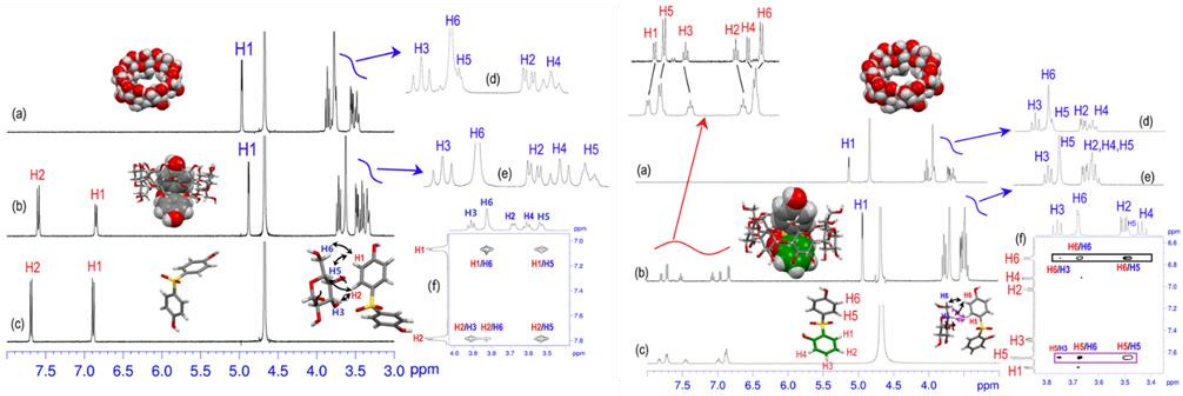
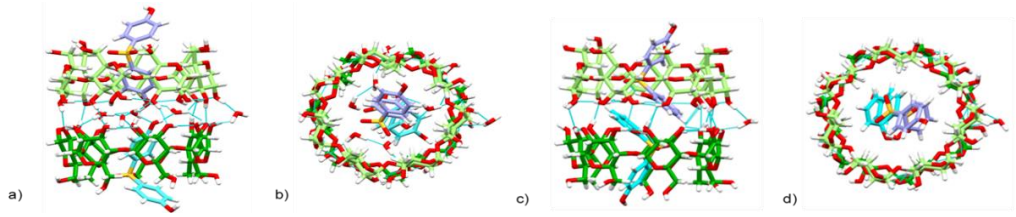


Figure 2. *Side and top views of the solid state of bisphenol@β-CD dimeric complexes: (a, b) (4,4´–BPS@β-CD)$_2$; (c, d) (2,4´–BPS@β-CD)$_2$*



Finally, the formation of inclusion complexes between 4,4´-BPS or 2,4´-BPS and β-CD was also confirmed by FT IR, DSC and TGA analysis. DSC curves evidenced significant changes in material properties of 4,4´-BPS@β-CD and 2,4´-BPS@β-CD complexes in comparison to starting raw materials; unexpectedly no thermic stabilization was detected by TGA analysis for both 4,4´-BPS and 2,4´-BPS upon inclusion inside the β-CD cavity.

Acknowledgements

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NOVEL STUDIES ON SILK SERICIN BIOFUNCTIONALIZATION BY ATOM TRANSFER RADICAL POLYMERIZATION

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1. Introduction

Silks are natural protein materials constituted of various assemblies of polypeptide and protein subunits which are generally classified as fibrous proteins. The proteins are produced by the larvae of domesticated *Bombyx Mori* moth. They are very promising biomaterials with different relevant applications tissue engineering, regenerative medicine, or drug delivery.[1] The major protein in the silk assembly is the fibroin being also the most abundant (70-80%). Sericin, the second main protein component of the silk, has been also acknowledged as a potential biomaterial in recent years.[2] Silk sericin was less studied and used as compared to fibroin. In most of the cases, the water-soluble sericin is removed from silk to purify the fibroin and to obtain a more biocompatible material. Therefore, silk sericin was hypothetically considered to have allergenic activity. The latest literature has shown that this issue was highly speculative and based on misinterpreted research results. The experimentally research had demonstrated that silk sericin can function as a substrate for the *in vivo* regenerative medicine or as a powerful tool innovative nanotechnology in drug delivery and gene therapy. The delivery of exogenous DNA fragments offers a promising approach for the treatment of numerous genetic disorders including cancer. Numerous research studies had successfully reported gene delivery based on recombinant spider silk proteins or silk fibroin nanocomplexes.[3] In this regard, silk sericin is the next silk protein taken in sight for such mission.

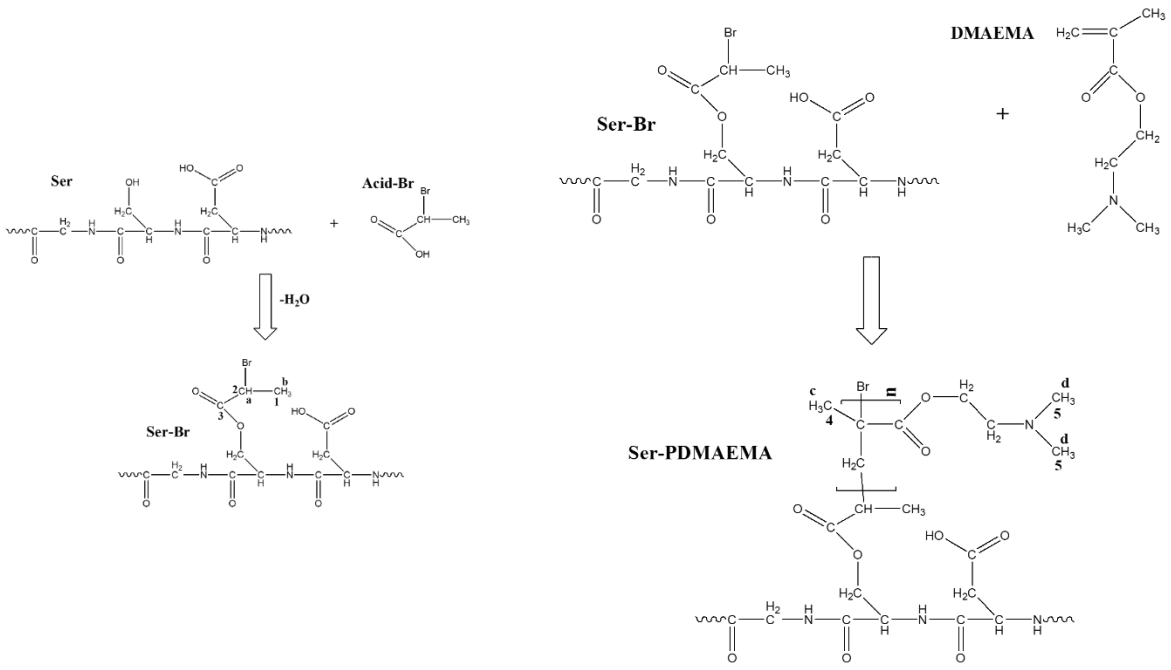
2. Experimental

The present study reports the silk sericin biofunctionalization based on atom transfer radical polymerization (ATRP) technique for the development of self-assembled nanocarriers. In this context, the silk sericin was reacted with alkyl halogens in order to provide the available halogen sites. The synthesis product (Ser-Br) was purified via dialysis p for one week using special cellulose membrane. The modified silk sericin was studied in terms of solubility behavior using several organic-inorganic solvents. The next step involved the growth of polymeric synthetic chains by a grafting procedure based on ATRP. Polymeric chains of poly-(2-dimethylamino ethyl methacrylate) (PDMAEMA) were grown in a controlled manner in order to design a biofunctionalized silk sericin with the desired chemistry. The final synthesis product (Ser-PDMAEMA) was purified by filter washing with dimethylformamide. The two synthesis pathway products were successfully characterized by physico-chemical means in order to reveal the chemical modifications (FTIR, RAMAN, NMR).

3. Results and discussion

The first product, Ser-Br, was investigated by FTIR, RAMAN and NMR (H and C) to prove the esterification reaction between the hydroxyl groups from the silk sericin backbone and the carboxyl groups of the alkyl halogen. The investigation results revealed the silk sericin modification. The final synthesis product, Ser-PDMAEMA, was also investigated by FTIR, RAMAN and NMR (H and C) in order to reveal the proper and controlled growth of the PDMAEMA chains. The results showed the presence of PDMAEMA chains with a reduced number of DMAEMA units on the silk sericin side chains. The biofunctionalized silk sericin was investigated in terms of solubility using various solvents. The solubility was mainly studied to choose the proper solvent for the further self-assembly process to generate nanocarriers. The two synthesis reactions are presented in Figure1.

Figure 1. *Modification of the silk sericin with alkyl halogen (left); PDMAEMA chains growth on the silk sericin backbone as side chains (right)*



4. Conclusions

In conclusion, we showed here the functionalization of silk sericin protein with PDMAEMA by ATRP. The biofunctionalization of silk sericin was evaluated by modern and powerful analytical techniques. Further investigation regarding the molecular weight distribution and precise determination of the grown units is under research. The final product was solubilized in proper solvents as an important step for further development of the nanocarriers.

Acknowledgements

This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P4-ID-PCE-2020-1448, within PNCDI III.

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3D BIOPRINTED SCAFFOLDS BASED ON FUNCTIONALISED GELATIN AND PEGDA FOR SOFT TISSUE ENGINEERING

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1. Introduction

3D bioprinted scaffolds has been proposed as an alternative approach of the tissue engineering in order to restore the damaged tissues.[1] Basis of the bioprinting process are bioinks that contain polymeric biomaterials, especially hydrogels, obtained from natural or synthetic polymers.[2] Natural polymers are used often due to the fact that they present biocompatibility and provide a favorable environment for cell attachment and proliferation. In order to improve these properties, the polymers undergo modifications, being subjected to physical and chemical crosslinking.[3] This paper presents the obtaining of 3D bioprinted scaffolds using bioinks based on gelatin methacrylate (GelMa) and poly(ethylene glycol diacrylate). The supports made by bioprinting were characterized and compared to establish the optimal composition of the biocernel and their applicability in soft tissue engineering.

2. Experimental

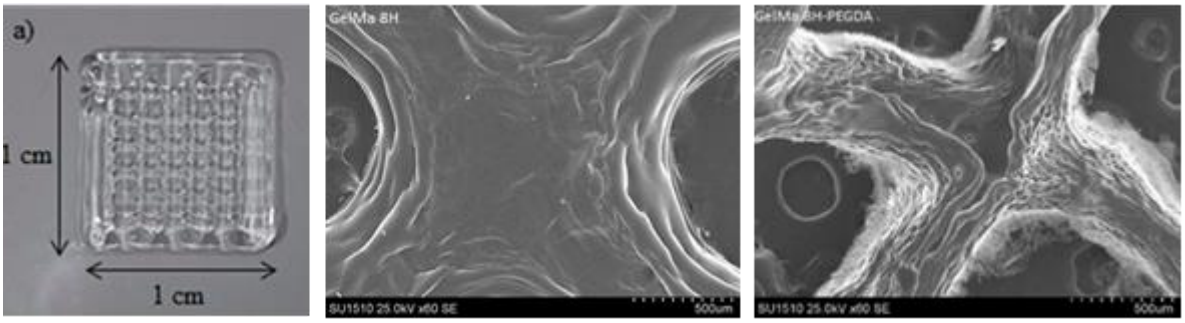
Gelatin was modified according to the protocol described by Camci-Unal and collaborators,[4] adding some changes to the method. Briefly, a 10% (wt/wt) solution of gelatin was prepared by dissolution of the biopolymer in PBS (0.01M, pH 7.2) and methacrylic anhydride was then added dropwise; the reactions were carried out for different time intervals, respectively for 2, 4, 6 and 8 hours, at 50°C.The resulting mixtures were then dialyzed against distilled water for one week to remove unreacted reagents and then freeze-dried. For bioinks preparation, GelMa products (20% wt/wt) were dissolved in PBS (pH 7.2, 0.01M), poly(ethylene glycol diacrylate) (PEGDA, as a crosslinker) and lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP, as a photoinitiating agent) were added and the mixtures, homogenized, bioprinted (Celllink Inkredible bioprinter) and after that freeze-dried for characterization. The bioink rheological behavior was evaluated with an MCR 302 Anton Paar rheometer equipped with parallel-plate geometry and Peltier temperature controller. The upper plate radius was of 30 mm and the selected gap was of 500 μm. The shear flow behavior of the samples was followed at different constant temperatures of interest (25°C, 37°C, and 60°C). The obtained scaffolds were characterized for their structure, morphology (SEM microscopy), and swelling behavior in simulated physiological conditions and *in vitro* degradability. I*n vitro* evaluation of citocompatibility (normal fibroblasts from albino rabbit) was also performed by the direct contact method, supported by morphological analysis of cell culture.

3. Results and discussion

Gelatin modification and bioink rheological properties. FT-IR spectroscopy and NMR data indicate that the primary amino (-NH_2) and hydroxyl (-OH) groups of gelatin had reacted with methacrylic anhydride, which was grafted onto the protein chain and the degree of modification is dependent of the reaction time. The flow curves obtained in stationary conditions permitted to reveal that the prepared bioinks present a Newtonian behavior at very low shear rates (when the structure is similar to the rest state). With increasing the shear rate, they have a shear thinning behavior (a decrease in viscosity). The hydrogel structure is disturbed by the applied shear forces, leading to new interactions.

Scaffolds Morphology: The 3D structure of the scaffold depends on the condition of the material bioprinting and crosslinking, and scanning electron microscopy indicated that the synthetic polymer PEGDA reacted with GelMA, leading to a significant development of the pore diameter which make them suitable for cell growth and proliferation.

***Figure 1**. SEM images of GelMa and GelMa-PEGDA scaffolds*



Swelling behavior and in vitro degradation of the scaffolds. Degree of swelling of materials in contact with phosphate buffer solution were subjected to analysis for both GelMa and GelMa-PEGDA scaffolds. The addition of the PEGDA polymer has the effect to diminish the capacity of swelling and the effect was more pronounced for highly modified biopolymer. *In vitro* degradation kinetics in the presence of collagenase for all modified types of GelMa porous materials and mixtures showed a significant influence between the type of GelMa (reaction time between gelatin and methacrylic anhydride) and PEGDA on the rate and degree of degradation. The introduction of the PEGDA polymer into gelatin matrices causes a decrease in the degradation rate of the material.

Scaffolds cytocompatibility and morphological analysis of cell culture. All materials intended to be used for medical applications must be tested by means of biocompatibility. One of the standard assays is MTT study for *in vitro* evaluation of citocompatibility by the direct contact method and morphological analysis of cell culture. Cell viability values at 72 hours demonstrate that cells in the culture are not affected by direct contact with materials (cells viability > 90%). In addition to the MTT test, a live/dead staining assay was performed. Sterile hydrogel samples were put in direct contact with cells. Cells were fixed using formic aldehyde for 24 hours and then stained by the May-Grünwald-Giemsa method. According to the obtained data it is obvious that the cells adhered to the substrate, forming a uniform monolayer and have a characteristic shape of fibroblasts.

4. Conclusions

The present paper aimed to obtain scaffolds by 3D printing of new bioinks based on methacrylate gelatin and PEGDA. According to the results of tests performed, it was observed that the bioprinted scaffolds have pores that favor the diffusion of nutrients for cell development; their degradation rate can be controlled by composition and bioprinting conditions. A careful rheological characterization of hydrogels was done in order to optimize the formulations. Quantitative rheological properties for defining biomaterials are analyzed to enable easier choice of the targeted network structure. Moreover, it has been found that the scaffolds based on GelMa and GelMa-PEGDA does not have a cytotoxic effect on the biological elements.

Acknowledgements

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HIFU EFFECT ON MAGNETIC POLYELECTROLYTE MICROCAPSULES

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1. Introduction

Drug targeting is defined as being selective drug delivery to specific physiological sites (organs, tissue, cells) where their pharmacological activity is required, and targeted drug delivery is one of the main challenges of todays' medical world. The major drawback is the fabrication of a biocompatible system, capable of maintaining the host in a good state/condition while delivering the drug to the target point and then remotely releasing it in a controlled manner. Several systems have been suggested as delivery hosts, including liposomes, block copolymers, dendrimers.[1]

Recently efforts have been devoted to the design of microcapsules that break on demand in response to external stimuli, thus releasing the content entrapped inside the shell. One such type of capsule is composed of polyelectrolytes, a class of polymers that carry charged functional groups.[2]

Ultrasound has been used for diagnostic medical imaging as well as therapy. A variety of ultrasonic processors and instruments exists and are available in clinics. Lately, High Intensity Focused Ultrasound (HIFU) was used as a surgery tool and is clinically evaluated in breast, kidney, and liver tumors.[3]

2. Experimental

Microcapsules consisting of alternate layers of poly(styrene sulfonate) (PSS, 70 kDa) and poly(allylamine hydrochloride) (PAH, 15kDa) were prepared following LbL technique. One layer of iron oxide nanoparticles (Fe_3O_4, 15nm) was embedded between the polyelectrolyte layers as the 4th, 6th, 8th or 10th layer of a total of 12 layers. The model chosen for the drug to be encapsulated was the readily available protein bovine serum albumin (BSA) labelled with Rhodamine B isothiocyanate (RBITC) dye.

A solid gel matrix designed to mimic the body was used. The gel loaded with dispersed capsules was placed in a degassed water bath (13-14˚C) on a holder. Ultrasonic irradiation was performed using a Therapy and Imaging Probe System (HAIFU, China). The frequency of focused ultrasound was 1 MHz.[4]

The samples were exposed to continuous high intensity focused ultrasound (HIFU) for a predetermined time to mimic possible 'real life 'treatment durations. Single point exposures were performed; the power and time of exposure were varied.

3. Results and discussion

The integrity and lifespan of the microcapsule play a crucial role in the transportation and deployment of drugs to the target site.

In this study different types of microcapsules composed of twelve layers with iron oxide (Fe_3O_4) nanoparticles (15 nm) in one or other layers. The immediate result of nanoparticle incorporation is an increase in size compared with control capsules of 12 layers without nanoparticles (Figure 1).

After the ultrasonic HIFU irradiation the surviving capsules intact capsules were recovered by dissolving the gel mimic sample in hot water (50 °C), centrifuging the mixture and removing and throwing away the supernatant liquid, which contained the ruptured capsules.

Figure 1. *Mean capsule size diameter*

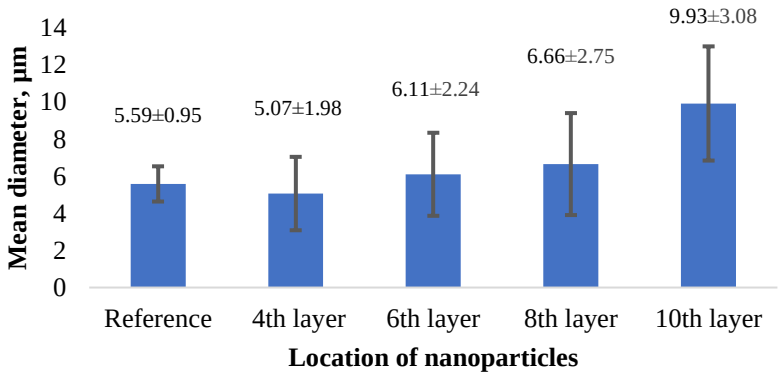
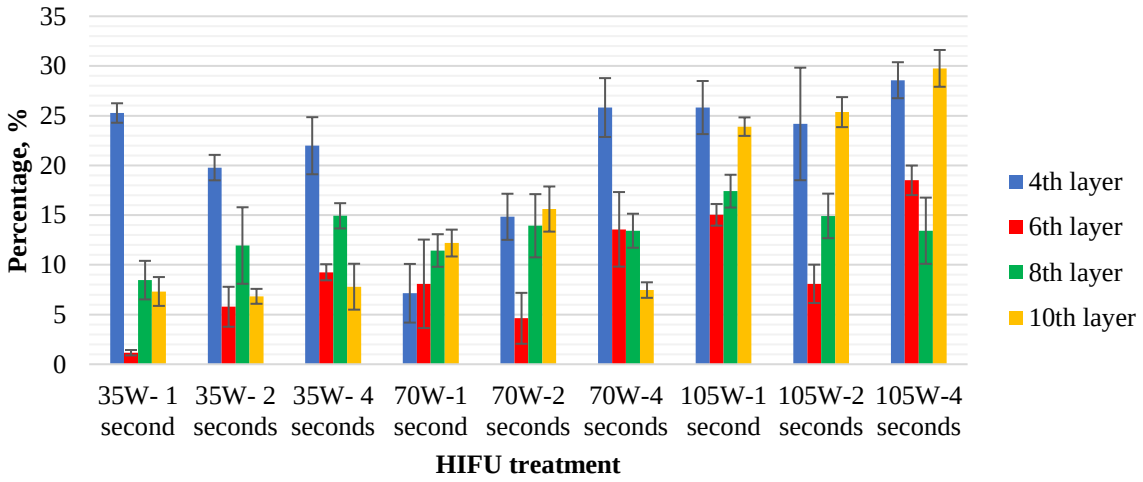


Figure 2. *% Ruptured capsules after HIFU treatment*



The number of ruptured capsules of each sample type was determined via hemocytometer readings post HIFU treatment and calculated as a percentage of the untreated original sample (Figure 2).

4. Conclusions

Polyelectrolyte capsules having iron oxide as one layer qualify as future "smart" carriers as they bear two very important features: controlled transportation and remote triggered release. Taking into consideration the specific behavior of each type of capsule used in this investigation, and the function of the placement of the nanoparticles within the shell layers, they can be designed to serve a certain purpose: release of encapsulated content by placing iron nanoparticles closer to the central core or complete breakage of the capsule carrier by placing the particles closer to the shell surface.

Acknowledgements

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BIOCOMPATIBLE HYDROGELS WITH BROAD-SPECTRUM ANTIMICROBIAL ACTIVITY

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1. Introduction

Infections caused by microorganisms are a serious problem related to human healthcare, which may appear in both wound healing and in biomedical implant fouling. There are many opportunistic pathogens which generate infections, among which *Staphylococcus aureus, Escherichia coli* and *Candida spp.* are the widest spread, causing problems from tissue morbidity, sepsis or implant replacement.[1]

Therefore, in this context, the development of new materials with broad antimicrobial properties are needed. Among the materials used in the treatment of microbial infections, hydrogels based on chitosan are intensely used due to their intrinsic properties. On the other side, chitosan's oligomers, present even a higher potential for the obtaining of antimicrobial materials, due to their superior biological properties, compared to chitosan.[2]

In this context, the present study had as objective the synthesis of systems based on chitosan oligomer with broad spectrum antibacterial activity, with specially designed and tailored properties, at multiple levels. The systems were designed as hydrogels, meeting the requirements for wound healing and biomedical applications, due to their structural building blocks and also due to their morphological particularities.

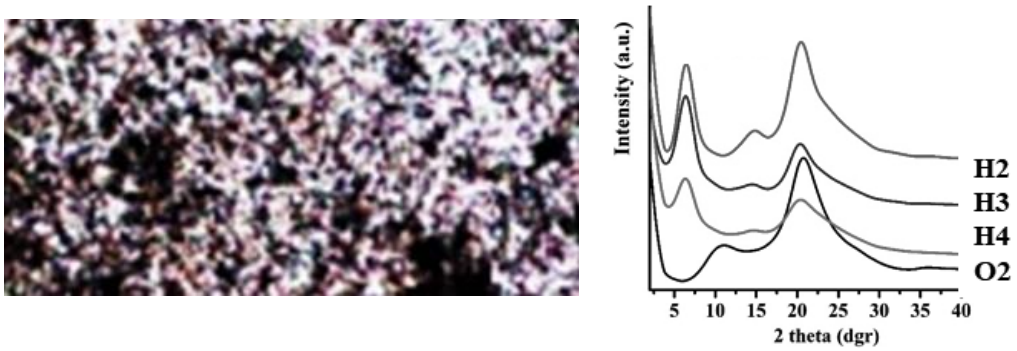
Moreover, the systems contain 2-formylphenylboronic acid (2-FPBA), a monoaldehyde known in the literature for its ability to induce chitosan gelation, possessing also strong antifungal activity against Candida, both albicans and glabrata on planktonic yeast and biofilm.[3]

2. Results and discussion

Eighteen hydrogels were synthesized by the acid condensation reaction of chitosan oligomers with different polymerization degrees and 2-FPBA, by varying the molar ratio of their functionalities.

The hydrogels and the corresponding xerogels were characterized from the structural point of view by FTIR and NMR spectroscopy, both techniques revealing the formation of reversible imine linkages between the reagents.

Figure 1. *POM image of CHOS20-1 (a) sample's emission under UV-lamp illumination (b) and WXRD diffractograms of some representative samples*



(a) (b)

The supramolecular architecture of the hydrogels was investigated by polarized optical microscopy and Wide-Angle X-ray diffraction. All the samples presented birefringence under polarized light (Figure 1a) indicating a highly ordered structure. These data were also confirmed by WXRD, the xerogels' diffractograms presenting three diffraction peaks which indicated a three-dimensional layered architecture of the investigated samples (Figure 1b).

The swelling degree was assessed by calculating the mass equilibrium swelling, reaching a maximum of 25 in water and 9 in PBS for the most hydrophilic sample. The enzymatic degradability was evaluated in the presence of lysozyme, both the gravimetric measurements and the SEM images post-enzyme contact revealing that the hydrogels were easily erodible. The rheological measurements demonstrated the gel like behavior of the samples and their thixotropy, important characteristic for their future biomedical applications. The new synthetized hydrogels were tested for their antimicrobial activity against common and virulent microorganisms, proving very good antibacterial properties against *S. aureus* and outstanding antifungal properties. These data, along with the *in vivo* biocompatibility of the hydrogels, demonstrated by their administration in mice, recommend them as materials with broad antibacterial spectrum, adequate for bioapplications.

Acknowledgements

This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PD204/2020, within PNCDI III and by the project H2020-MSCA-RISE-2019: Smart Wound Monitoring Restorative Dressings (SWORD) (no. 873123) and by the project "Petru Poni Institute of Macromolecular Chemistry-Interdisciplinary Pol for Smart Specialization through Research and Innovation and Technology Transfer in Bio(nano)polymeric Materials and (Eco)Technology", InoMatPol (ID P_36_570, Contract 142/10.10.2016, MySMIS: 107464).

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SILOXANE/SILANE DERIVATIVES BASED ON 5-AMINO-1,3,4-THIDIAZOLE-2-THIOL AND THEIR GOLD COMPLEXES: INTERFACIAL PHENOMENA BASED ON PHOTOLUMINESCENCE

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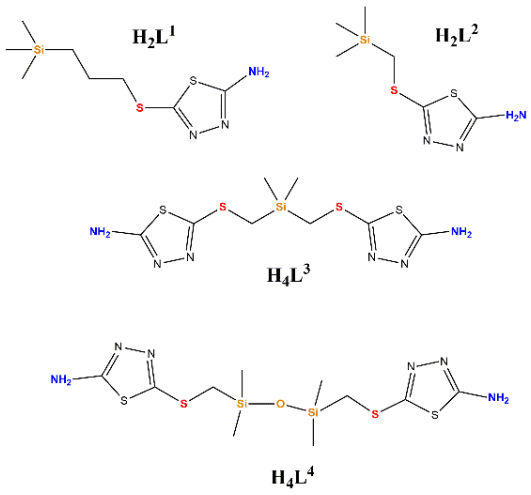
1. Introduction

Aggregation induced emission luminogens represent a special class of molecules for high fidelity imaging.[1] In order to enhance photoluminescence, an original idea is coupling 1,3,4-thiadiazole with a siloxane/silane moiety able to induce self-assembly capacity, biocompatibility and hyperconjugation between the moieties. This work is a continuation of our previous studies,[2] wherein several experimental observations arise some questions. For instance, what would be like to determine critical micelle concentration and couple it with fluorescence? What would be like to take a deep insight on the rigidity of aggregates and their influence on emission? What would be like to create supramolecular structures in water for further biocompatibility? All these questions shall be answered herein.

2. Results and discussion

Herein, 5-amino-1,3,4-thidiazole-2-thiol has been reacted with (3-chloropropyl)trimethylsilane (H_2L^1), (chloromethyl)trimethylsilane (H_2L^2), bis(chloromethyl)dimethylsilane (H_4L^3) and 1,3-bis(chloromethyl)tetramethyldisiloxane (H_4L^4) by an analogous Williamson reaction of thiols, obtaining four ~~4~~-new amines (Figure 1). These compounds were completely characterized by FTIR, NMR, XRD and elemental analysis. The aggregation behavior has been highlighted by Wilhelmy method in DMF solution, successful only for H_2L^1 and H_4L^4 with critical micelle concentration (CMC) ranging around 10^{-2}-10^{-1} M. Photoluminescence studies by varying concentrations revealed that once the micelles appear then emission occurs (Figure 2).

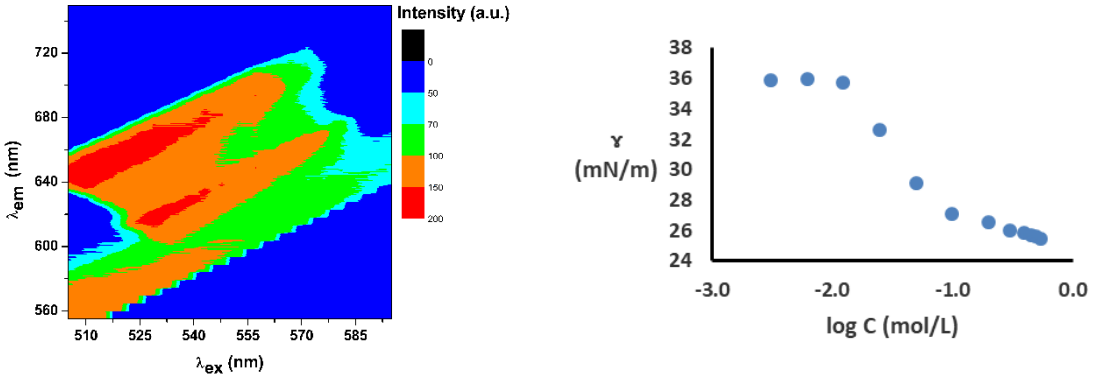
Figure 1. *Chemical structures of the new four amines*



The determined quantum yield was about 20% and the emission lifetime, of the order of nanoseconds, indicated two processes in excited state, assigned to the excimer formation. Fluorescence anisotropy revealed low orientational order around 0.2, perfectly resembling TEM and DLS analysis, wherein low ordered micelles were noticed with high diameter, around 2000 nm. To avoid the toxic effect of DMF and high CMC, the micelles were prepared in water/ethanol mixture, successful for all compounds. The emission of micelles in water was red shifted, but roughly with the same quantum yield. The emission lifetime indicated the same processes in excited state and also of the order of nanoseconds. The orientational

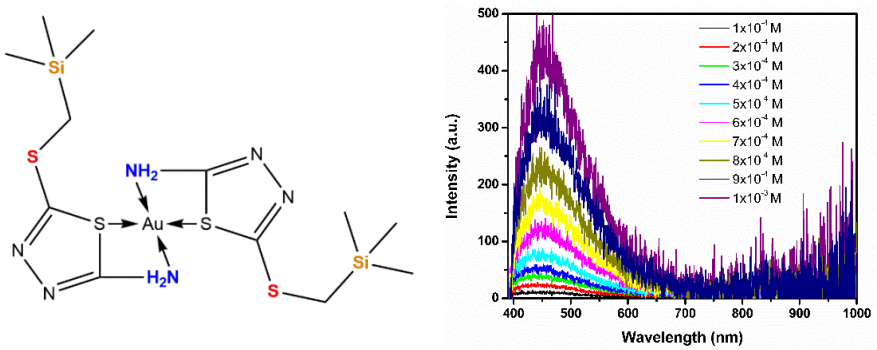
order determined by fluorescence anisotropy in water was around 0.9 that resembles TEM and DLS analysis, wherein spherical micelles were observed with diameter of 500 nm. Besides, the determined zeta potential indicates good electrokinetically stability, about -17 mV.

Figure 2. *Excitation emission matrix and Gibbs adsorption isotherm for H_2L^1 micelles*



In order to enhance fluorescence, the four amines were further reacted with chloroauric acid. In our attempts, so far, only the gold complexes of H_2L^1 and H_2L^2 have been fully synthetized, the others being in progress. The products were characterized by FTIR, NMR and MALDI-MS.They show good photoluminescence activity, starting from concentrations around 10^{-4} M (Figure 3). The most excitingfact is that the gold complexes showed near infrared (NIR) excitation band, so promisingfor further studies, since phototaxis by NIR might be employed. The latter shouldrespond at photo-stimulus, throughproperties such as mechanical, thermal and emission, all at the same time.[3]

Figure 3. *Proposed structure and emission intensity variation with concentration of H_2L^2 gold complex*



3. Conclusions

The essence of this study was coupling the critical micelle concentration with photoluminescence. It was fulfilled by synthesis of the silane/siloxane diamines, which obeyed the aforementioned. The compounds assessment revealed surface activity, good electrokinetically stability, quantum yields about 20%, lifetime of the order of nanoseconds and high orientational order in water. Not in the end, our work will be continued by completely synthesis of the gold complexes and boosting their scientific and applied value.

Acknowledgements

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ENERGY-EFFICIENT DYNAMIC POLYMER-BASED NANOCOMPOSITES FOR THERMAL COMFORT

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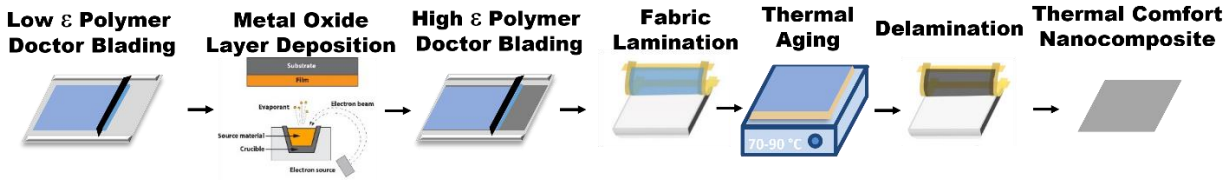
1. Introduction

Thermal management has potential applications in multiple areas such as buildings, electronics, and clothing. The animal kingdom provides inspiration for materials with application in thermal management – the mirror spider (*Thwaitesia argentiopunctata*) can dynamically shift its skin color and light reflectance due to guanine patches found on the abdomen which are switched by the muscle cells between contracted and expanded states. This architecture provided inspiration for development of polymer nanocomposite materials with active control of infrared radiation, replicating the capability of spider to change the reflectance and transmittance of light in the infrared wavelength range. Such a polymer-based materials are prepared without use of volatile organic solvents and are safe for human use.

2. Experimental

The procedure at laboratory scale (Figure 1) involves doctor blading a layer of linear polymer with low thermal emissivity (10–100 micron thick), followed by another nanometer thick metal oxide layer with pulsed laser deposition, doctor blading of a layer of high emissivity polymer (10–100 micron thick), lamination of support fabric, thermal aging on hot plate, and delamination from substrate resulting in patches of functional material. This is a material with two dissimilar sides - one side active for cooling the skin by removing heat through infrared radiation emission to the environment, and the other side active for heating the skin by emitting infrared radiation towards the skin.

Figure 1. *Preparation steps for thermal comfort nanocomposite materials*



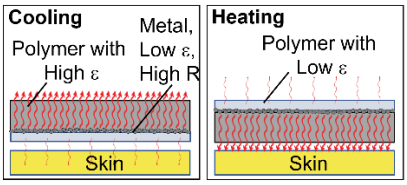
The resulting nanocomposite films were characterized in terms of mechanical (Instron 3365 Universal Testing System, USA), morphological (SEM Thermoscientific Verios G4UC), and thermal infrared (FLIR C2 infrared video camera, USA) properties.

3. Results and discussion

Currently, thermal management employs either “passive” or “active” systems. While active clothing has on-demand control of temperature, it is also complex and requires continuous energy input. An ideal thermal management platform should bring together the advantages of both passive and active systems. While space blanket demonstrates a wonderful combination of low weight, compactness, and manufacturability, it is a static technology that can not dynamically change the amount of heat reflected in the form of infrared radiation – the space blanket is either worn on or it is taken off by the user. We took inspiration from the dynamic capabilities of the mirror spider to change its skin color for preparation of polymer nanocomposites which can be actuated electrically or mechanically to modify their reflectance and transmittance for infrared radiation in the electromagnetic spectrum. Thus, we developed a scalable platform for which no analogue exists and that enables adaptive control of thermal radiation exchange, with polymeric substrates which regulate a heat flux of >40 W/m^2. The mechanism for the modulation of radiative heat flux is based mostly on the difference in emissivity of each of the two sides of the

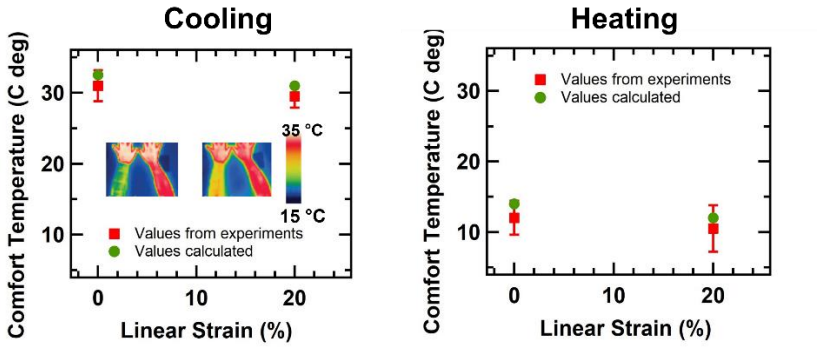
nanocomposite thermal comfort material (Figure 2) and also with actuation (mechanical or electrical) of the nanocomposite.

Figure 2. *Setups for cooling and heating for the two sides of the nanocomposite thermal comfort material*



For developing a thermal model for these materials, there are multiple initial hypothesis which must be considered and for each side of the thermal comfort nanocomposite we can draw the different heat flows affecting the material and the skin. Using these equations, together with experimental data on the temperature of the inner and outer sides of the material for cooling setup and for heating setup, we can choose polymer materials with desired IR properties, and we can also change the air gap thickness so that the total cooling or heating capability of the composite material balances the total heat generation or heat loss rate. From these equations, we can find the maximum (for cooling setup) or minimum (for heating setup) ambient temperature which can be sustained without compromising personal thermal comfort.

Figure 3. *Measurements for cooling and heating for the two sides of the nanocomposite thermal comfort material*



The measurements with the cooling setup show the maximum temperature at which the total cooling capability of the composite material balances the total heat generation rate varies from around 31 °C for unstretched material to 29 °C for material stretched with 20% (Figure 3). The images recorded with the IR camera demonstrate this mechanism, where the temperature recorded for the arm covered with unactuated nanocomposite shows a temperature close to the environment (20 °C), while under strain the temperature recorded with IR camera gets close to that of the skin (34 °C) (Figure 3).The measurements with the heating setup show the maximum temperature at which the total heating capability of the composite material balances the total heat loss rate varies from around 12 °C for unstretched material to 10.5 °C for material stretched with 20%.

4. Conclusions

The nanocomposite described here can be integrated with textile cloth for development of an artificial thermoregulatory platform. It demonstrates capacity to control in a dynamic manner both cooling and heating within a single piece of material due to its two sides with different thermal properties. Such nanocomposites can be manufactured from affordable scalable polymers, with potential for significant energy savings when applied on a global scale.

Acknowledgements

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THERMALLY REARRANGED MIXED MATRIX MEMBRANES FILLED WITH FUMED SILICA FOR CO_2 SEPARATION

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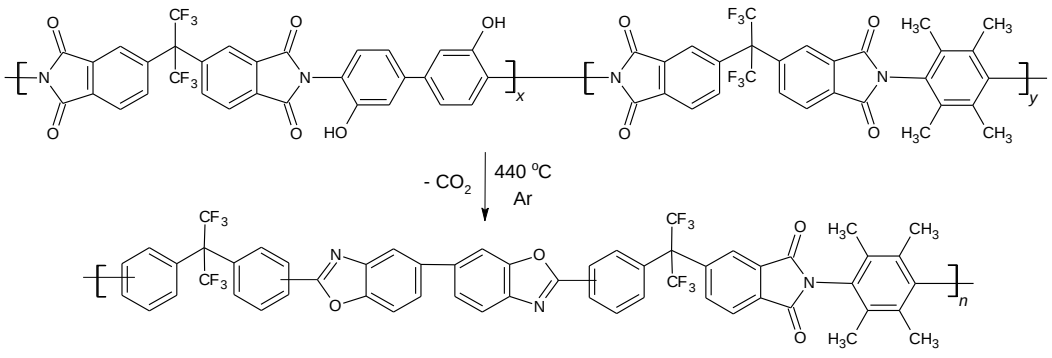
1. Introduction

Tackling the problem of global warming involves, among others, the control of greenhouse gas emissions to the atmosphere. To reduce the amount of CO_2 emission, new efficient and economical solutions are required. One of the developing directions is post-combustion carbon dioxide capture using selective polymer membranes. In comparison to conventional methods, membrane gas separation has many advantages, such as low membrane fabrication and energy costs, simplicity and compactness of membrane modules, as well as ease of their adaption to already existed installations. To be competitive to other methods, membrane technology requires the availability of membranes with high separation parameters, good mechanical strength, and thermal stability. To overcome limitations resulting from Robeson's upper bond, different kinds of modification of polymeric membranes have been performed. One of the current researches is thermal treating, where the formation of new functional groups and cross-linking is occurred, such as a thermal rearrangement of polyhydroxyimide to polybenzoxazoles (PBO). Another type of modification concerns dispersing inorganic fillers in a polymer matrix to obtain high-performance mixed-matrix membranes (MMM). The combination of high selectivity of sieves and good processability of the polymer has been expected to occur. In this work, the effect of the presence of nonporous fumed silica particles on physical, thermal, mechanical, and gas transport properties of MMMs before and after their thermal rearrangement to PBOs has been investigated and discussed.

2. Experimental

In this work copolyimide from 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), and a mixture of 3,3'-dihydroxybenzidine (HAB) and 2,3,5,6 tetramethyl-1, 4-phenylene diamine (4MPD) in 3:1 molar ratio was synthesized and investigated (Figure 1). The typical two-step polycondensation reaction of 6FDA dianhydride with 4MPD and HAB diamine mixture was carried out in N-methyl-2-pyrrolidone and *o*-dichlorobenzene solution. MMMs were obtained by the addition of the required amount of fumed silica (from 15 to 45 wt.%) to the poly(amic acid) solution. The membranes were cast directly from the reaction mixture on the glass plate. After the drying procedure, membranes were thermally rearranged to polybenzoxazoles to receive TR-MMM. The effect of the fumed silica particles presence on membrane properties was examined and analyzed by using TGA, DSC and the tensile test methods. The permeability of pure N_2, O_2, He, and CO_2 through the membranes was measured using the constant volume gas permeation apparatus.

Figure 1. *The reaction of thermal rearrangement of copolyhydroxyimide to polybenzoxazole*



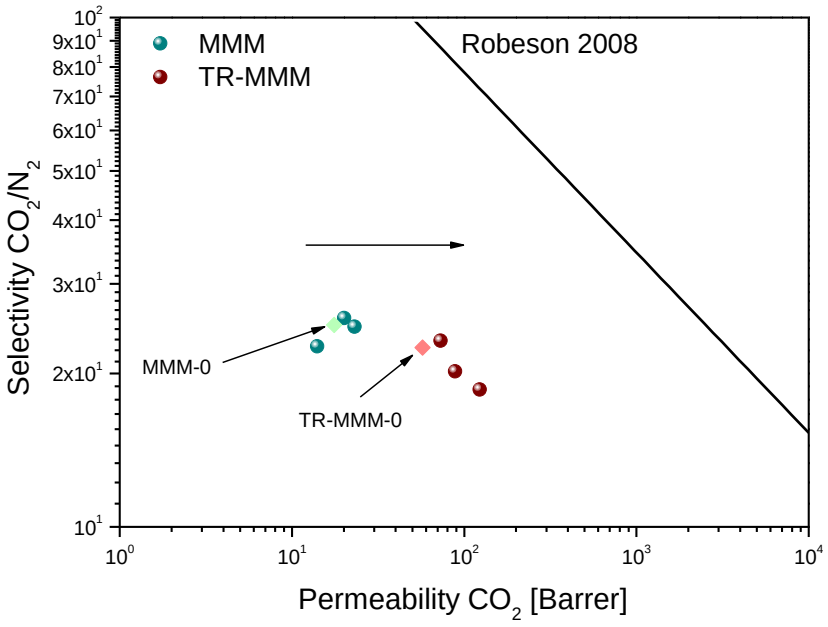
3. Results and discussion

Table 1. *Thermal properties were investigated by TGA and DSC methods for both pure and filled membranes*

Sample	T_g [°C]	T_{TR} [°C]	T_{deg} [°C]
MMM-0	379	474	563; 677
MMM-15	378	466	568; 678
MMM-30	361	472	577; 673
MMM-45	354	409	561; 673

Thermal properties were investigated by TGA and DSC methods for both pure and filled membranes and the data are summarized in Table 1. As can be seen, the presence of SiO_2 in a polymer matrix decreases the glass transition temperature and temperature of thermal rearrangement of the membranes. This effect is greater the higher the filler content. Fumed silica does not significantly affect the degradation of the polymer matrix. Considering the gas transport results, the addition of 15 wt.% of silica particles increases permeability of MMM, whereas the higher amount tends to reduce membrane permeability and slightly improve selectivity. On the other hand, a distinct increase in CO_2 permeability (by 115%) accompanied by only a small decrease in CO_2/N_2 selectivity (by 17%) can be observed for 45 wt.% filled membrane after conversion to PBO compared to its unfilled PBO counterpart. Moreover, as can be seen in Figure 2, all the received TR-MMMs are closer to the Robeson's upper bound than the unfilled PBO membrane, which makes them attractive for gas separation technology.

Figure 2. *Robeson's plot for the CO_2/N_2 gas pair*



4. Conclusions

A series of the new TR-MMMs containing fumed silica particles were developed and investigated, to determine their structure, physical and gas permeation properties. The results show that this approach allows membranes with superior properties compared to those of their unfilled counterparts to be obtained. This refers to both polyimide membranes incorporated with up to 30 wt.% of silica and all the thermally rearranged MMMs which demonstrated a permeability increase of up to 115% over the pure polymer. Moreover, adding SiO_2 particles to a polymer matrix reduces glass transition temperature and the temperature of thermal conversion to PBO that is important from a practical point of view, because it creates the possibility of forming membranes in a more convenient and energy efficient way. In conclusion, the CO_2 permeability/selectivity can be tailored by incorporation of the fumed silica particles into the polyimide matrix. In particular, thermally rearranged membranes filled with silica seem to be suitable for this kind of applications.

CONTROLLING THE SURFACE PATTERNING AND SELF-ASSEMBLY OF INORGANIC NANOPARTICLES BY MACROMOLECULAR DESIGN OF POLYMERIC BRUSH COATINGS

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1. Introduction

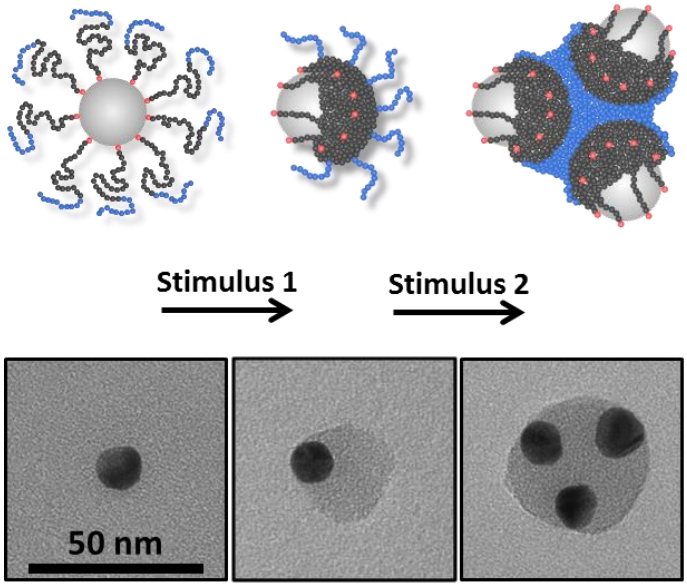
The way in which inorganic nanoparticles interact with their environment is controlled by their surface coating. Heterogeneities in their surface coating can lead to non-uniform "patchy" nanoparticles. Controlling the spatial distribution of polymer ligands on the nanoparticle surface (i.e. "patchiness") allows one to render nanoparticles with functions that are otherwise unattainable, and is thus of critical importance. Recently, a thermodynamically controlled approach for producing patchy nanoparticles has been proposed by the group of Kumacheva.[1]

For surface-grafted polymer brushes, the reduction of solvent quality may lead to the formation surface-pinned micelle (patches) in, driven by the minimization of the surface free energy of the system.[1] This underlying mechanism posed the question about the colloidal stability of thus-produced patchy nanoparticles, the dynamic properties of the patches, and the secondary assembly of patchy nanoparticles into supracolloidal clusters. These aspects are addressed in this presentation.

2. Results and discussion

The process of surface patch formation under reduced solvency conditions was investigated in the native solvent environment using plunge freezing and cryogenic transmission electron microscopy.[2] Patch formation was externally controlled and induced by heating an aqueous solution of poly(*N*-isopropylacrylamide)-grafted gold nanoparticles above the polymer's lower critical solution temperature.[2] However, in such approach involving homopolymer brushes, attractive surface-polymer patches form, and surface pattern formation and secondary agglomeration processes thus occur concomitantly.

Figure 1. *Schematic illustration (top row) and corresponding transmission electron micrographs (bottom row) of nanoparticles decorated with diblock copolymers after casting from good solvency conditions for both blocks (left), poor solvency conditions for the inner block and good solvency conditions for the outer block (middle), and poor solvency conditions for the inner block combined with cross-linking of the outer block (right)*



A strategy was developed to separate the processes of surface patch formation and secondary self-assembly into larger clusters. The developed approach rests on surface-grafted diblock copolymers, in which a nanoparticle-adjacent block is exploited for surface-patch formation, whilst an outer nanoparticle-remote block provides colloidal stability to the patchy NPs.[3] Furthermore, this outer block can be addressed separately from the first block (using orthogonal stimuli), thereby "staging" surface-patch formation and self-assembly of patchy NPs into clusters (Figure 1).

Aging effects of surface patch structures created in such manner were also investigated, by exploring the time-temperature superposition in patch morphology and distribution. These investigations revealed that above a threshold temperature, polymer ligands gain lateral mobility and ultimately, can desorb from the nanoparticle surface.[4]

3. Conclusions

Targeted macromolecular design of polymeric surface coatings of nanoparticles opens up the possibility to create adaptive systems that allow surface patterning induced by external stimuli. The surface patterns can be stabilized in colloidal solution by employing diblock copolymer brushes. Diblock copolymer surface coatings also enable the controlled, on-demand assembly into defined nanoparticle clusters.

The individual patches are preserved up to moderately temperatures. Higher temperatures lead to a reconfiguration of the surface patch structure.

Acknowledgements

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LOWERED BAND GAP OF CONJUGATED POLYAZOMETHINES VIA SUPRAMOLECULAR ORGANISATION INDUCED BY MODIFICATION OF ALKYL SUBSTITUENTS

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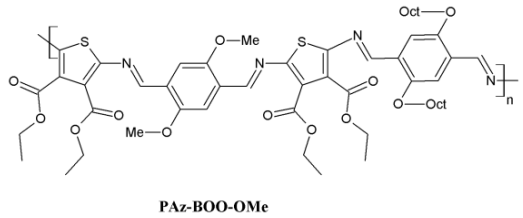
1. Introduction

An interesting group of conjugated materials for optoelectronics are compounds containing an imine bond in their structure, such as azomethines and polyazomethines. The imine bond shows isoelectronic character with the vinylene bond,[1] and subsequently condensation of aromatic amines and aldehydes leads to the formation of π-conjugated compounds, characterised by many valuable physicochemical properties,[2] and also showing activity in optoelectronic devices, including photovoltaic cells.[3] Due to the limited solubility of conjugated compounds, in order to enable the application of thin films of these materials by wet methods, additional substituents are often introduced into the chemical structure of conjugated compounds to improve solubility. However, these groups, usually containing long or branched alkyl groups, can have an adverse effect on the supramolecular organisation,[4] hindering π-π interactions and consequently reducing the crystallinity and conductivity of the compounds.[5] To counteract this, some of the large n-alkyl substituents were replaced with shorter chains, and the effect of such modification on the physicochemical properties relevant for photovoltaic cell applications were investigated.

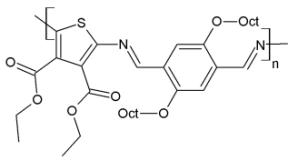
2. Results and discussion

To follow such effect, bulky side chains have been partially replaced by shorter substituents with a similar electronic effect (Figure 1) what was expected to affect the supramolecular organisation of polymers, due to enhanced planarity of conjugated backbone, through removal of the steric hindrance.

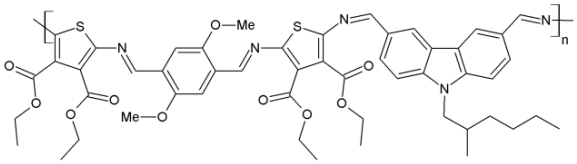
Figure 1. *Chemical structures of investigated polyazomethines*



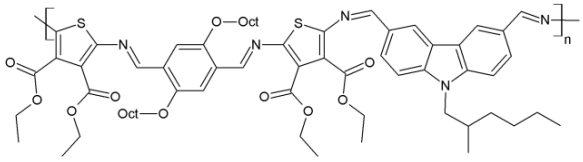
PAz-BOO-OMe



PAz-BOO-OOct



PAz-Carb-OMe



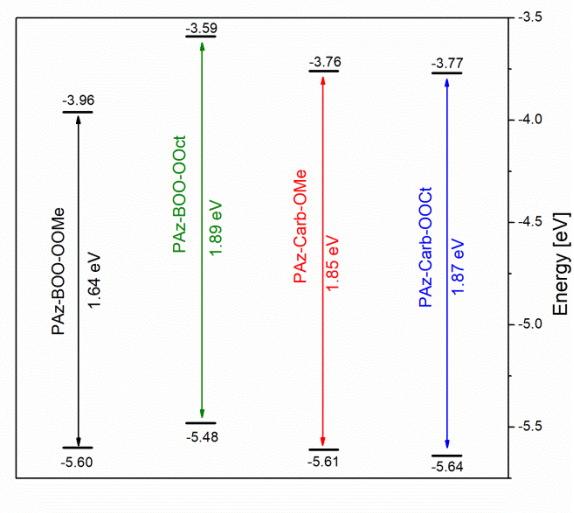
PAz-Carb-OOct

This effect has been followed in compounds with linear (PAz-BOO) and branched (PAz-Carb) alkyl groups, investigating thermal stability, UV- Vis absorption spectra and electrochemical behaviour of such compounds. Additionally, thin films have been deposited and their morphology has been observed using X-ray diffraction (XRD) technique. As a concluding task, the photovoltaic activity of synthesised compounds has been studied, while acting as a donor component of bulk-heterojunction solar cell.

Thermal properties of all materials met the requirements for photovoltaic applications, showing values of initial weight loss in a similar range (331.3 - 350.0 °C), regardless of the modification of the substituent

structure. Determined values of molecular orbitals energies have shown that the partial replacement of linear alkoxy substituents in the PAz-BOO-OOct compound by methoxy groups (PAz-BOO-OMe) have tuned the energy of LUMO level, only slightly affecting the HOMO energy (Figure 2). This change probably results from the improved planarity of the PAz-BOO-OMe polymer, adopted by the chain after removal of some large octyloxy groups, which constitute a steric hindrance. A similar modification of the octyloxy substituents in a polymer consisting of branched 2-ethylhexyl groups (PAz-Carb) has not shown such pronounced changes, probably due to the excessive planarity disorder, induced by the branched substituents.

Figure 2. *Energy levels of investigated polyazomethines*



An analogue effect of the studied polymers supramolecular organisation could be observed on the UV-Vis absorption spectra where a distinct bathochromic shift of the low-energy absorption band has been observed after a partial modification of the linear substituents length. For polymers containing branched 2-ethylhexyl groups (PAz-Carb), the change has been less pronounced. Such observations are consistent with the results of XRD measurements performed for thin films of these polymers, where a partial modification of the linear substituents length (PAz-BOO) has caused an increase in thin film crystallinity, while no changes have been observed in polymers containing branched alkyl groups (PAz-Carb). All obtained compounds have been applied as a donor component in bulk heterojunction solar cells, where they have shown activity together with a fullerene acceptor, reaching efficiencies of 0.09 - 0.17%.

3. Conclusions

The research allowed to obtain new conducting polymers using an economic and ecological methods of synthesis. These compounds have shown high thermal stability, suitable for application in photovoltaic cells. The influence of the supramolecular organisation could be observed during electrochemical and optical properties studies, where the replacement of some linear, octyloxy substituents with methoxy groups allowed to reduce the width of the energy gap, allowing for electron transitions of lower energy, consequently shifting the absorption band towards longer wavelengths. In the case of polymers containing branched N-2-ethylhexyl groups, the modification of the alkoxy groups length did not affect the supramolecular organisation to a greater extent.

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STUDY OF NEW IMINES CONTAINING A PHENANTHROLINE CHROMOPHORE

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1. Introduction

A representative class of compounds in coordination chemistry is composed by imine-based materials, also known as azomethine or Schiff bases, due to their widely reported coordinating ability. As a result of their physical and chemical properties, this class of materials may be used in various domains of applications including: analytical chemistry, food and dye industry, catalysis, as well as diverse biological areas.[1,2]

The appealing characteristics of imines like facile synthesis coupled with synthetic tailor capacity, biodegradability, pronounced photophysical properties and ability to coordinate to metal ions tag azomethines as one of the most widely explored molecular chemosensors. Imines can also be utilized for heavy metal sensing, for the removal of pollutant from the environment, as well as spectrophotometric and fluorimetric agents, among others. As a consequence of these features Schiff base complexes have drawn an increasing attention in the area of ionic binding.[3,4]

A versatile starting material for organic, inorganic and supramolecular chemistry is represented by 1,10-phenanthroline which is a chelating bidentate ligand for transition metal ions that still has a significant influence in coordination chemistry. 1,10-Phenanthroline is a rigid planar, hydrophobic, electron-poor heteroaromatic system who is responsible for its coordination ability toward metal ions.[5]

Taking the advantages of these structural features, 1,10-phenanthroline derivatives and their metal complexes have been used as intercalating or groove binding agents for DNA and RNA, as building units for the construction of efficient luminescent materials and photo-switchable molecular devices.[5-8]

Taking into account the aforementioned literature data it should be interesting to combine imine with a phenanthroline heterocycle in a conjugated molecule with the aim to enhance the conjugation length, light emission efficiency and the charge carriers. Along these lines, here we report on the influence of some metal ions on the physico-chemical properties of new phenanthroline-based imines with emphasis on electronic absorption, fluorescence and cyclic voltammetry behaviour. This study is meant to survey their application as luminescent materials.

2. Experimental

A phenanthroline-based aldehyde was obtained by the oxidation of active methyl group from 4-methyl-1,10-phenanthroline with selenium dioxide in dioxane and water at reflux. The aldehyde was purified and used afterwards in the synthesis of three imine-based compounds by using the condensation reaction involving three aromatic diamines bearing various aromatic or heteroaromatic units.

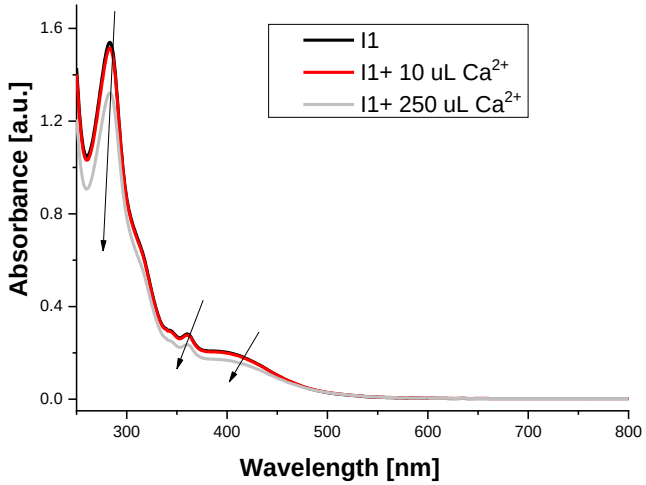
The structure of all compounds was confirmed by spectral methods including FTIR spectroscopy and ^{1}H-NMR analysis. The imines were further characterized by solubility tests, UV-vis and fluorescence spectroscopy as well as by cyclic voltammetry tests. The last three methods were involved to monitor the complexation ability of imines with various metal ions. The thermal stability was assessed on the basis of differential scanning calorimetry and thermogravimetric analysis.

3. Results and Discussions

Three aromatic imine-based compounds containing phenanthroline chromophoric unit were obtained and characterized. The FTIR spectra and ^{1}H-NMR analysis confirmed the presence of the imine units by their characteristic absorption band and singlet peak, respectively. A good solubility was found for the imines both in polar and non-polar solvent which enabled a diverse range of solvent utilization for spectroscopic

measurements. The best results were obtained when tetrahydrofuran (THF) was used which allowed the complexation studies with a large number of metallic salts. Figure 1 shows the UV-vis spectra of imine I1 after the addition of Ca^{2+} ions.

***Figure 1**. UV-vis absorption spectra of phenanthroline-based imine I1 upon complexation with Ca^{2+} ions*



The thermal stability of the new synthesized imines was high with onset temperatures and char yields well correlated with their corresponding chemical structure.

The complexation studies with various metal ions were also performed by using PL and cyclic voltammetry measurements confirming the ionochromic response of these imines towards several metallic ions. Moreover an enhanced fluorescence was observed after complexation in some cases that may be exploited for their further use as luminescent materials.

4. Conclusions

New phenanthroline-based imines were obtained with the aim to contribute to the domain of coordination chemistry in the frame of molecular chemosensors and luminescent materials. The synthesized structures proved to be highly soluble and thermally stable. They exhibited an optical response towards a series of metallic ions which was evidenced by UV-vis, PL and cyclic voltammetry measurements, thus being demonstrated the potential use of these imines in sensing and other opto-electronic applications.

Acknowledgements

This work was supported by a grant of the Romanian Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, Project PN-III-P2-2.1-PED-2019-3993, 485PED/2020, within PNCDI III and by the project "Petru Poni Institute of Macromolecular Chemistry-Interdisciplinary Pol for Smart Specialization through Research and Innovation and Technology Transfer in Bio(nano)polymeric Materials and (Eco)Technology", InoMatPol (ID P_36_570, Contract142/10.10.2016, MySMIS: 107464).

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INTERLABORATORY ASSESSMENT FOR REPRODUCIBILITY IN NMR METABOLOMICS

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1. Introduction

Metabolomics has become an important topic in a wide range of scientific areas, including medicine, pharmacology, nutrition and metabolism, food sciences and environmental research. Metabolomics involves simultaneous detection of a large number of compounds from a living system or a naturally occurring ecosystem. As metabolomics requires processing of large numbers of multiple parameters, the reproducibility of data for statistical purposes is a key issue.

2. Experimental

Bruker Avance Neo 600 and 400 MHz and Bruker Avance III HD 600 MHz NMR instruments have been used. All three instruments have been equipped with 5 mm z-gradient inverse detection (BBI) probes. TopSpin software has been used for controlling the spectrometers and data processing. Spectra have been recorded with noesypresat pulse sequence which allows fast acquisition of ^{1}H NMR spectra using 32 scans, a 90° pulse, 4 s relaxation delay with simultaneous CW irradiation and 2.7 s acquisition time with an ERETIC type of signal as quantitation reference.

3. Results and discussion

We have been involved in one of the first interlaboratory quantitation trials of metabolites in blood plasma.[1] Since then, we continued to be involved in metabolomics studies,[2-6] using NMR equipment which evolved from the generation 1990 (Varian Gemini 300), through generations 1995 (Bruker DRX 400), 2000 (Bruker Avance III 400), 2010 (Bruker Avance HD 600) until 2016 the latest NMR generation (Bruker Avance Neo 400 and 600). In order to assess the reproducibility of the current equipment and the level of confidence in the reported data we have designed an interlaboratory trial involving several instruments and operators.

Figure 1 presents an overview of the operator deviations as percentage from the averaged values for over 4000 pipetting-weighing experiments and Figure 2 presents the variability of the integral of the methyl signal from the same sample recorded in different NMR tubes in over 260 experiments performed in 16 different days.

Figure 1. *Deviations as percentage from the averaged values for all pipetting- weighing experiments*

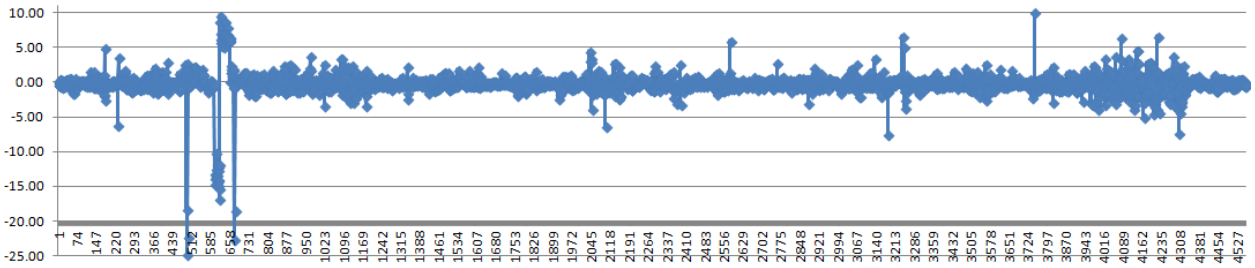
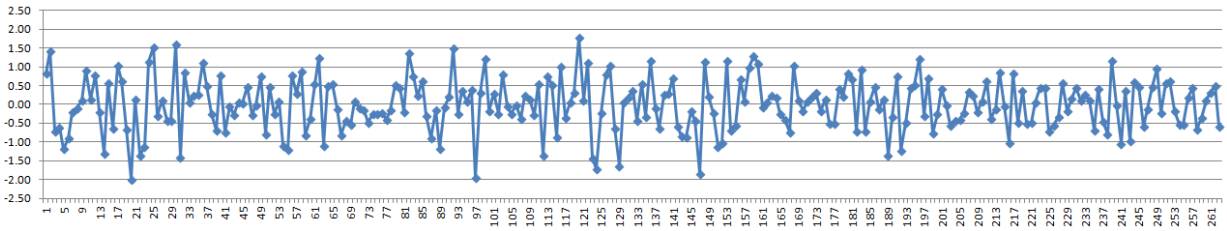


Figure 2. *Tubes and electronics induced variability of the methyl integral on one NMR instrument recorded in 16 different days*



4. Conclusions

The estimated reproducibility error in NMR quantitation for metabolomics purposes with our current instrumental setup using both NMR operators and non-NMR personnel (researchers involved in chemical synthesis and students), is about 4%. This value is matching the acceptable values for biomedical research specified by the NMR manufacturers.

Acknowledgements

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COMPLEXATION OF ACETOPHENONE SUBSTITUTED BENZIMIDAZOLIUM SALT WITH NATIVE AND MODIFIED CYCLODEXTRINS – AN NMR STUDY

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1. Introduction

Benzimidazolium salts are largely used as intermediates in synthesis of various bioactive pyrrolo[1,2-c] benzimidazole and pyrrolo[1,2-c]quinoxaline derivatives.[1,2] According to literature data, some benzimidazolium salts proved also anticancer activity in vitro against HeLa cell lines, acting as bifunctional DNA intercalators.[3] These biological and pharmacological properties, make them attractive for host-guest studies, as they are known to have quite low water solubility. Native cyclodextrins and their derivatives can form stable inclusion complexes in aqueous solution with a variety of inorganic, organic, and biological molecules by accepting them into their cavity. Cyclodextrin inclusion complexes are widely used with various aims including changing the solubility, drug/compound delivery carriers, structural or theoretical studies. NMR spectroscopy is one of the most important analytical methods used to follow cyclodextrins' interactions. From different 1D and 2D NMR techniques, detailed information about the structure of cyclodextrins and their inclusion complexes can be obtained. The present paper discusses the NMR characterization of inclusion complexes of β-cyclodextrin and some chemically modified cyclodextrins with 1-ethyl-(2-phenyl-2-oxoethyl)-5,6-dimethylbenz imidazolium bromide.

2. Experimental

The NMR spectra have been recorded on a Bruker Avance III 400 instrument, equipped with a 5 mm multinuclear inverse detection z-gradient probe. For the benzimidazolium bromide-cyclodextrins mixtures, the chemical shifts are reported in δ units (ppm), and were electronically referenced to the residual peak of the solvent (ref.: H_2O 4.8 ppm). The H, H-ROESY experiments were recorded using standard pulse sequence, with water suppression, as delivered by Bruker with TopSpin 2.1 PL6 spectrometer control and processing software.

3. Results and discussion

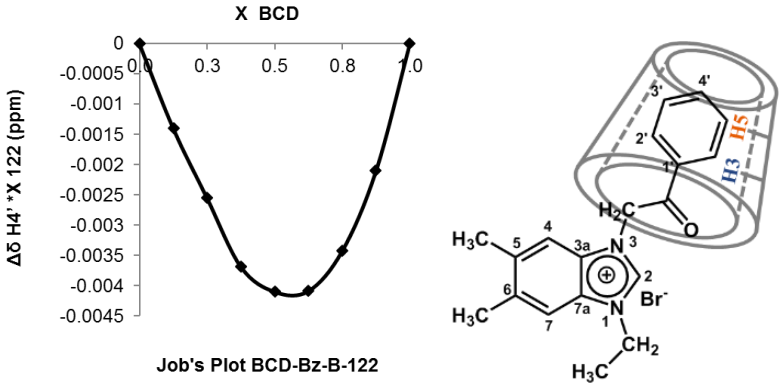
Determination of stoichiometry by NMR Spectroscopy

The stoichiometry of the complexes was determined using the continuous variation method (Job's method). The total concentration was kept constant (10^{-2} M) and the molar fractions (X) of the components were varied between 0 and 1. From the graphical representations of $X_{salt}*\Delta\delta=f(X_{CD})$ we obtained plots that show inflexion points at 0.5 indicating a 1:1 stoichiometry. An example of Job's plot is shown in Figure 1 for benzimidazolium salt and beta-cyclodextrin.

Determination of stoichiometry by UV-VIS Spectroscopy

The stoichiometry of the complex was determined using the Job's method. The total concentration was kept constant ($5x10^{-5}$M) and the molar fractions of the components were varied between 0 and 1. The plots obtained from the graphical representations of $X_{salt}*\Delta A=f(X_{CD})$ show inflexion points at 0.5 indicating a 1:1 stoichiometry.

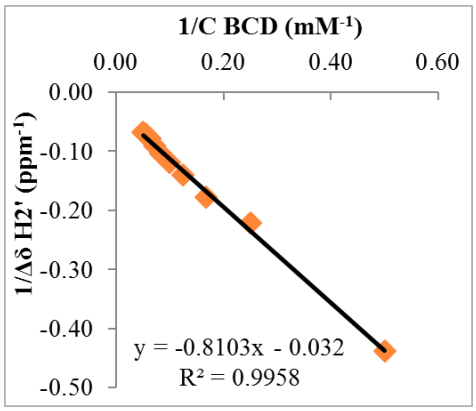
Figure 1. *Job's plot for benzimidazolium salt and beta-cyclodextrin mixtures indicating the 1:1 stoichiometry*



Determination of association constants

For each set of samples, the concentration of benzimidazolium salt was kept constant (10^{-3} M) and the concentration of cyclodextrins was increased up to 20 fold excess. The Benesi-Hildebrand data treatment (example in Figure 2) was used to determine the association constants by using the chemical shifts of the peaks with the largest chemical shift variation upon titration.

Figure 2.*Chemical shifts variations of benzimidazolium salt H-2' proton as a function of BCD concentration*



For recording the ROESY experiments, 1:1 (molar ratios) mixtures in D_2O of the benzimidazolium salt and BCD, Me-BCD and 2HP-BCD were prepared. Correlation peaks were observed between the inner cavity protons of the cyclodextrin's molecule (H-3 and H-5) and ones from the benzimidazolium residue and its phenyl substituent, meaning that the salt molecule resides inside the cavities of the cyclodextrins.

4. Conclusions

Cyclodextrin inclusion may be successfully used for improving the water solubility of benzimidazolium derivatives.

Acknowledgements

The research was supported by the EEA Norway-Romania Grants and Romanian National Authority for Scientific Research, CNCS-UEFISCDI, project number RO-NO-2019-0540 (STIM4+) and by the project InoMatPol (ID P_36_570, Contract 142/10.10.2016, MySMIS: 107464).

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SALICYL-IMINE-CHITOSAN HYDROGELS FOR PROLONGED DRUG RELEASE

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1. Introduction

In recent years, researchers are aiming on developing new materials which can be used as local therapy alternative, to load and release various drugs. Among them, chitosan-based hydrogels are a promising alternative, due to their versatile properties: they are non-toxic, biodegradable and biocompatible, have capacity to absorb various fluids and to swell.[1] Even that, in order to improve and control their delivery potential an important research direction was dedicated to the chitosan modification. It was demonstrated that by physical or chemical crosslinking of chitosan with various agents is possible to adjust the morphology and viscoelastic properties.[2] The research activity of our group proved the possibility to obtain hydrogels based on chitosan and different natural monoaldehydes with good properties for bioapplications: biocompatibility, mechanical strength, biodegradability, thixotropy, high drug-loading capacity and its controlled release.[3-5] By using salicylaldehyde was possible to obtain hydrogels with excellent thixotropic and self-healing properties which recommend them to act as matrix for drug delivery systems.[6] To demonstrate the achievability of this newly developed chitosan-based hydrogel to act as a matrix, the present paper reports the preparation and characterization of new drug delivery systems by *in situ* hydrogelation of chitosan and salicylaldehyde in the presence of diclofenac sodium salt (*DCF*) as a model drug.

2. Experimental

Materials: low molecular weight chitosan (193 kDa, DA=82%), salicylaldehyde (SA) (98%), ethanol, glacial acetic acid, phosphate buffer (PBS) (pH=7.4), diclofenac sodium salt (*DCF*), lysozyme (40 000 units/mg protein) were purchased from Aldrich and used as received.

Synthesis: a series of four formulations with different crosslinking degrees were prepared by *in situ* hydrogelation of chitosan with salicylaldehyde in the presence of *DCF* by varying the molar ratio between the glucosamine units of chitosan and salicylaldehyde.

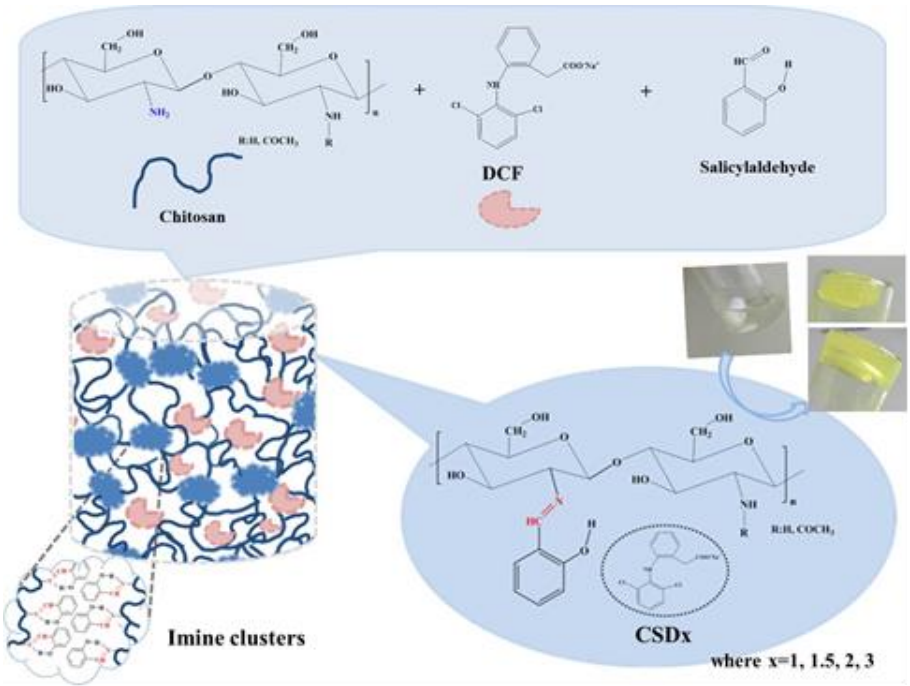
Equipment and methods: the formulations have been characterized from the structural and supramolecular points of view by Fourier transformed infrared spectroscopy (FT-IR Bruker Vertex 70 Spectrofotometer), Wide angle X-ray diffraction (Bruker D8 Avance diffractometer), Polarized light microscopy (Olympus BH-2) and Scanning Electron Microscope (Scanning Electron Microscope SEM EDAX – Quanta 200). Swelling studies, *in vitro* enzymatic biodegradation and release profile of *DCF* were investigated in similar conditions mimicking the *in vivo* environment (PBS, pH=7.4 at 37°C). The *in vitro* release kinetics of ***DCF*** was evaluated using UV-visible spectroscopy, by recording the characteristic absorption band at 275 nm, and fitting its absorbance on a predetermined calibration curve. Also, the release mechanism was assessed by fitting the *in vitro* release data on five mathematical models. The biocompatibility of these formulations was assessed *in vivo*, on experimental rats.

3. Results and discussion

A series of four formulations with different crosslinking density have been prepared by varying the molar ratio between glucosamine units of chitosan and aldehyde group of salicylaldehyde (Figure 1). To prove that the hydrogelation in the presence of *DCF* take place due to the self-ordering of the newly formed imine units into clusters which play the role of crosslinking nodes, the formulations were characterized from structural and supramolecular points of view by FTIR, X-ray, SEM and POM techniques, and data were compared to those obtained for the reference hydrogels. The FTIR spectroscopy demonstrated the formation of the imine linkage between chitosan and salicylaldehyde around 1630 cm^{-1} and confirmed the presence of *DCF* in the resulted systems. Wide angle X-ray diffraction and optical polarized microscopy revealed the formation of organized supramolecular 3D systems, while SEM showed highly porous morphologies.

Both X-ray and SEM techniques proved that the *DCF* was anchored by physical interactions into the pores walls at submicrometric level.

Figure 1. *Schematic representation of the synthesis of the DCF delivery systems*



The *in vitro* release kinetics of *DCF* in phosphate buffer solution (pH=7.4) was evaluated using UV-visible spectroscopy, revelling that these formulations are able to provide a sustained release of the encapsulated *DCF* during 10 days, the release rate being correlated to the crosslinking density and hydrogelation speed of the systems. The biodegradation occurred in three main stages, reaching a mass loss of 48% after 21 days.

The formulations showed *in vivo* biocompatibility on experimental rats, no influence on the hematologic profile, liver, kidney or immune defence capacity being detected after 7 days of subcutaneous implantation.

4. Conclusions

New drug delivery systems were prepared by *in situ* hydrogelation of chitosan with salicylaldehyde in the presence of *DCF* as model drug. The formulations presented attractive properties, such as: biodegradability, biocompatibility, swelling ability and capacity to release DCF in a controlled manner, suggesting these formulations as valuable materials for biomedical applications.

Acknowledgements

The research leading to these results has received funding from the Romanian National Authority for Scientific Research, MEN-UEFISCDI grant, project number RO-NO-2019-0540 (no. 14/2020) and the European Commission through the project H2020-MSCA-RISE-2019, SWORD- DLV-873123.

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ELECTROSPUN COMPOSITE FIBROUS MATERIALS FROM BIODEGRADABLE POLYMER AND CHEMICAL FUNGICIDE FOR GRAPEVINE PROTECTION

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1. Introduction

Esca is one of the earliest described diseases in grapevines that cause trunk damages and sudden wilting of the entire plant caused mainly by species *Phaeomoniella chlamydospora* (*P. chlamydospora*) and *Phaeoacremonium aleophilum* (*P. aleophilum*). In practice, there are no known curative approaches for fighting with esca directly, which is a huge problem for preserving the vineyards[1].

The progress in the field of nanotechnology during recent years, and the possibilities that it offers have enhanced the interest of researchers and industry in composite materials, especially those based on biodegradable polymers. This interest is due to a great extent to the various and increasing possibilities of application of materials from these polymers in a growing number of areas of social and economic importance, such as agricultural application. Electrospinning is currently regarded as one of the most promising nanotechnologies for the preparation of fibers having micro- and nanoscale diameters and a large specific surface area which is a prerequisite for the attainment of high effectiveness in a number of applications[2], e.g., medicine and agriculture[3]. In this respect, among the polymers from renewable sources particularly, polyesters and polysaccharides deserved special attention. Cellulose acetate (CA) is one of the most important esters of cellulose. The advantages of CA are its low cost, an easily feasible production and wide variety of applications. Recently, great attention has been paid to fibers from cellulose and cellulose derivatives due to their biodegradability, good mechanical and barrier properties.

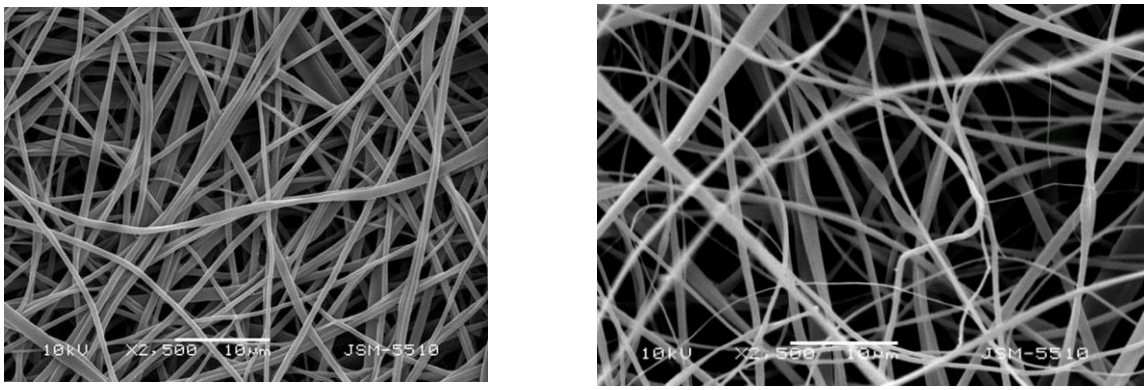
The present study aims at preparation of electrospun composite materials from biodegradable polymer and 8-hydroxyquinoline derivative with antifungal activity. The effect of the incorporated biologically active compound on the morphology, wetting and physic-chemical properties was studied. Microbiological test against *P. chlamydospora* and *P. aleophilum* were performed as well.

2. Results and discussion

The research concept is based on the assumption that by using the electrospinning method, it is possible to find effective experimental approach to obtain innovative composite micro- and nanostructured fibrous materials with fungicidal activity against *P. chlamydospora* and *P. aleophilum*. Moreover, the advantage of the so-called "active dressing" made of electrospun polymer membrane will be not only its fungicidal activity against some of the esca `s causes, but also will allow the plant wound to “breath”. In the present study, the versatility of electrospinning was exploited in order to create innovative polymer materials with fungicidal activity against two strains ascomycete fungi - associated with esca - the most devastating disease of grapevines.

In the present study we have used SEM analysis to observe the morphology of the obtained materials. SEM micrographs of the obtained CA and CA/5-Cl8Q fibrous materials are shown in Figure 1. Electrospinning of CA solution under the selected conditions reproducibly resulted in obtaining continuous defect-free fibers with mean fiber diameter of 780 ± 100 nm. The addition of 5-Cl8Q to the spinning solutions resulted in slight decrease of the fiber diameters.

Figure 1. *SEM micrographs of fibrous materials:* **A**. *CA and* **B**. *CA/5-Cl8Q*



A. **B.**

Contact angle analysis was used to give an indication of the surface wettability depending on the composition of the prepared membranes. It was found that CA and CA/5-Cl8Q membranes were hydrophobic with water contact angle of ca. 120°.

8-Hydroxyquinoline derivatives display a broad range of biological activities, including antifungal activity against pathogenic fungi causing diseases in humans and in animals. The determined by us low MIC values of 5-Cl8Q against *P. chlamydospora* and *P. aleophilum*[4] give reason to expect that incorporation of 5-Cl8Q in fibrous materials will result in obtaining efficient antifungal membranes. Because of the growth characteristics of *P. chlamydospora* and *P. aleophilum* fungi their development was followed 96 h. The membranes containing 5-Cl8Q completely inhibited the fungi growth within 96 h. This is due to the fact that the 5-Cl8Q content in the fibrous materials was much higher than the determined MIC of 5-Cl8Q, and, in addition, the release profile of 5-Cl8Q provided sufficient amount to be released still in the early stages of the experiments.

Figure 2. *Digital images of the zones of inhibition against P. chlamydospora and P. aleophilum after contact of the membranes with fungi cells*

3. Conclusions

Composite micro- and nanofibrous materials of biodegradable polymer containing 5-chloro-8-hydroxyquinolinol were obtained by electrospinning. The incorporation of 5-Cl8Q into the fibers imparted a considerable antifungal effect against *P. chlamydospora* and *P. aleophilum* fungi. These features indicate that the obtained novel fibrous materials are suitable candidates for application in agriculture for plant protection against two main causative agents of esca disease.

Acknowledgements

Financial support from the Bulgarian National Science Fund (Grant KP-06-OPR03/2) is gratefully acknowledged.

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CRYOGELS OF CARBOXYMETHYLCHITOSAN FOR 3D-CELL CULTURE

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1. Introduction

Targeted search of efficient drugs, first of all, anti-tumor ones, requires screening of numerous substances under conditions the most similar to those of tumor formations in the human organism. Traditional methods of cells cultivation and manipulation in 2D systems are now insufficient to solve new tasks of cell biology, biochemistry, and pharmacology. About 67 % of anti-tumor drugs are excluded from clinical tests at later stages due to their low efficiency and safety, which were not manifested at early screening stages with application of 2D cell models. There is an opinion that in many cases the experiments on cells in 2D cultures cannot be physiologically relevant with respect to complex in structure, heterogeneous in cell composition, and constantly changing over time tumors in the human organism.[1] It was shown that HCT 116 cells (human colon cancer cells) in the composition of tumor spheroids were 1.5–3.5-fold less sensitive to some anti-tumor drugs than the same cells cultivated in 2D systems.[2] Organization of actinic filaments in human liver carcinoma cells at 3D cultivation is different from that of cells in the monolayer on the surface of the culture vessels.[3]

Achievements in the fields of materials chemistry, materials fabrication and processing, and biology resulted in creation of 3D matrices, which reflect more adequately the geometry, chemistry, and signal medium of the natural outer-cell matrix for cell cultivation.[4] Such matrices enable one to analyze spatial interaction between cells and between them and the outer-cell matrix. 3D porous matrices based on biodegradable and biocompatible polymers are of great interest simultaneously for creating tissue engineering structures and cell cultivation for in vitro studies. The main problems of the development of macroporous materials based on chitosan are related to its insolubility in alkaline media and, simultaneously, to the absence of efficient crosslinking agents working in acidic media, except high-toxicity dialdehydes.[5] Broadly applied at present in the synthesis of porous materials lyophilization of chitosan solutions with subsequent neutralization or treatment by water-alcohol or water-acetone mixtures with stepwise increase of the fraction of the aqueous phase has numerous disadvantages: the main ones are related to the necessity of using special vacuum equipment, solubility of the fabricated material in acidic media, and instability of the 3D structure.

Here we suggest the method of fabrication of supermacroporous biodegradable materials with pore sizes of no less than tens of microns for three-dimensional cultivation of mammal cells to create 3D models of tumor tissues for testing in vitro effectiveness of anticancer drugs and investigation of cell-cell interactions.

2. Experimental

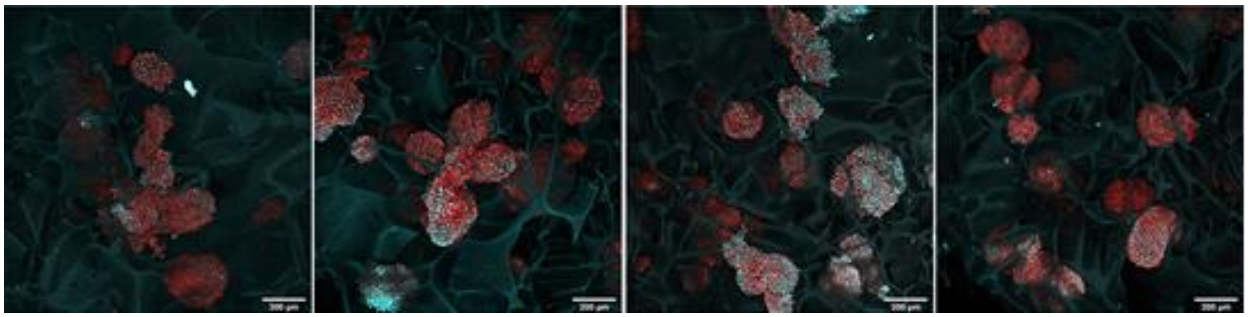
Low molecular weight N,O-(carboxymethyl)chitosan (CMC) with deacetylation degree of 0.75 and degrees of N- and O-carboxymethylsubstitution of 0.29 and 1.20, respectively, was purchased from Biolog Heppe GmbH (Germany). Cross-linking agents 1,4- butanediol diglycidyl ether (DGE-1,4-BD) and ethylene glycol diglycidyl ether (DGE-EG) were purchased from Sigma–Aldrich and J&K Scientific Ltd. (China), respectively. Monolith CMC cryogels have been fabricated from 3% aqueous CMC solution at cross-linker:CMC molar ratios from 4:1 to 1:2 at -10°C, freezing time was set to 7 days. The growth and formation of 3D structures by tumor lines of human cells of intestines (HCT116) have been investigated in flow-through systems. The dynamics of changes in the morphological and functional state of cells was analyzed using a complex of immunocytochemical and fluorescent dyes: TRITC-labeled phalloidin, TO-PRO-3, DAPI. Analysis of stained single cells was carried out by flow cytometry (Beckman-Coulter, USA). The analysis of cells in the composition of the spheroids was carried out on a laser scanning confocal microscope LSM 780.

3. Results and discussion

It has been shown that the degree of modification of CMC with DGE was significantly lower than we have reported earlier for chitosan,[6] which can be explained by the substitution of most reactive primary amino groups and C-6 hydroxyl groups in CMC. Despite the low degrees of functionalization with the crosslinking agent (from 3.8 to 13% according to the elemental analysis data), mechanically strong CMC cryogels were obtained over the entire range of molar ratios. The CMC cryogels supported solution flow rate through the monolith up to 200 column volumes per hour. Due to the insignificant difference in the degree of modification by the cross-linking agent, the mechanical properties of CMC cryogels obtained with DGE-1,4-BD differed insignificantly - Young's modulus, determined from the compression curves of a cylindrical cryogel sample, varied in the range of 6.5-13.3 kPa, while for the chitosan cryogels obtained with the same type of cross-linking reagents, Young's modulus reached 90 kPa[6]. The morphological features of the CMC cryogels depending on the crosslinking reagent and the molar ratio were studied by laser scanning confocal microscopy, the minimum pore size was determined as 118 ± 32 μm, the maximum - 213 ± 67 μm.

Several set-ups of three-dimensional cultivation of tumor human cells in monolithic CMC cryogels have been tested. The higher efficiency of the flow-through system has been confirmed using laser confocal microscopy, and the optimal flow rate of the medium has been determined. It has been found that the cell aggregates morphology and their distribution in the polymer matrix depended on the cryogel characteristics. The highly cross-linked cryogels showed the lowest efficiency for 3D cell culture. Cultivation of HCT116 cells in CMC cryogel cross-linked with DGE-1,4-BD in a flow-through system at a medium flow rate of 7-8 bed volume/day after 7 days led to the formation of multiple spheroids with a diameter of about 150 μm or more (the average cell size of this culture is 8 –16 μm) – Figure 1.

Figure 1. *3D structures of HCT116 tumor cells in monolith CMC cryogel cross-linked with DGE-1,4-BD at cross-linker : CMC molar ratio 1:1, 7 days of cell culturing at flow rate 7 bed volume/day (scale bar - 200 μm, blue color - cell nuclei, red - actin cytoskeleton of cells)*



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SAMPLE CONTROLLED THERMAL ANALYSIS – A PROMISING APPROACH FOR COMPLEX SYSTEMS

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1. Introduction

For the majority of technical applications, the knowledge of the thermal stability of polymers is essential in order to avoid decomposition during the processing or the service life of polymers. Thermal stability defined as the ability of the polymeric material to resist to action of heat and maintain its properties (strength, toughness or elasticity) at a given temperature is usually determined by thermogravimetric analysis. A weight loss as a function of temperature is monitored and some characteristic temperatures $T_{x\%}$ (where x is the mass loss) and the maximum rate of weight loss are determined from the thermogravimetric profile.[1] The most common temperature program is the one in which the temperature changes linearly with time, so that the heating rate is constant.

The quality of TGA measurements is directly related to the accuracy and precision of determination of every single decomposition step. From this point of view, especially in the case of complex polymeric structures containing multiple building blocks the conventional TGA presents some limitations. These are related to complex thermal scans with broad or overlapping weight losses evidenced by multiple peaks and shoulders. This pattern was noticed for two types of structures:

- ✓ β – cyclodextrin – based polyurethane hydrogels containing two or three building blocks: β – cyclodextrin, polyethylene glycol based urethane sequence and oligolactide;
- ✓ mixture containing poly(lactic acid).

The present study focuses on studying the ability of the sample controlled thermal analysis to better separate the overlapping thermal events emphasized in a conventional TGA experiment of a complex system. The advantages and disadvantages of the sample controlled thermal analysis are discussed.

2. Experimental

Dynamic rate High Resolution TGA analysis was performed using 20°C/min and 50°C/min heating rates and resolution from 3 to 6, sensitivity 1, from ambient to 700°C. For comparison, a series of constant heating rate experiments were carried out using 5°C/min, 20°C/min and 50°C/min heating rates.

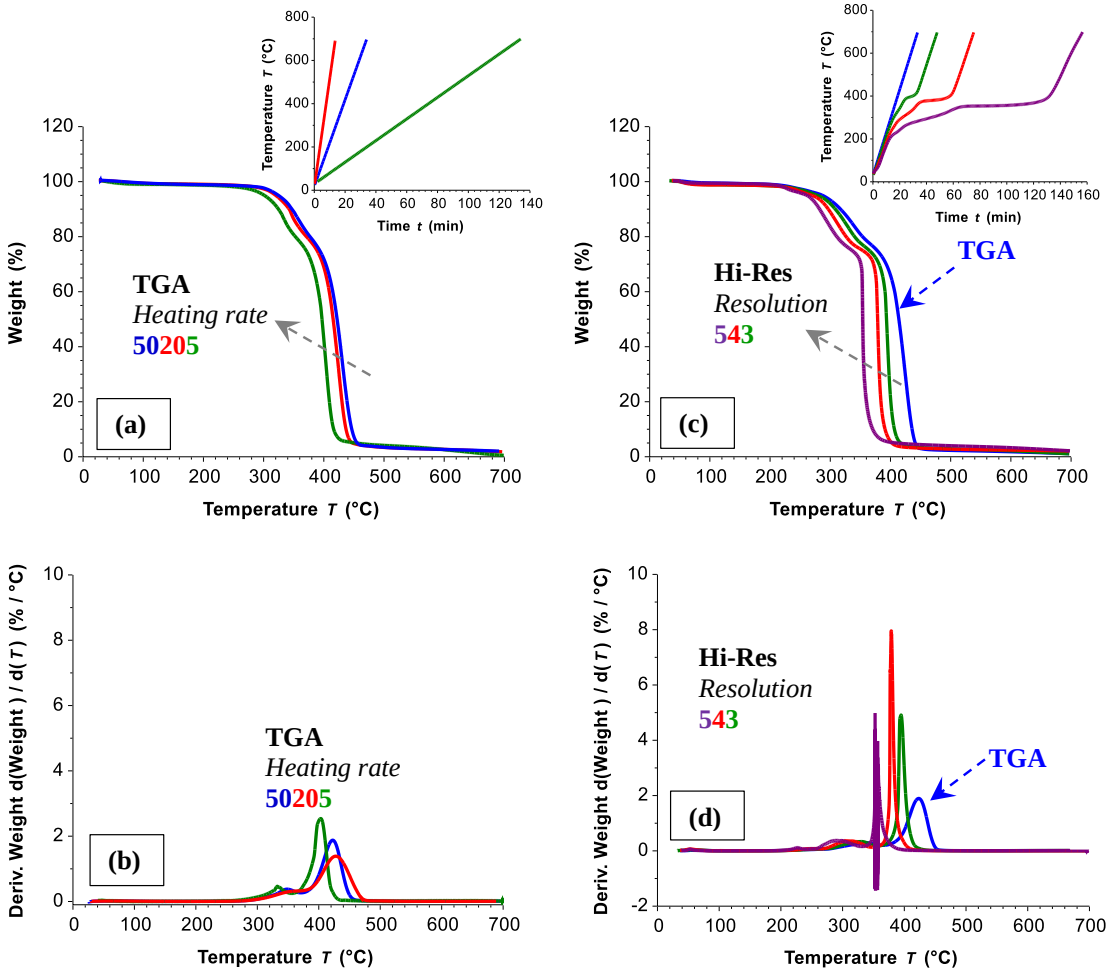
3. Results and discussion

Very small samples or very low heating rates have proven to be a very a particularly effective method for enhancing resolution in TGA. However, these conditions cause problems, either of sensitivity, or of a very long time needed for the experiment, perhaps several hours if isothermal or at a very slow heating rate. Another approach which delivers enhanced TGA resolution without the time trade-off is the sample-controlled thermal analysis developed by TA Instruments (HiRes™), which uses the feed-back from the sample in order to control its heating profile.[2-4] High heating rates are used during no weight loss regions, while small heating rates are applied during weight changes.

A series of experiments were run to find the optimum conditions to perform the dynamic rate High Resolution TGA experiments.

The thermal curves show a β – cyclodextrin based polyurethane hydrogel with or without oligolactide sequence run by both techniques.

Figure 1.*TGA versus High Resolution TGA for a cyclodextrin based polyurethane hydrogel without (Figure 1 a, b) or with lactide segment (Figure 1 c, d)*



Reducing the heating rate generates only subtle differences in the weight loss curve of the cyclodextrin network, evidenced by a shifting of the two decomposition steps to lower temperatures, but with an increase in the experimental time. Increasing the resolution from 3 to 5 in a Hi-Res TGA performed on the cyclodextrin lactide network has emphasized the degradation of lactide segments and an increased the separation of the quite broad weight loss region between 300°C and 440 °C.

4. Conclusions

The Hi-Res technique has some advantages compared to the conventional constant heating rate. It improves the resolution of successive/overlapped TGA weight losses by revealing fine characteristics of the degradation with a right choice of experimental conditions (heating rate, resolution, and sensitivity).

Acknowledgements

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ANTIFUNGAL PROPERTIES OF NEW MULTICOMPONENT POLYMER SYSTEMS AS FLAME RETARDANT COATINGS

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1. Introduction

Epoxy resins are versatile reactive compounds possessing very good properties, such as: good adhesion to different substrates, great resistance to corrosion, chemicals and abrasion, flexibility, moderate toughness, etc. being widely used in domains like engineering and construction, aeronautics, printed circuit boards etc.[1] Within this context, semi–interpenetrating polymer networks (S–IPNs) were obtained from diglycidyl ether of bisphenol A (DGEBA) cured with aromatic, cycloaliphatic and aliphatic hardeners and having as linear component an aromatic oligophosphonate, which were tested in terms of long time antifungal resistance.

2. Experimental

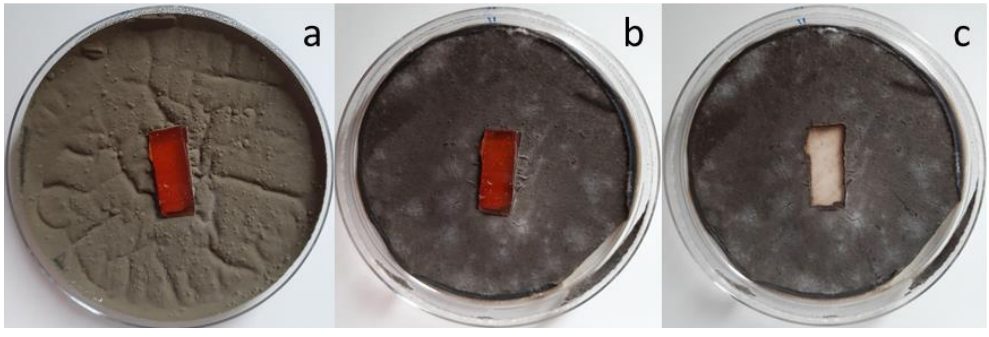
The samples resistance against decay was tested against three different fungal strains: *Penicillium chrysogenum* ATCC10106, *Cladosporium cladosporioides* ATCC16022 and *Aspergillus brasiliensis* ATCC 9642. The samples were placed on Petri dishes with proper media and inoculated with a fixed amount of test-microorganisms (0.5 McFarland standard) and afterwards incubated for 10 weeks at 25°C. Visual aspect of the fungus colony on the samples surface was monitored at each 7 days interval during the 10 weeks of incubation.

After 10 weeks of exposure to fungal attack, the samples were extracted from the culture plates and the mycelium present on their surfaces was rinsed repeatedly. The wet samples were oven-dried at 100ºC for 3 hours until they reached constant weight. The previously resulted suspension was serially diluted and, in order to quantify the fungistatic properties of the samples against fungal attack it was used CellTiter 96sAQueous One Solution Cell Proliferation Assay, MTS (Promega, Madison, WI USA), by following the protocol recommended by the manufacturer. Experiments were done in triplicate and cell viability was expressed as percentage of control cells' viability. Graphical data were expressed as means ± standard error of the mean.

3. Results and discussion

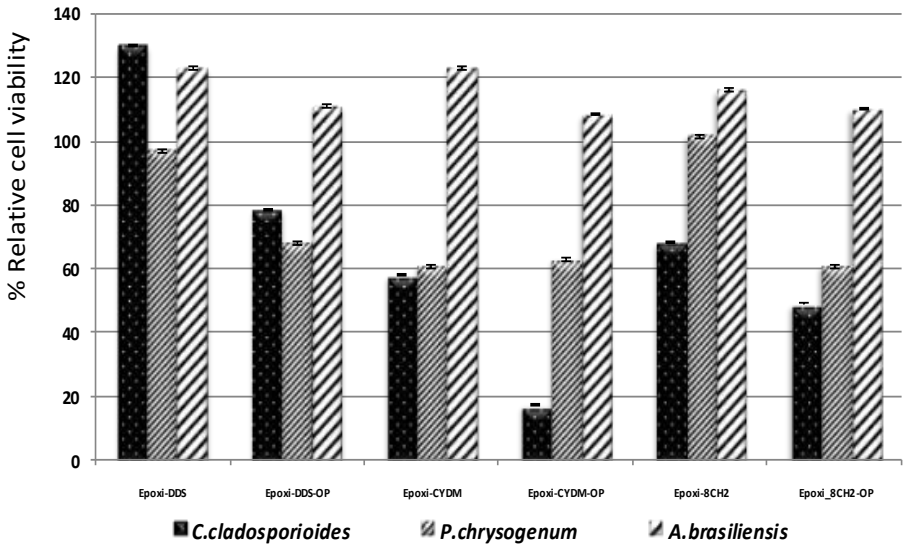
First the assessment of degradation degree after 10 weeks of exposure was based on visual observations and the measure of the weight loss. As it may be noticed in Figure 1, during the decay test, all surfaces of samples were not covered by the fungal colonies. It was not noticed a mass lost for all of the tested samples, excepting those incubated with *A. brasiliensis*. Even in this case the weight loss was much reduced, less than 1% for most of the samples.

Figure 1. *The S–IPN cured with aromatic hardener, as example, exposed to C. cladosporioides for 1week (**a**), 10 weeks (**b**), and inhibition zone after the sample being removed at the end of the incubation (**c**)*



Even if there were not noticed weight variations, and also there was not distinguished a notable growth of the colonies on the samples, the fungistatic properties when compared with a control varied from having excellent fungistatic properties against *C. cladosporioides* and being slightly efficient against *A. brasiliensis* adherence in other cases (Figure 2).

Figure 2. Fungistatic efficacy of the samples against the reference strains



4. Conclusions

There were obtained new epoxy–based semi–interpenetrating polymer networks with very good fungistatic properties.

Acknowledgements

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CARBON BASED NANOMATERIALS-DNA-GOLD NANOPARTICLES HYBRID ASSEMBLIES FOR SERS BIOIMAGING

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1. Introduction

Reliable, fast detection and imaging of living cells is becoming an urgent need in medical diagnostic. The ability to study cellular and molecular processes has the potential to impact many aspects of biomedical oriented research and clinical patient management in terms of early diagnosis of disease, monitoring and therapy. An interesting approach to overcome major disadvantages of the currently available techniques (magnetic resonance imaging, computed tomography, optical bioluminescence and fluorescence, high frequency ultrasound, flow cytometry, etc.)[1,2] is represented by Raman technique that is gaining extensive approval for biomedical applications during the last decade.[3] Conventional Raman spectroscopy is able to distinguish the spectral fingerprint of many molecules, but it is often limited by the extremely low efficiency of the scattering process. However, the discovery of the surface enhanced Raman scattering (SERS) phenomenon offers an exciting opportunity being capable of detecting even at single-molecule scale. The SERS effect typically appears when molecules are either adsorbed onto nano-roughened noble metal surfaces or positioned between noble metal nanoparticle surfaces (hot spot) which results in a dramatic increase of the incident electromagnetic field, resulting in high Raman intensities comparable to fluorescence.[4] However, the complexity and difficulties in design and construction of Raman agents still constitute a major disadvantage in the implementation of SERS. Herein, we present a facile strategy for the DNA-assisted decoration of carbon-based nanomaterials (CBNs) with gold nanoparticles (AuNPs) and their application in SERS bioimaging.

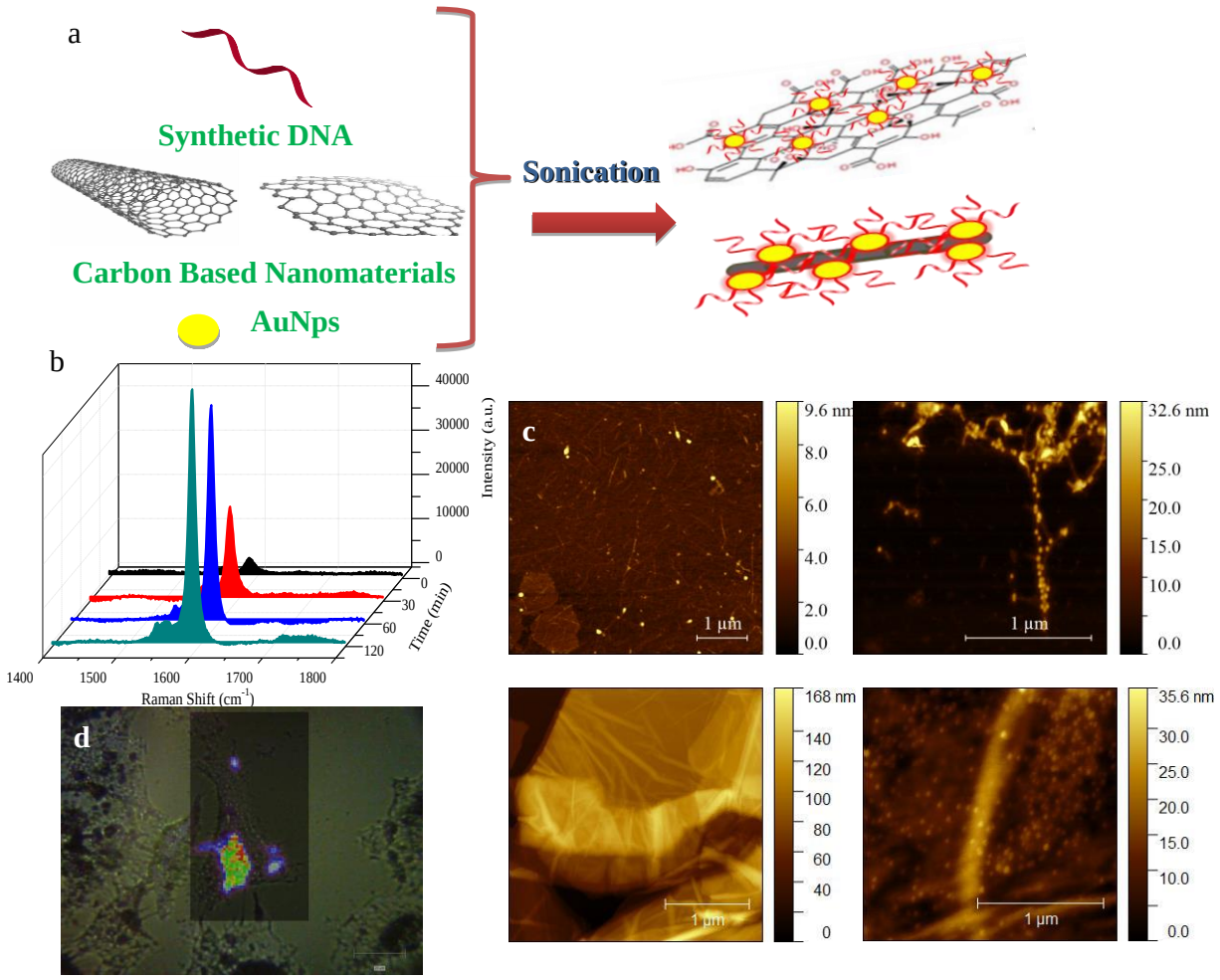
2. Experimental

Citrate coated AuNPs were synthesized using standard and adapted Turkievich methods[5] and subsequent functionalized with synthetic DNA. By ultrasonication at room temperature of CBNs (single walled carbon nanotubes (SWNTs) and graphene oxide (GO)) with DNA-AuNPs, CBNs-AuNPs hybrid assemblies with enhanced Raman signal were obtained. The physico-chemical properties were investigated by UV-Vis spectroscopy, zeta potential, atomic force microscopy (AFM), TEM, and Raman spectroscopy. The cytotoxicity of the CBNs-AuNPs assemblies was tested prior to SERS experiments on HeLa cells.

3. Results and discussion

A facile strategy for the DNA-assisted decoration of CBNs with AuNPs by sonication at room temperature was developed and the process was monitored using Raman spectroscopy (Figures 1a, 1b). The reaction mixture after 60 min of sonication was analyzed by AFM on freshly cleaved mica, pretreated with $MgCl_2$ for better attachment of DNA modified nanostructures (Figure 1c). Analyzing the AFM images, we could observe that AuNPs were attached to the carbon nanotubes or graphene oxide surface yielding dispersed hybrid nanomaterials. Cell toxicity test carried out for the synthesized SWNT-AuNPs nanocomposites revealed a cell viability higher than 75% at all tested concentrations (Figure 1e). Further, HeLa cells were incubated with SWNT-AuNPs nanohybrids for 24 hours, washed with ultrapure water and then fixed with 2.5% glutaraldehyde prior to Raman imaging (Figure 1d). The colored areas in the fig. 1d corresponded to G-band characteristic to SWNTs and can be used as an indicator of the SWNT-AuNPs nanostructures presence in the HeLa cells, making these hybrid nanocomposites suitable for Raman bioimaging applications.[6]

Figure 1. *(a) Schematic illustration for the fabrication of water-soluble CBNs–AuNPs nanohybrids; (b) dependence of the Raman signals intensity of SWNT-AuNPs on sonication time; (c) AFM images of the SWNT-AuNPs (top) and GO-AuNPs (bottom) after 60 min sonication; (d) overlapped optical and Raman images of HeLa cells incubated for 24 hours at 37°C with SWNT-DNA*



4. Conclusions

A DNA-assisted method for the attachment of gold nanoparticles to CBNs has been developed, yielding hybrid nanocomposites which exhibited enhanced SERS effect. The possibility to label and Raman image cells was successfully demonstrated. The presence of free DNA around the CBNs-AuNPs is one of the key advantages of the proposed strategy, as it allows post-synthetic modification of obtained hybrid assemblies through hybridization of complementary DNA stands containing molecule of interest.

Acknowledgements
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HYDROPHOBIC BIOCOMPATIBLE $CaCO_3$/CELLULOSE MATERIAL WITH POTENTIAL APPLICATION IN WOUND DRESSING

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1. Introduction

Due to their antibiofouling, self-cleaning and strain resistance properties, hydrophobic surfaces have been used in a variety of applications in recent years.[1-3] In nature, composite materials with these characteristics include teeth, bones or shells, which contain both biopolymers and crystalline phases.[4] Calcium carbonate is one of the most abundant minerals in the world, having three anhydrous crystalline polymorphs, calcite being the most stable form.[5] Several studies investigated the selective nucleation of calcium carbonate using chemically modified templates,[6,7] in order to obtain hydrophobic materials. As such, we report a simple method for the potentially large-scale coating production of calcium carbonate *via* diffusion-controlled crystallization, using as substrate a cheap, versatile and super-hydrophilic nonwoven material (NWM). Our aim was to obtain hydrophobic surfaces, maintaining the support's biocompatible properties, as possible matrix to load/release different medications in dry wound dressing.

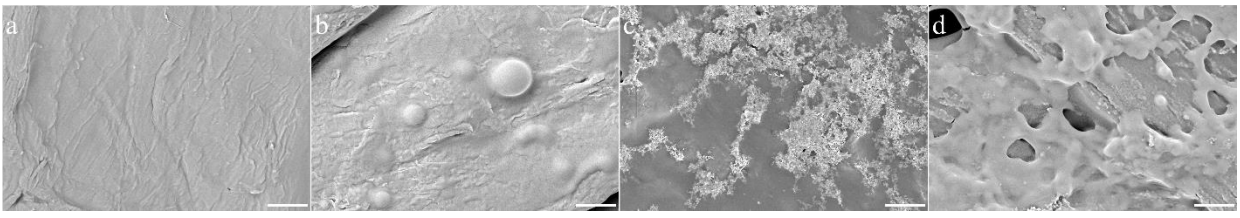
2. Experimental

The NWM material was treated with chitosan (CS) polycation solution, at room temperature. Next, $CaCO_3$ crystals were grown by placing the samples in $CaCl_2$ solutions, without or with poly(2-acrylamido-2-methylpropanesulfonic-*co*-acrylic acid) (PSA), left in a desiccator for 5 days, with NH_4HCO_3 as the carbonate source. The composite materials were analyzed by SEM, XRD, contact angle, and further for tetracycline hydrochloride loading/release, and antibacterial and biocompatibility test.

3. Results and discussion

The polyanion was used to control the $CaCO_3$ crystals' grown on the surface of the NWM material treated with CS polycation (NWM_{CS}). The initial material has a structure made of intermingled fibers with a mean diameter of 152±31 μm, the fibers surface morphology being smooth (Figure 1).

***Figure 1**. SEM images of NWM (a), NWM_{CS} (b), NWM_{CS}-$CaCO_3$ (c) NWM_{CS}-$CaCO_3$/PSA (d) (10 μm)*



After treating the material with CS, the corresponding NWM_{CS} images show the presence of a thin polycation layer at the fibers surface. The chosen method for growing crystals was based on the ammonium carbonate diffusion, the $CaCO_3$ precipitation being induced by exposing the solution containing calcium ions to the vapors released by the ammonium carbonate decomposition, in desiccator. When the samples treated with CS (NWM_{CS}), were introduced in the crystallization medium, the fibers surface was covered by a thin layer of $CaCO_3$. The structures observed on the fibers surface, determined by the presence of a thin layer of $CaCO_3$ or $CaCO_3$/polymer, is expected to decrease the surface energy of the materials, thus obtaining hydrophobic surfaces. The initial material (NWM) is superhydrophilic, making the measuring of the contact angle impossible. After the surface modification with CS the measured contact angle classifies all the obtained composite materials as hydrophobic, the water contact angle exceeding 119°. The contact angle values depend very much on the ability of the complex structure formed by $CaCO_3$ and PSA to cover

the surface and on the pattern formed on the surface. Sample NWM_{CS} - $CaCO_3$/PSA show some large crystals at the materials surface along with a thick polymer layer at fibers surface.

TCH loading and release

The maximum sorption capacity was determined taking into account the initial TCH concentration in aqueous solutions and the residual concentration of the supernatant after sorption. NWM and NWM_{CS} have a good TCH sorption capacity, while the materials with $CaCO_3$ show an increase of the sorption capacity, especially when PSA was used. Also, the sorption capacity was nearly constant in the initial TCH concentration domain of 0.5 – 1.0 g/L, decreasing up to almost 50% when the initial solution concentration decreased to 0.25 g/L. Thus, the samples resulted after the TCH sorption from 0.5 g/L solution were tested for drug release behaviour. The TCH release in phosphate buffer solution at pH 7.4 show a continuous drug release in the first 480 minutes, until reaching a plateau. The highest cumulative release percent, of approximately 30%, was obtained for the samples prepared with NWM_{CS} covered with $CaCO_3$/PSA, while the initial material, NWM, or the one covered with CS, NWM_{CS}, enabled the release of only 6-7% of TCH, while the sample with $CaCO_3$ released approximately 18% in 480 minutes.

Antibacterial activity and biocompatibility tests

The tested samples (NWM, NWM_{CS}, NWM_{CS}-$CaCO_3$ and NWM_{CS}-$CaCO_3$/PSA) did not present antibacterial activity but *E. coli* did not adhere to the materials' surface, while *S. aureus* formed a biofilm on the surface of NWM_{CS} and NWM_{CS}-$CaCO_3$ samples. However, the presence of polyanion did not permit the adhesion of microorganisms in both cases. The antibacterial activity was also tested for the samples loaded with tetracycline (TCH). All the tested samples after the TCH loading showed antibacterial activity for both of the tested strains. The NWM sample loaded with TCH presented the best antibacterial activity, especially agains *S. aureus*. The NWM_{CS}-$CaCO_3$ and NWM_{CS}-$CaCO_3$/PSA samples are equally efficient against *S. aureus*, but less efficient than NWM. The MTS assay showed that the cells treated with NWM_{CS} and NWM_{CS}-$CaCO_3$/polyanion samples had a relative to control viability of 92% and 86%, respectively. The cells treated with NWM showed a proliferation with a relative viability of 118%. On the other hand, the cells treated with NWM_{CS}-$CaCO_3$ did not show significant differences of their viability compared to the control cells.

4. Conclusions

This paper proposes a straightforward technique for the potentially large-scale coating manufacture of calcium carbonate by diffusion-controlled crystallization, using a cheap, adaptable, and super-hydrophilic NWM as a substrate. The goal was to alter the NWM's hydrophilic qualities in order to create hydrophobic composite materials while keeping the NWM's biocompatibility as a loading/release matrix for various drugs. The surface morphology was first modified by polycation (CS) sorption at fibers surface and further on by $CaCO_3$ growth under ammonium carbonate diffusion in the absence or in the presence of PSA polyanion. The NWM's initial super-hydrophilicity changed as a result of surface modification in hydrophobicity, the contact angle values being in the range of 119° - 125°, depending on the ability of the complex structure to cover the surface and on the pattern formed on the surface. The antibacterial test showed that the investigated samples have antifouling capability against *E.coli* and partially for *S. aureus*. The biocompatibility test showed that the cells treated with NWM_{CS} and NWM_{CS}-$CaCO_3$/PSA have a relative to control viability of 92% and 86%, respectively, whereas cells treated with NWM_{CS}-$CaCO_3$ show a 100% viability.

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THIOPHENE END-GROUP-FUNCTIONALIZED OLIGO(2-METHYL-2-OXAZOLINE) AS AN AMPHIPHILIC REACTIVE MACROMONOMER AND AS A NON-CONVENTIONAL INTRINSIC LUMINESCENT MATERIAL

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1. Introduction

Poly(2-alkyl-2-oxazolines) (POXA), also known as peptide-mimetic polymers have received growing attention in the context of biomaterials and polymer therapeutics outperforming polyethylene glycol (PEG), the gold standard in polymer-based applications,[1] in many asspects.[2] POXA provide higher stability, tunability, and functionalization than PEG, while retaining the requisite features of biocompatibility, "stealth" behavior, and low dispersity.

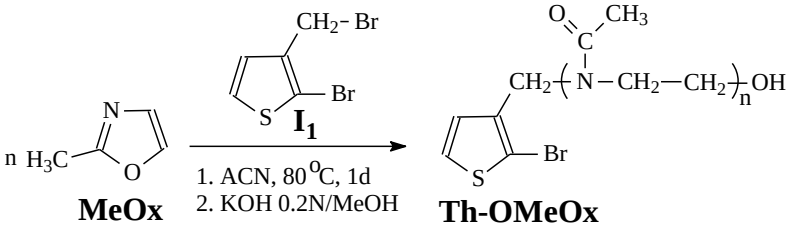
The excellent properties of POXA polymers enable their use in a wide variety of different biomedical applications, from targeted drug delivery and drug formulation to tissue engineering and tissue adhesives. In particular, the extraordinary synthetic versatility of POXA allows the construction of complex polymeric architectures with finely tunable physical properties in a defined manner, for a large range of applications, including nanomaterial formulations. The hydrophilic character of POXA in combination with conjugated polymers (CPs) hydrophobicity will render to the obtained materials an amphiphilic character.

Amphiphilic π-conjugated rod–coil molecules in "hairy-rod" brunched architecture could be of great interest as nanofunctional materials, being excellent candidates in creating well-defined, fluorescent micellar structures,[3] by self-assembling in aqueous solutions with advantages in terms of environmental friendliness and direct applicability as biomaterials.[4-7] As such, exploration and synthesis of new electroctive and photoactive thiophene macromonomers, derived from oligo/polymers already known for their biocompatibility and/or biodegradability, able to work as synthons in the obtainment of new biomaterials, is a hot current topic.[8-10]

2. Experimental

In the present study, we report about the design and synthesis of a new oligo(2-methyl-2-oxazoline)-(OMeOx)-based macromonomer which contains at one chain end a photo- and electroactive 2-bromo-substituted thiophene ring (Th-OMeOx in Scheme 1).

Scheme 1. *Synthesis pathway of macromonomer Th-OMeOx*



3. Results and discussion

Th-OMeOx was engineered as a geometric shape and electronic character dissymmetrical, amphipathic compound, with hydrophobic and aromatic thiophene at one the extremities of the biocompatible, hydrophilic, aliphatic oligo(2-oxazoline). As the cationic ring-opening polymerization (CROP) reaction, used for its synthesis, was quenched by the addition of KOH methanolic solution, the placing of the hydroxyl functionality at the opposite chain end of the OMeOx was possible. The presence of the reactive bromine and of the hydroxyl groups in the Th-OMeOx structure endows this compound with

multifunctionality. Thus, it was used as a reactive intermediate in synthesis, by Suzuki coupling, of a new, polymerizable bithiophene macromonomer and by self-acid-assisted polymerization (SAAP) in solid state a grafted polythiophene amphiphile, having OMeOx as side chains, was obtained.[11] Also Th-OMeOx is an interesting material in its-self. In selective solvents for its constitutive building blocks, (such as water and chloroform), Th-OMeOx showed self-assembling (SA) capability into micellar nanoparticles by the so-called "direct dissolution" method. The SA was demonstrated by different techniques (DLS, UV-vis, fluorescence, AFM) and was due mainly to the solvophobic/solvophilic interactions with the contribution of aromatic thiophene ring (allowing for π-π intre-rings interaction) as well of the hydroxyl end-functional groups able to drive intermolecular hydrogen-bonding. Interestingly, the photophysical properties measurements revealed that the intensity of fluorescence emissions increases with the increasing concentration of dispersion and that the self-assembled structures showed that λ_{ex}-dependent luminescent properties. This clusterization-triggered emission was attributed to abundant presence in the OMeOx structure of electron rich moieties (carbonyl and N) that by "through-space" conjugation ignited this uncommon luminescence form the common OMeOx.[12]

The results of these studies confirm that Th-OMeOx is a versatile, multifunctional compound.

4. Conclusions

In summary, considering critical roles of structural complexity and special functions in advanced polymer materials, we have successfully achieved the synthesis of a new amphiphilic, reactive oligo(2-methyl-2oxazoline) macromonomer (OMeOx) containing thiophene (Th), Th-OMeOx, endowed with multiple functionalities that are encoded in its structure.

Acknowledgements

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DESIGNING PHENOTHIAZINE-BASED MATERIALS WITH HIGH LUMINESCENCE IN SOLID STATE

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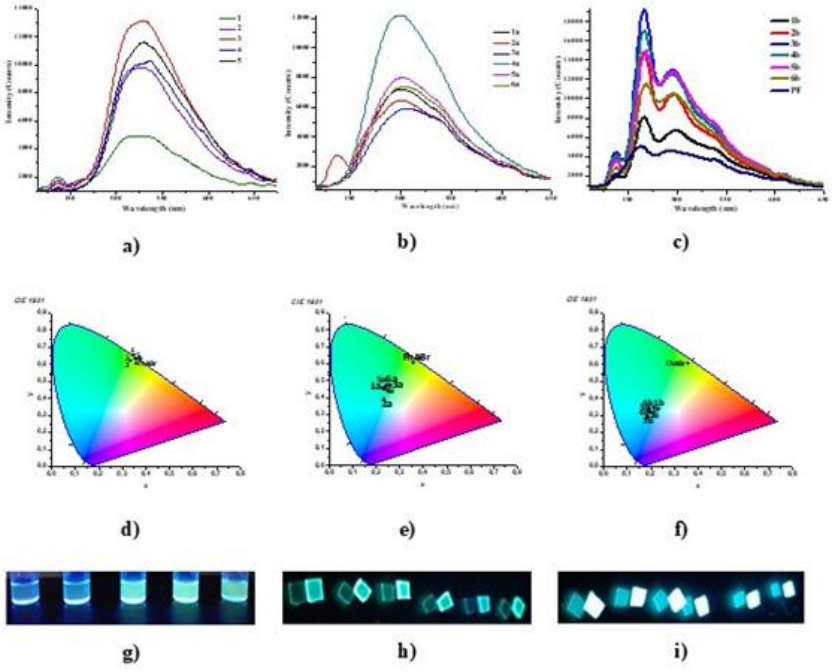
1. Introduction

In this contribution we report the preparation of two types of materials, nanocrystals and cocrystals, based on a phenothiazine derivative bearing bromine and carbonyl units. Their design has been thought in order to improve the quantum efficiency in solid state. The phenothiazine nanocrystals were obtained as water suspensions by the reprecipitation method, and as nanohybrid films by dispersing in polymethylmethacrylate (PMMA) and polyfluorene (PFL) matrix. Their morphological features were investigated using dynamic light scattering technique (DLS), scanning electron microscopy (SEM), atomic force microscopy (AFM), polarized light microscopy (POM) and their photophysical behavior was monitored by UV–vis and photoluminescence spectroscopy. Further, a series of binary phenothiazine-based co-crystals were prepared by combining a host dibromine functionalized phenothiazine (B) with a guest formyl-based phenothiazine (A) in various molar ratios, from 1:1 up to 9:1, to form single crystals and thin films as well. Single crystal X-ray diffraction (XRD), polarized light microscopy, nuclear magnetic resonance (^{1}H NMR) and infrared spectroscopy (FTIR) indicated the successful formation of supramolecular synthons *via* halogen bonds. POM and AFM indicated the formation of submicrometric crystals into the co-crystal films. The photophysical behavior was investigated by UV–vis and photoluminescence spectroscopies.

2. Results and discussion

Nanocrystals based on a phenothiazine chromophore were successfully prepared, in both water and a polymeric matrix, namely PMMA and PFL. Nanocrystals with diameter around 113 nm were obtained by reprecipitation in water, and around105 nm by solvent induced phase separation in PMMA and PFL matrix.

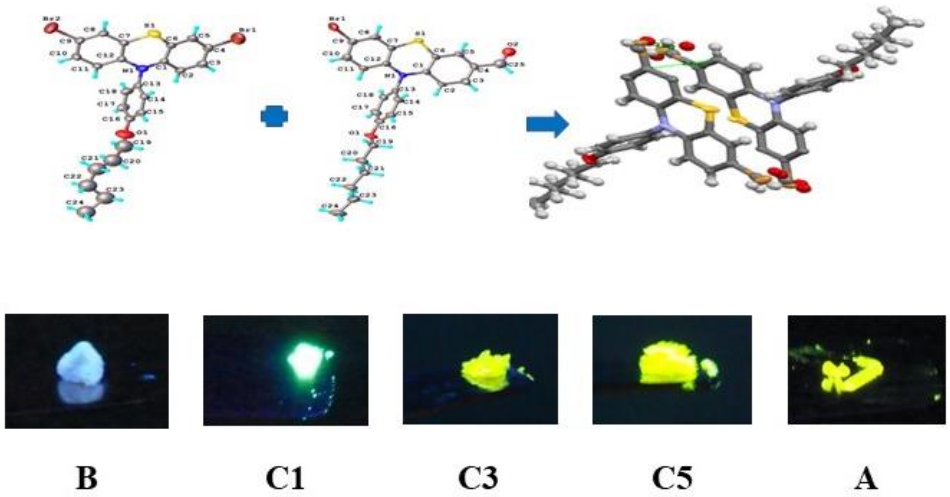
Figure 1. *Emission spectra, chromaticity diagram and images of the samples illuminated with an UV lamp of the nanocrystals in a), d), g) water, b), e), h) PMMA and c), f), i) PFL, when excited at 395 nm*



They presented highly efficient luminescence when excited with visible light (Figure 1), reaching an absolute quantum yield of 35% in water, 45% in PMMA, and 39% in PFL. The high luminescence efficiency of the nanoparticles in the water bio dispersant, when excited with light of low energy makes them attractive for bio-applications, while the high efficiency of the nanoparticles in solid films recommends them as reliable candidates for optoelectronics.

In order to obtain the cocrystals, a guest containing bromine and formyl units (7-Bromo-10-(-4-hexyloxyphenyl)-10H-phenothiazine-3-carbaldehyde (noted A)) was doped into a dibromine containing host (2,7-Dibromo-10-(4-hexyloxy-phenyl)-10Hphenothiazine (noted B)), in different molar ratios, giving new materials with improved photophysical properties (Figure 2). The photophysical behavior was investigated by UV–vis and photoluminescence spectroscopies, and showed a remarkable improvement of the quantum yield, reaching values of 27% for single co-crystals and of 42% for thin films of nano-co-crystals.

Figure 2. *Representation of the co-crystal's preparation and their images under UV lamp*



Acknowledgements

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PMMA-BIOGLASS SCAFFOLDS OBTAINED BY PHASE SEPARATION METHOD: ANALYSIS OF ITS STRUCTURE, MORPHOLOGY, MECHANICAL AND BIOLOGICAL PROPERTIES

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1. Introduction

There are over 1 million cases of bone defects annually due to trauma, congenital anomalies, osteoporosis, and tissue resection caused by cancer that require surgical procedures employing artificial or autologous bone grafting techniques as a treatment.[1] The design and engineering of synthetic 3D scaffolds with ordered architectures has recently received particular attention in medical engineering sectors including genetic, and tissue engineering. Moreover, the synthetic bone graft substitutes can overcome the limitations associated with currents treatments e.g. transmitting infectious diseases and immunological rejection. The scaffold will serve as a template for bone cell regeneration and support the formation of new tissue. While designing a scaffold for bone regeneration, the following properties are essential: biocompatibility, porosity, pore size, surface properties, mechanical properties, and biodegradability.

Mesoporous bioactive glasses used in synthetic scaffolds preparation are attractive materials because of their outstanding properties e.g. optimal surface area, pore-volume, and ability to induce in vitro hydroxyapatite mineralization.[2] Poly methyl methacrylate (PMMA) acrylic bone cement has been used extensively in surgical fixation of artificial joints for more than 50 years. It first used orthopedics is credited to English surgeon, Dr. John Charnley, who used "dental acrylic" in 1958 for total hip arthroplasty.[3] Several techniques such as solvent casting,[4] freeze drying,[5] phase separation,[6] and rapid prototyping technologies[7] have been used to produce scaffolds-based polymer matrix with adequate properties for bone tissue engineering. The phase separation method is an easy and simple way of introducing porosity into a polymer matrix.[3]

This study aimed to obtain PMMA-bio-glass scaffolds containing cerium up to 3 mol %, by phase separation method with suitable properties for bone regeneration treatment. Furthermore, the effect of cerium addition on the properties of the obtained scaffolds was assessed.

2. Experimental

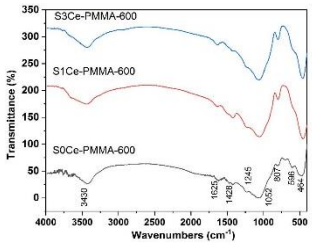
PMMA-bioglass scaffolds were prepared by the phase separation method. The bioglass precursor sol was directly used to obtain the scaffolds. In brief, Ce-doped mesoporous bioglass in the $70SiO_2$-(26-x) CaO-P_2O_5-$xCeO_2$ system (where x stands for 0, 1 and 3 moles %) were synthesized as described in paper.[8] Pluronic P123, was used as structure directing agent. For PMMA bioglass scaffolds fabrication, 15 % PMMA with a molecular weight of 550000 and a density of 1.18 g cm^3 was dissolved in ethanol and water mixture. Equal volumes of the bioglass solution and the polymer mixture were mixed to obtain the scaffold materials. The as prepared scaffolds were thermally treated at 600 °C with the heating rate of 1° /min and 2h plateau at maximum temperature.

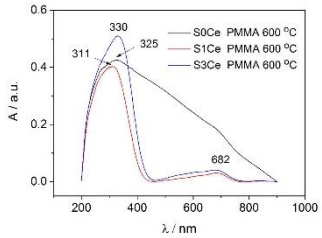
Structure, Ce^{3+}/Ce^{4+} ratio, morphology, porosity, compressive strength, bioactivity, citotoxicity, and biodegradation rate of the resulted scaffolds were investigated. The obtained scaffolds were labeled as follow: S0CePMMA, S1CePMMA and S3CePMMA for as prepared scaffolds and S0CePMMA600, S1CePMMA600 and S3CePMMA600 for thermally treated ones.

3. Results and discussion

XRD patterns confirmed the amorphous structure of the thermally treated scaffolds. UV–vis measurement was performed to determine the Ce^{3+}/Ce^{4+} ratio in PMMA-bioglass scaffolds. As can be observed in Fig. 1 the absorption bands of Ce^{4+} and Ce^{3+} are overlapped. Particularly, cerium can switch in the oxidation states between Ce^{4+} and Ce^{3+} during redox reactions in physiological fluids with formation of free radicals including superoxide anion radical, consequently inducing anti-inflammatory, pro-osteogenesis, and pro-angiogenesis activities. The identification of the functional group by FTIR is shown in Figure 2:

Figure 1. *Absorption spectra of the scaffolds* ***Figure 2***. *FTIR spectra of the scaffolds*





The bands at 1100 and 482 cm^{-1} correspond to the Si-O-Si stretching and bending vibrations respectively. The band at 598 cm^{-1} is assigned as P-O bending vibrations. After immersion in Simulated Body Fluid (SBF) the intensity of this band increases confirming the formation of hydroxyapatite layer. Table 1 shows the properties defined as essential when design a scaffold such as porosity, surface properties, mechanical properties and biodegradability.

Table 1. *Porosity, BET surface area, compressive strength and weight loss of the scaffolds*

Samples	Porosity % (Archimedes method)	BET surface area (m^2/g)	Compressive strength (MPa)	Weight loss 196 h (%)
S0CePMMA600	46	97	27	15.68
S1CePMMA600	54	137	29	8.43
S3CePMMA600	52	114	28	8.13

4. Conclusions

PMMA–bioglass scaffolds were obtained by the phase separation method. UV–vis measurement allowed us to determine the Ce^{3+}/Ce^{4+} ratio in the PMMA-bioglass scaffolds. According to the data from Table 1 and the literature study, it can be concluded that the obtained scaffolds are suitable for tissue engineering applications. Quantitative MTT assay showed that all the scaffolds were cytocompatibles within the concentration range tested. The cell viability significantly decreased at the highest tested concentrations (100%) for all the scaffolds.

Acknowledgements
The financial support of the PN-III-P2-2.1-PED-2019- 0598 project is gratefully acknowledged.

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CHITOSAN BIOCOMPATIBLE HYDROGELS AS DRUG DELIVERY MATRICES FOR ANTICANCER APPLICATIONS

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1. Introduction

Chitosan is a biocompatible biopolymer with good bioadhesivity and biodegradability in human body by an enzymatic metabolism.[1] Based on these favorable properties, various forms of chitosan and its derivatives were developed for application as drug delivery systems. This research activity evidenced a new hydrogel based on chitosan and a monoaldehyde with proper properties for local drug delivery in tumors: rapid hydrogelation in physiological pH and excellent *in vivo* biocompatibility.

2. Experimental

NMR spectra of the hydrogels were registered with a BRUKER AvanceDRX400 MHz spectrometer, FTIR spectra were recorded on the xerogels of the neat hydogels and of the drug delivery systems with a FT-IR Bruker Vertex 70 Spectrophotometer. The supramolecular ordering of the hydrogels and of the drug delivery systems was investigated by Wide Angle X-ray Diffraction (WAXD) on a Bruker D8 Avance diffractometer and on Olympus BH-2 Polarized Light Microscope (POM). Further, their morphology was monitored with a Scanning Electron Microscope SEM EDAX – Quanta 200 equipment. The hydrogels' rheological properties were determined Using a MCR302 Anton-Paar rheometer equipped with a Peltier device. The *in vitro* cytotoxicity of the hydrogels was investigated on HeLa cells and the drug release has been studied *in vitro* by Perkin Elmer Lambda 35 UV-vis spectrophotometer. In addition, the drug release has been investigated *in vivo* on experimental rats.

3. Results and discussion

3.1. The obtaining of hydrogels and of drug delivery systems

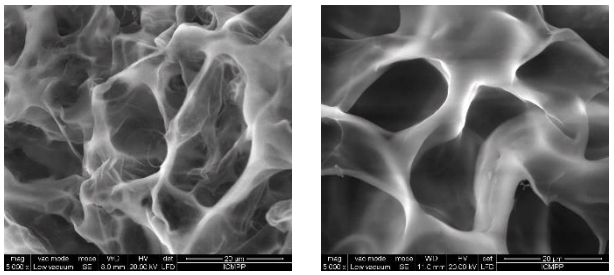
The hydrogels were obtained by acid condensation reaction between the amino groups of chitosan and aminoaldehyde, 2-hydroxy-5-nitrobenzaldehyde,[2] by varying the molar ratios between amino and aldehyde groups. In this way, a series of hydrogels with different crosslinking degree was obtained and noted N1-N7. Drug delivery systems were prepared (N1D-N4D) by *in situ* encapsulation method, during hydrogelation, using the diclofenac sodium salt as model drug.

3.2. Structural and supramolecular characterization

The hydrogelation has been confirmed by complementary methods such as FTIR, NMR, X-ray diffraction and POM, which demonstrated the formation of ordered cluster of imine units, acting as crosslinking nodes of the chitosan chains. Thus, the FTIR and ^{1}H-NMR spectroscopy demonstrated the formation of the imine linkage by the appearance of the characteristic stretching vibration band at 1613 cm^{-1} and specific imine signal at 8.7 ppm chemical shift, respectively. On the other hand, X-ray diffractograms proved the supramolecular ordering of the imine units by occurrence of a sharp reflection band around 6°, characteristic to the formation of layered architectures. Further, POM images displayed strong birefringence in line with the supramolecular organization demonstrated by WAXD.

Encapsulation of the drug into the hydrogel matrix did not significantly affect the X-ray diffractograms, which is confirmed by POM, indicating its anchoring at submicrometric level. Comparative SEM images of both xerogels, with and without the drug, suggested the encapsulation produced mainly into the xerogels' walls (Figure 1).

Figure 1.*SEM images of the N3 xerogel and N3D drug delivery system xerogel*



N3 **N3D**

3.3. Rheological measurements

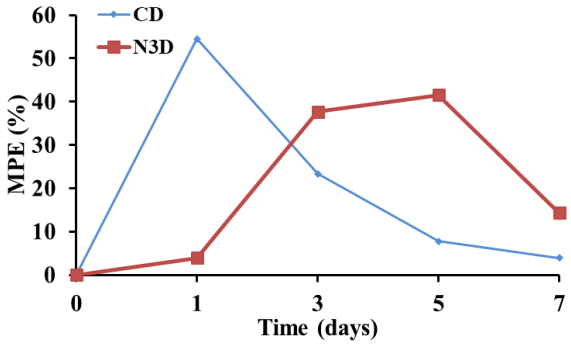
By rheological experiments it was confirmed the gel-like behavior of the studied samples and their ability to recover the mechanical properties after applying a high strain. Moreover, it was demonstrated that the hydrogels' elasticity increased along the crosslinking density.

3.4. In vitro and in vivo biologic experiments

Circular pellets obtained from the xerogels of the hydrogels and drug delivery systems were used for both experiments, *in vitro* and *in vivo*. For the *in vitro* study, phosphate buffer solution was used as a release medium and in case of the *in vivo* study, the biocompatibility and the somatic antinociception, during the release of the drug were monitored. *In vitro* anticancer activity on HeLa cells proved that the hydrogels suppressed the HeLa cell viability around 60%, after 48 h.

The *in vitro* and *in vivo* release tests proved a prolonged release of the drug, during 7 days (ND3), compared to the drug control (chitosan-diclofenac (CD) pellet), which was released during 24 hours (Figure 2). The blood parameters, biochemical response and immune systems were not affected during the period of testing, indicating the biocompatibility of both tested xerogels, with and without the drug.

Figure 2. *Maximum possible effect (% MPE) of the pellet implantation over 7 days*



4. Conclusions

All these results revealed the new hydrogels as a reliable matrix for the development of prolonged release drug delivery systems with good *in vivo* biocompatibility and bioactivity. Therefore, these novel synthesized hydrogels represent biomaterials with potential application in the anticancer therapy, as drugs or as matrices for drug encapsulation.

Acknowledgements

This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PD 197/2020, within PNCDI III and by the project InoMatPol (ID P_36_570, Contract 142/10.10.2016, cod MySMIS: 107464).

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REACTIVITY ANALYSIS FOR 4-(AZULEN-1-YL)-2,6-BIS((E)-2-(THIOPHEN-2-YL)VINYL)PYRIDINE USING CALCULATED QUANTUM PARAMETERS

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1. Introduction

Estimated global reactivity parameters derived from the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), as stated by Koopmans,[1,2] are reported for the structure of 4-(azulen-1-yl)-2,6-bis((E)-2-(thiophen-2-yl)vinyl)pyridine in order to assess its complexing properties for electrochemical applications.

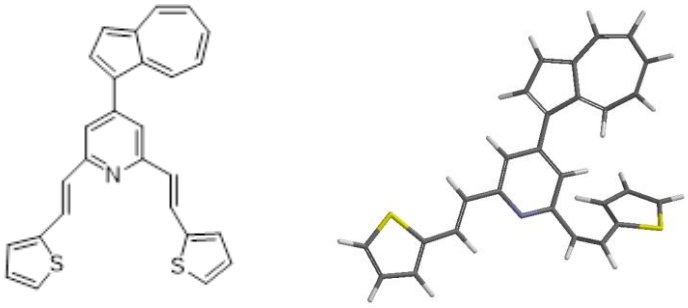
2. Experimental

The optimized 3D structure was obtained by energy minimization using molecular mechanics force fields[3] with Spartan'18 software from Wavefunction, Inc. Irvine, U.S.A. Property computations were performed using Density Functional Theory (DFT) and hybrid B3LYP functional[4] with 6-31G (d, p) polarization basis set for equilibrium geometry at ground state.[5]

3. Results and discussion

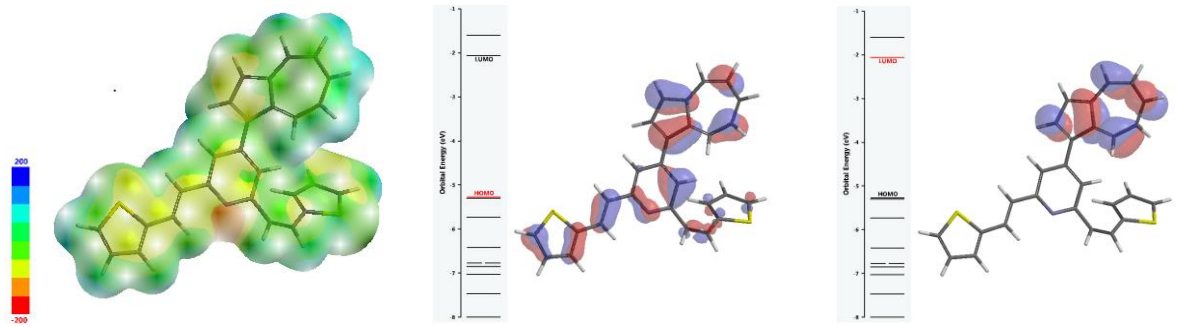
DFT calculations for the lowest energy conformer of the investigated compound in terms of predicted energy levels of the frontier molecular orbitals HOMO and LUMO were conducted. The global reactivity parameters (ionization potential, electron affinity, electronegativity, global hardness, softness and electrophilicity index) along with local reactivity descriptors as Mulliken and electrostatic charges, electrostatic potential and local ionization potential, were obtained. Figure 1 reveals the structure of the studied compound, as 2D (a) and optimized 3D structure (b). Furthermore, in Figure 2, the electrostatic potential map is represented (a), along with the energy diagrams of HOMO (b) and LUMO (c).

Figure 1. *Structure of 4-(azulen-1-yl)-2,6-bis((E)-2-(thiophen-2-yl)vinyl)pyridine*



The used relationships are: $IP = -E_{HOMO}$ (eq.1); $EA = -E_{LUMO}$ (eq.2); $\Delta E = IP - EA$ (eq.3); $\chi = (IP + EA)/2$ (eq.4); $\eta = (IP - EA)/2$ (eq.5), $\sigma = 1 / \eta$ (eq.6) and $\omega = \mu^2 / 2\eta$ (eq. 7) were: IP is the ionization potential, E_{HOMO} is the energy of HOMO, EA is the electron affinity, E_{LUMO} is the energy of LUMO, ΔE is the energy gap between HOMO and LUMO, χ is the electronegativity, η is the global hardness, σ is the softness, μ is the chemical potential and ω is the electrophilicity index.

Figure 2. a) *Electrostatic potential representation;* ***b).*** *HOMO diagram;* ***c).*** *LUMO diagram*



a). b). c).

Table 1. *Calculated chemical reactivity parameters using B3LYP level of theory*

Parameter	***IP***	***EA***	***ΔE***	***χ***	***η***	***σ***	***ω***
Value (eV)	5.27	2.06	3.21	3.67	1.61	0.62	4.18

IP and *EA* can be furthermore correlated with the experimental oxidation and reduction potentials as previously shown from other compounds of electrochemical interest.[6,7] Kinetic stability and reactivity useful to evaluate complexing ability toward heavy metals ions can be compared with results obtained for similar structures, helping in the rational design of modified electrodes.

4. Conclusions

Starting from reactivity analysis by computational means based on electron density properties, we can evaluate a series of quantum parameters useful for electrochemical applications in heavy metal ions recognition. Electrophilic and nucleophilic sites quantitatively approximated using DFT theory improve our strategy efforts in designing better ligands.

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GREEN INTERPENETRATED SILICONE-BASED ELASTOMERIC WEBS ENGINEERED AS WAVE ENERGY HARVESTERS

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1. Introduction

Wave Energy Harvesting using Dielectric Elastomers (DE) as power take-off (PTO) systems is a recently developed technology with great potential.[1-7] The Dielectric Elastomer PTO (DE-PTO) system is a "sandwich" consisting of a dielectric elastomer coated on both sides with compliant electrodes, thus forming a stretchable polymeric capacitor capable of converting mechanical energy into electric energy.[8]

Recently, a DE-PTO system with two polymeric layers (approximately 20 cm in diameter) gave a remarkable average performance of 3.8 W/cycle.[3] The obtained results demonstrated the possibility of designing dielectric elastomer-based PTO systems that can be considered for large-scale electrical energy production.

Silicone-based electromechanical transducers represent one of the most studied classes due to their great properties: high flexibility, low toxicity, resistance to weathering, good dielectric strength and operating on various temperatures (-120 to 200 ºC). Besides these remarkable properties, they possess a relatively low elongation at break and a low dielectric permittivity.

The main aim is to increase the conversion efficiency of silicone-based PTO systems by increasing the elongation at break and the dielectric permittivity of silicone elastomers in an original approach which consists in obtaining new silicone-based interpenetrated polymer networks (IPNs).

2. Experimental

Hydroxyl-ended (HEP) and vinyl-ended (VEP) PDMSs were synthesized by Heterogeneous Cationic Ring Opening Polymerization of the monomer octamethylcyclotetrasiloxane and CT175 as catalyst. Water and 1,3-divinyltetramethyldisiloxane were used for end-capping and to control the molecular weights.

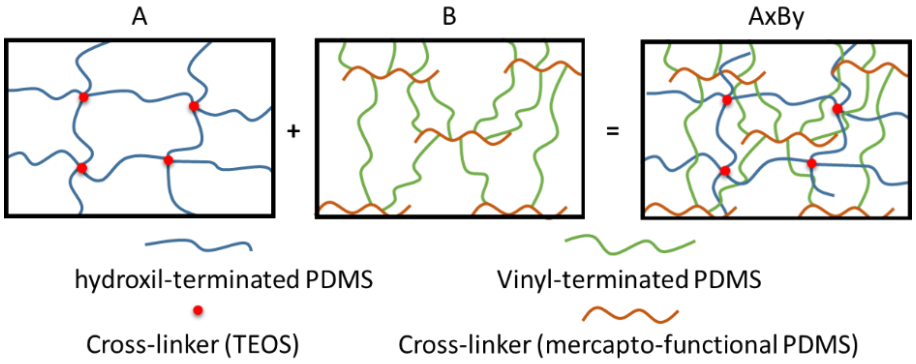
The polymerizations were carried under mechanical stirring at roughly 90 degrees Celsius for 6 hours. The catalyst was filtered out of the mixture and the unreacted monomers were separated from the resulting polymer through distillation. The resulted polymers have molecular weights as described in the table below.

***Table 1**. GPC data of the synthesised polymers*

Polymer	Mn [g/mol]	Mw [g/mol]	PDI
HEP	226000	340000	1.50
VEP	16800	35000	2.00

The silicone-based interpenetrated polymer networks (Si-IPNs) were obtained by mixing five different weight ratios between HEP and VEP (1:1, 1:2, 2:1, 1:4, 4:1). The HEP polymer was cross-linked with tetraethyl orthosilicate (TEOS) throughout a condensation curing reaction (elastic network, A) and VEP polymer was cross-linked using a mercapto functional siloxane oligomer by UV induced thiol-ene addition (rigid network, B), Figure 1.

Figure 1. *Schematic representation of the silicone-based IPNs formation*



After a stepwise homogenization of the components with a speed mixer (DAC 150), the final mixtures were poured on Teflon coated substrates, irradiated for 5 minutes, and kept in a special lab-made chamber (with high humidity) for maturation and dust deposition prevention.

Acknowledgements

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HIGH-DRUG-LOADING MAGNETIC NANOPLATFORMS

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1. Introduction

Nanomedicine is regarded as one of the most promising applications of nanotechnology, as it would allow the development of tailored therapies, with a high level of selectivity and efficacy.[1] Although much research has been performed, translation from academia to commercial application remains disappointingly low. Formulating drugs onto nanoparticles endows drugs with new properties such as improved bioavailability and pharmacokinetics, reduced toxic side effects, controlled release, and possibility of elevating drug dose.[2]

Most nanomedicines have low drug loading (few weights percent 10÷20%) and the clinical translation of such nanomedicines is challenging due to high production cost, issues in scale-up productions, irreproducible properties and toxic side-effects from the nanoparticles. To achieve a drug therapeutic window, very high particle concentration is required, but the very viscous solution of such high NP concentration leads to many difficulties[3] and it is critical to increase drug loading.[4] Therefore, high drug-loading nanoparticles would be ideal to achieve the high drug dose with a reduced amount of carrier material.[5]

The present study aims to design, assemble and fabricate a new generation of multifunctional nanoplatforms for performing controlled drug loading for biomedical applications. The proposed tasks are made possible by combining two components within the nanoplatforms *(i)* Fe_3O_4magnetic nanoparticles that allow high drug load and *(ii)* self-assembled drug-drug co-crystal (Captopril-Losartan potassium) attached to the surface of the magnetic particles in high weight (>30%) that allow selective delivery of the structure to target receptor. The individual building blocks (*Fe_3O_4 NPs*) and their assemblies (*Fe_3O_4-Captopril-Losartan co-crystal*) are comprehensively characterized with respect to physical, chemical and biological characteristics in order to assess their controlled integration into periodic structures with the potential benefits including the creation of magnetically tunable nanoplatforms capable of simultaneous binding of organic and inorganic components.

2. Experimental

All reagents used for the precipitation reactions, i.e., ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$ 98%), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 98%) were purchased from Alfa Aesar. Sodium hydroxide (NaOH, 98%) and hydrochloric acid (HCl, 37%) were purchased from Sigma-Aldrich. The reagents were used without any further purification.

The MNPs synthesis followed a modified mechano-chemical hydrothermal approach showed in our previous studies.[6] For this study, 1.47 g $FeCl_2 \cdot 4H_2O$ and 4 g $FeCl_3 \cdot 6H_2O$ (Fe^{2+}/Fe^{3+} molar ratio ≈1:2) were mixed with 1 ml HCl and 3 ml distilled water and heated at about 60 °C. Under fume hood, 5.5 g NaOH were added and quickly mixed until the color of solution turned to black. After adding 40 ml distilled water under mechanical mixing, the MNPs were magnetically separated and washed until the pH of solution decreased to 6.5.[7]

Drug loading process was performed by adding Fe_3O_4 MNPs into an equimolar solution of Captopril-Valsartan Potassium under stirring at RT for 24h.

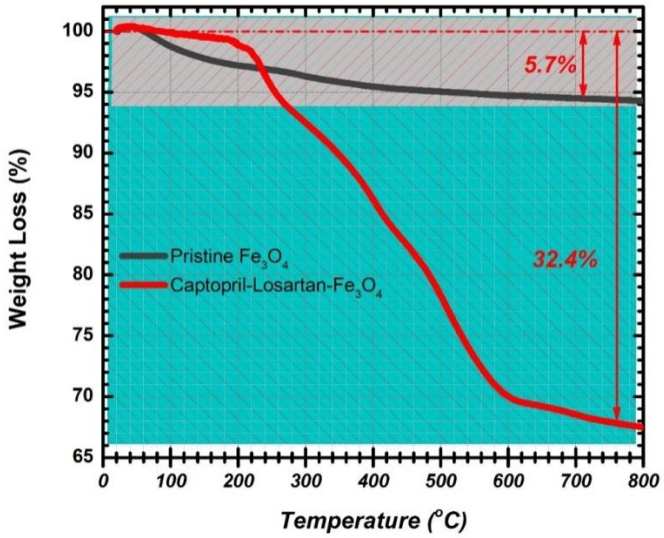
Evaluation of the *in vitro* biocompatibility of Fe_3O_4 nanoparticles loaded with Captopril-Losartan potassium was performed on a normal cell culture (human fibroblasts), the cell viability being quantified through the MTT test (3-(4,5-Dimethyl-2-thiazolyl)-2,5-diphenyl-2H-tetrazolium bromide). To perform the viability test, the culture plates (96 wells) were seeded with fibroblasts at a density of 1 x 10^5 cells/well and incubated for 24 hours at 37 ° C (95% humidity, 5% CO_2). After 24 hours, Fe_3O_4 nanoparticles loaded with Captopril-Losartan potassium were added over fibroblasts and incubated for another 24 hours. Finally, the

culture plates were read on a spectrophotometer (Synergy HTX multi-mode reader Elta 90 MR), at an incident wavelength of 570 nm.

3. Results and discussion

The thermogravimetric analysis was used to evaluate the thermal stability of the magnetic nanoplatforms and to quantify the drug amounts on the magnetic Fe_3O_4 nanoparticles. The TG thermogram shows different decomposition steps in the temperature range 25–800°C. For, pristine Fe_3O_4 nanoparticles, the weight loss of max. 5.7%, is observed between the temperatures range of 25–800 °C and is due to the evaporation of physically adsorbed water on the surface. For Captopril-Losartan co-crystal-Fe_3O_4 magnetic nanocomposite, it may be observed that in the temperature range of 90–250 °C no mass loss occurs, confirming a good thermal stability of the nanocomposite. The major thermal event which occurs in the temperature range 250-600°C a linear mass loss can be observed up to 32.4% which can be assigned to the decomposition process of the drug attached to the Fe_3O_4 nanoparticles. The TGA results confirmed that the embedded Fe_3O_4 nanoparticles with Captopril-Losartanco-crystal (wt.32.4%) has been done successfully.

Figure 1.*TGA thermograms of pristine Fe_3O_4 magnetic nanoparticles and Captopril-Losartan co-crystal -Fe_3O_4 magnetic nanocomposite*



4. Conclusions

"Post-loading" strategy to fabricate nanoplatforms was successfully applied in this work to achieve high drug-loading nanoparticles (*Fe_3O_4-Captopril-Losartan co-crystal with 32.4 wt.%*)

The results of the viability assay showed that Fe_3O_4 nanoparticles loaded with Captopril-Losartan potassium are not toxic to the normal cells tested.

Acknowledgements

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EFFECT OF THE WASHING ON THE RESISTIVITY OF THE POLYAMIDE TEXTILES COATED WITH DOPED POLYANILINE

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1. Introduction

The interest in conductive textiles increased due to new applications as flexible optoelectronic devices. The polymers as polythiophene, polyaniline and polypyrrole have been extensively studied because of the conducting properties near elasticity and low cost. Polyaniline (PANI) is the most commercial promising conducting polymer because of low cost of monomer, thermal and chemical stabilities, easy preparation, and eco-friendly. Polyaniline is an intrinsic conjugated polymer containing aromatic rings and amino groups. In polyaniline conduction is given due to delocalization of the electrons in double bonds. Processing and intrinsic conductivity of the polyaniline are critical established by types of doping ions used in the process.

In this work polyaniline doped with para-toluene sulfonate acid (p-TSA) were deposited on polyamide textiles by in situ polymerization. The molar ratio between aniline: p-TSA was 3:1. The structure and morphology of polyamide textiles before and after coating with doped polyaniline was studied using infrared spectroscopy and scanning electron microscopy (SEM). Electrical properties were recorded on fresh obtained coated textiles and on the textiles after washing with water (neutral), HCl 10% (acid media) and detergent without phosphate (basic media), according to patent number SR EN 1149-1:2006. Conductive textiles exhibited a rough but uniform, coherent coating with good electrical surface resistivity.

2. Experimental

The wet polyamide textiles of size 10 cm x 10 cm, was introduced in the mixture of the aniline and p-TSA into a reactor. Then an aqueous solution of ammonium persulfate (0.02M) was poured over time to 30 minutes. The complete reaction was finished after another one hour and 30 minutes. The temperature of polymerization was 10 °C. The molar ratio aniline: dopant: ammonium persulfate was 1:3:1.

The textiles were characterized by Attenuated Total Reflectance (ATR); scanning electron microscopy (SEM), surface electrical resistivity measurements and washing tests. Attenuated Total Reflectance was carried on a Cary 630 infrared spectrometer at room temperature with 32 scans and sensitivity of 4 cm^{-1}. Surface morphology of textiles was observed using scanning electron microscope (Quanta 250 -FEI). The textiles were inspected before and after coating with doped polyaniline. The surface resistivity was measured according SR EN 1149-1:2006 employing the 2 electrodes method; using a PROSTAT 800 meter.

3. Results and discussion

The morphology of the textiles covered with p-TSA doped polyaniline are shown in figure 1.A uniform thin film was deposited on the textiles.

In figure 2 is presented the infrared spectrum between 1800 cm^{-1} and 600 cm^{-1}. Main bands are identified and assigned. Infrared spectroscopy brings valuable information on the structure of polymer obtained.

Polyaniline bands highlight the following issues:

- ✓ Stretching bands of chinoid ring (Note Q) of type N = Q= N are observed at 1620 cm^{-1}
- ✓ Stretching bands of the benzenoid ring (note B)N-B-N type are observed at 1514 cm^{-1}
- ✓ Stretching bands such as CN^{+} of the polar on structure are observed in 1232 cm^{-1}

Figure 1.*SEM images of coated fabrics at different magnifications*

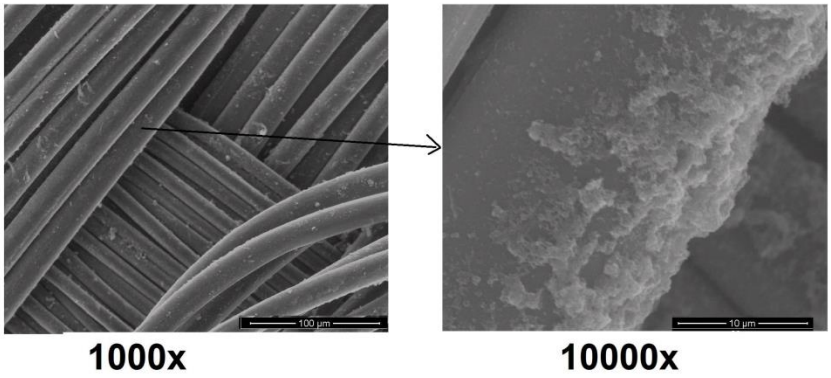
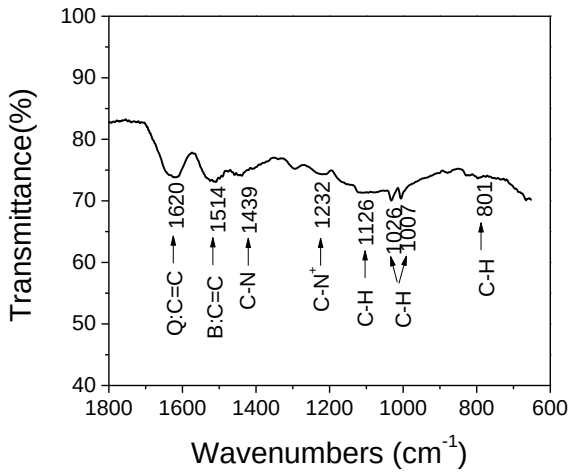


Figure 2.*ATR spectrum of coated textile and identification of bands*



Similar intensity bands at 1620 cm^{-1} and 1514 cm^{-1}demonstrated the obtaining of emeraldine, 50% oxidized form. From spectrum it can be conclude that the conductive polyaniline was obtained.

In the Table 1 the results of electrical resistivity measurements on coated fabrics according to standard SREN1149-1:2006 were presented.

Table 1.*The results of the resistivity measurements of the coated fabrics before and after washing; according SR EN 1149-1:2006*

	Coated polyamide	**After washing with water**	**After washing with HCl 10%**	**After washing with detergent**
Surface Rezistivity (Ωcm)	$3.8*10^4$	$3.7*10^4$	$1.1*10^4$	$5.7*10^6$

The surface resistivity in all experiments shows good values. The surface resistivity decreased after 10 circles in the washing machine with detergent, but the value in maintained in the interval proper to applications.

4. Conclusions

The polyamide textiles prepared by *in situ* polymerization were coated uniformly and showed good electrical resistivity of 10^4 -10^6 Ωcm after washing with water, acid and detergent. They can be used as flexible conductive textiles.

ALGINATE-DERIVED TANNING AGENTS FOR BIODEGRADABLE LEATHER

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1. Introduction

Sustainability is a global level challenge for tanning industry whose production lies on Cr (III) salts for more than 90%, negatively impacting both biotic and abiotic factors in an ecosystem. However, leather has accompanied mankind since its first technological attempts and remains a non-replaceable material, in particular towards synthetic alternatives.

Nevertheless, societal challenges are strongly pushing tanning industry to develop a more sustainable leather value chain. Consequently, our research re-focuses on the sustainability of leathers that are more biodegradable, and not just durable.

The main aim of our research has been to develop tanning and re-tanning agents from alginate for producing biodegradable leather. Alginate is a natural hydrophilic polysaccharide abundantly synthesized in nature by marine brown algae and widely used in food, cosmetics, medicine and tissue engineering due to its biocompatible, biodegradable and non-carcinogenic nature.[1] The ability of the oxidized sodium alginate (OSA) to crosslink collagen fiber in powder hide has been reported[2] and further tested on bovine hide at industrial-pilot level.[3]

2. Experimental

To this purpose novel safe and non-toxic tanning agents based on sodium alginate (SA) derivatives, from 100% renewable sources have been developed and tested at laboratory level. SA derivatives (SADs) were obtained using (ii) radical degradation by H_2O_2 under ultrasound[4] and (iii) ultrasonic treatment.[5]

Various treatment conditions (oxidants' concentration, treatment duration, ultrasound frequency and intensity) were tested to obtain the appropriate depolymerization degree and aldehyde content for ensuring re-tanning and tanning properties.

3. Results and discussion

This work involved a comparative study of the collagen interaction SADs and OSA using an analytical approach based on micro-Differential Scanning Calorimetry (micro-DSC) for characterizing the collagen-SAD matrix hydrothermal stability[6] complemented by unilateral nuclear magnetic resonance (NMR MOUSE), to understand the structuring ability of SAD to form matrices with collagen within hide.[7]

Infrared spectroscopy in attenuated total reflection mode (FTIR-ATR)[8] was also used to characterize the various SADs and compare the features of their spectra with that of OSA obtained by selective oxidation with KIO_4.

The results obtained so far have confirmed the suitability of the various SADs as non-toxic tanning or re-tanning agents for biodegradable leather production. The next research step concerns with developing an efficient, simple, fast and cost-effective industrial method to obtain alginate chains with a tailored length and tanning / re-tanning properties.

The use of renewable bioresources could confer more biodegradability to leather and significantly reduce the chemical and environmental footprint of leather production.

Acknowledgements

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β-CYCLODEXTRIN/CURCUMIN INCLUSION COMPLEX-LOADED HYDROGELS FILMS BASED ON BIOPOLYMERS. CHARACTERIZATION AND CURCUMIN RELEASE KINETIC STUDY

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1. Introduction

Curcumin has antibacterial, antioxidant, and anti-inflammatory activity. It was successfully used to treat dermatological diseases. The main drawback of using curcumin is its water insolubility and low bioavailability. The attenuation or elimination of these disadvantages has been attempted by preparing formulations based on micelles, liposomes, polymeric nanoparticles, complexes, emulsions. Polymer matrices can protect curcumin from adverse environmental conditions; improve the half-life of the bioactive compound, thus increasing its bioavailability both *in vitro* and *in vivo*.

2. Experimental

In this study, β-cyclodextrin inclusion complexes with curcumin at a molar ratio of 2:1 were prepared to increase the polyphenol water solubility, and the complexation degree obtained varies between 40-55%.

The bovine serum albumin (BSA) is used to increase the hydrogel film's biocompatibility. Electrostatic interactions could appear between amino groups from BSA and the carboxylic groups from pectin at a pH lower than the BSA isoelectric point (pKa=4.5), and the polyelectrolyte complexes can be obtained. The biopolymer films were prepared in two stages. Firstly, gellan/bovine serum albumin (BSA) films in which the β-cyclodextrin/curcumin inclusion complex was incorporated, were obtained by ionic cross-linking with magnesium acetate at pH=7.8. In the second stage, after drying, the films obtained were subsequently polyelectrolytically complexed by immersing them in a 1.5 % pectin solution at pH=3.5 for 20 minutes. The films were then dried at room temperature and kept in the dark at 4ºC until further characterizations. The experimental program is given in the table below.

Table 1. *Experimental program*

Sample*	Quantity of gellan, mg	Quantity of BSA, mg	Quantity of pectin, mg	Magnesium acetate concentration %	Quantity of curcumin from inclusion complex, mg	Immobilization efficiency, %
P1	200	100	600	0.5		
P2	150	100				
P3	100	100				
P4	100	200				
P1C	200	100			25	60.48
P2C	150	100				84.91
P3C	100	100				97.78
P4C	100	200				89.05

*Gellan solution volume: 20 ml, BSA solution volume: 5 ml; pectin solution volume: 60 ml; concentration of glycerine: 1% (w/w), magnesium acetate solution volume: 1 ml

The films obtained were characterized by the swelling degree (Q%), SEM, FT-IR, TGA, mechanical tests, and the cytotoxicity was evaluated. The encapsulation efficiency was evaluated. BSA possesses hydrophobic regions, and some hydrophobic interaction with curcumin may appear that lead to a higher percent of curcumin immobilization.

3. Results and discussion

The encapsulation efficiency increases when the gellan amount decreases. Some hydrophobic interaction between BSA and curcumin could appear, leading to an improved curcumin immobilization.

The swelling degree values depend on the cross-linking degree and pH. It increases at pH=7.4 and when the cross-linking degree decrease. The explanation is related to the fact that the films contain gellan and pectin, the basic PH having the effect of forming the carboxylates anions from the acid groups that did not participate in the cross-linking with Mg^{2+}. The electrostatic repulsion occurs between polysaccharides macromolecules, which cause the relaxation of the polymer network and facilitate the absorption of larger water quantities. The FT-IR spectroscopy demonstrates that electrostatic interactions occur. Films surface morphology analyzed by SEM microscopy shows a smooth surface with no micropores because the films based on gellan and BSA were covered with a pectin layer.

The MTT assay was used for the cytotoxicity test, and the analysis was performed with normal fibroblast cells from the human dermis. The results showed that the films tested did not show cytotoxicity. The antioxidant activity (expressed by IC50) for curcumin-loaded hydrogel film was improved compared with the one of free curcumin, and the polymeric matrix has a protective role for curcumin against UV radiations. The protective role of the polymer matrix was proved. The release kinetics studies of curcumin from the polysaccharides films were performed in two different pH media (5.5 and 7.4), and a higher release efficiency was observed in a slightly alkaline medium. The skin's curcumin permeability was also tested *in vitro* using a Franz diffusion cell. The release of curcumin is in concordance with the swelling degree. The higher release efficiency was obtained at pH=7.4 and depended on the cross-linking degree and the hydrophobicity of the sample. The permeability of curcumin released from the film on chicken skin was a study using the cell Franz. The test was performed for 24 h using two buffer solutions at pH=7.4 and pH=5.5. The results are also in concordance with the swelling degree.

4. Conclusions

Hydrogel films based on gellan/BSA/pectin were obtained by ionic cross-linking and polyelectrolyte complexation. The inclusion complex of β-cyclodextrin/curcumin can be immobilized in films with hydrogel character based on gellan/BSA/pectin leading to systems with increased bioavailability. The polymeric matrix of the films has a protective role for curcumin against UV degradation and maintained the antioxidant activity of curcumin. The swelling degree values are high and depend on the BSA quantity within the film, the biopolymer concentration, and the cross-linking degree. The inclusion complexes determined the increase of the hydrophilicity, and the swelling degree values for samples with curcumin were higher than at the samples without curcumin. Higher release efficiency was observed at pH=7.4, in concordance with the swelling degree behavior. The cytotoxicity test shows that the films maintain cell viability.

POLYHYDROXYBUTYRATE ACCUMULATION IN *RALSTONIA EUTROPHA* IN LIPID CONTAINING MEDIA

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1. Introduction

The specialized literature describes the use of vegetable oils for obtaining polyhydroxyalkanoates (PHA) through biotechnological processes. The most common type of PHA produced by microorganisms is poly-β-hydroxybutyrate, a short-chain homopolymer also called poly-D-(-)-3-hydroxybutyric acid, P(3HB) or PHB. Some heterotrophic microorganisms produce this polymer in batch or fed-batch crops.

The use of vegetable oils is closely related to the specifics and climate of each country, their field of interest and the need for efficient removal of their residues, resulting from various technological processes. For this, olive oil, sesame oil, palm oil, soybean oil, rapeseed oil, corn oil,[1] cold-pressed or heat-processed oils are used.

The use of sunflower oils is not described in the literature. It is estimated that sunflower oils represent only 8% of all vegetable oils used in the world, with palm oil in the first place (32%), followed by soybean oil (29%), other oils (27%), rapeseed oil (14%), peanut oil (4%), cottonseed oil (4%).[2]

Among the microorganisms used, *Ralstonia eutropha* grows well in mineral environments, at temperatures of 30°C, on many carbon sources, structurally correlated or not with our product of interest. Therefore, this microorganism was chosen for testing various vegetable oils for the production of PHAs and were tested the following: cultivation duration; the maximum amount of PHB for different oils; the maximum amount of dry biomass; the maximum amount of PHA in relation to dry biomass.

2. Experimental

The bacterium *Ralstonia eutropha* DSM 545 was cultured on three different ICCF media[3] with the following composition: sunflower oil in different quantities (0.92g%, 1g%, 1.38g%); $(NH_4)_2SO_4$ - 0.1 g; Na_2HPO_4 $2H_2O$ - 0.45 g; KH_2PO_4 - 0.15 g; $MgSO_4$ $7H_2O$ - 0.02 g; $CaCl_2$ $2H_2O$ - 0.002 g; Ammonium citrate and iron - 0.005 g; microelements - 0.2 ml; distilled water - 100 ml; microelement solution: H_3BO_3 - 0.3 g; $CoCl_2$ $6H_2O$ - 0.2 g; $ZnSO_4$ $7H_2O$ - 0.1 g; $MnCl_2$ $4H_2O$ - 30 mg; $NaMoO_4$ $2H_2O$ - 30 mg; $NiCl_2$ $6H_2O$ - 20 mg; $CuSO_4$ $5H_2O$ - 10 mg; distilled water - 1000 ml. The cultivation conditions are as follows: temperature: 30°C-34°C, initial pH = 7.5, aeration by stirring on a rotary stirrer at 220 rpm and 2 cm eccentricity of the stirrer. At the end of the 48 hours of cultivation, the main results are shown in the table below.[4]

3. Results and discussion

Following the study performed by culturing *Ralstonia eutropha* DSM 545 on a mineral medium containing sunflower oil in a concentration of 0.92g%, 1g% and 1.38g%, at an initial pH of 7.5, a temperature of 30-34ºC and within 48 hours of cultivation, higher results are obtained than those made with other oils known from the literature. They are directly related to the concentrations of oil used. The table below presents comparative results obtained from the three culture media with sunflower oil and those made with other oils known from the literature.

Table 1. *Comparative results obtained from the three-culture media with sunflower oil and other oils.*

Type of vegetal oils	Lipid substrate concentration (g%)	Bioprocess time (h)	Cells concentration (g/l)	PHA concentration g/l)	Yield (PHA/DB)x100
Sunflower oil 1	0,92	48	5,305	4,757	89,67
Sunflower oil 2	1	48	7,215	6,080	84,27
Sunflower oil 3	1,38	48	8,900	7,880	88,54
Soybean oil	1	72	6,100	3,500	57,00
Sesame oil	1	72	6,100	4,100	68,00
Rapeseed oil	1	72	8,500	4,590	53,90
Corn oil	1	72	8,590	5,660	65,90
Olive oil	1	72	7,198	5,261	73,09

4. Conclusions

Following the study, PHAs can be obtained in quantities and yields of biotechnological interest with the help of the microorganism *Ralstonia eutropha* DSM 545, based on an environment containing a lipid substrate, namely sunflower oil in different concentrations. We were obtaining PHA in different concentrations of 4.747 g/l, 6.080 g/l and 7.880 g/l. Therefore, PHAs are relative to dry biomass of 89.67%, 84.27% and 88.54% are obtained depending on the concentration of the lipid substrate (the concentration of sunflower oil).

Acknowledgements

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DOUBLE-FUNCTIONALIZED CHITOSAN NANOFIBERS FOR WOUND HEALING

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1. Introduction

Skin is the largest organ with a sensory role for protection and thermoregulation of the human body.[1] That is why it is important to treat the skin wounds using efficient dressings which favor a rapid healing while minimizing the side effects. In latest years it become obvious that for this aim, multifunctional materials which address the needs for a rapid healing should be developed.[2]

This category of materials also includes chitosan nanofibers (CS) that mimic the extracellular matrix of the body, being easily applied and removed from wounds, thus avoiding the traumatic debridement. Encapsulation of antimicrobial compounds in this type of nanofibers increases their value, assuring the prevention of invasive infection.[3] Of major importance is the control of the release rate of the antimicrobial compound and the monitoring of its bioavailability at the infected site.

To this end, this study proposed the functionalization of chitosan nanofibers by imination with a mixture of two aldehydes, 2-formylphenylboronic acid (2-FPBA) and citral (CI).Their choice was done anticipating a synergistic relationship between them, as CI has the ability to potentiate the antimicrobial activity of 2-FPBA by improving intracellular reactive oxygen species (ROS) and cell permeability.[4] It was assumed that the reversible imine bond will promote the release of both aldehydes in a humid environment, under the control of their consuming during the process of pathogens' inactivation.

3. Results and discussion

A series of five chitosan fibers mats were prepared by imination of neat chitosan fibers with a mixture of two aldehydes, 2-FPBA and CI, by maintaining a constant molar ratio of glucosamine units of chitosan /aldehyde groups, while varying 2-FPBA/CI ratio (Table 1).

***Table 1**. Reaction parameters and sample codes*

Code	C0	C0.25	C0.5	C0.75	C1
$NH_2/CHO_{2FPBA}/CHO_{citral}$ molar ratio	1/0/2	1/0.25/0.75	1/0.5/0.5	1/0.75/0.25	1/1/0
CS/2FPBA/Citral Weight (g)	0.1593/ 0/ 0.1512	0.1535/ 0.0037/ 0.1183	0.3142/ 0.1435/ 0.1599	0.1541/ 0.1118/ 0.0424	0.1639/ 0.1585/ 0
CD (%)	-*	11**	22**	39**	56**
η (%)	-*	44	44	52	56

2FPBA – 2 formylphenylboronic acid; CD- conversion degree of amino groups of chitosan into imine units generated by 2FPBA; η – imination yield with 2FPBA; * not determined; **determined from ^{1}H-NMR spectra

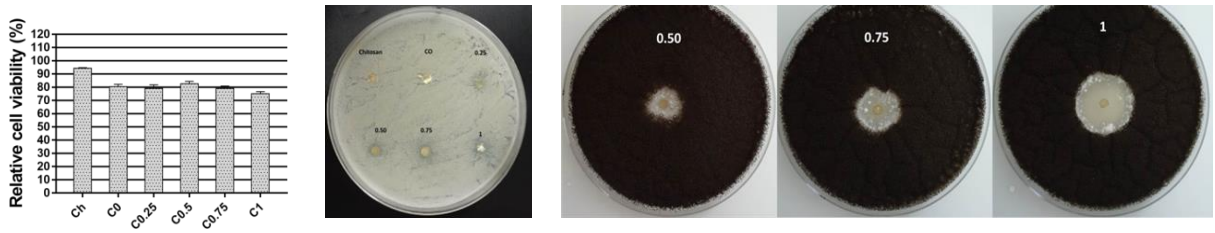
Two of five samples were prepared using only one aldehyde, in order to create references for the understanding of characterization data and properties of the mixed samples. The neat chitosan nanofibers were prior prepared by electrospinning of a chitosan/PEO mixture followed by PEO washing.

Structural characterization by FTIR and 1H-NMR confirmed the presence of imine bonds yielded by each aldehyde, reaching a maximum conversion degree of amine units into imines of 56% (Table 1). UV-vis analysis revealed the dynamic nature of the imine bonds, 2-FPBA being released much faster than CI in a PBS solution. This behavior was attributed to the hydrophilic character of 2-FPBA compared to the hydrophobic one of CI. The same cause influenced the diffusion of aldehydes into fibers during the imination reaction and consequently the site where the reaction took place: CI preponderantly reacted at the fibers' surface while 2-FPBA inside them.

The fibers had the diameter less than 200 nm and exhibited birefringence under POM indicating the alignment of chitosan chains during the electrospinning. From the swelling kinetics it was observed that the mass equilibrium swelling value of the functionalized fibers was lower than that corresponding to neat chitosan fibers, the swelling being influenced both by the reversibility of the imine bond and hydrophilic/hydrophobic nature of the two aldehydes.

The enzymatic biodegradation in the presence of lysozyme was also correlated with the hydrophilic/hydrophobic nature of the two aldehydes, a more intense biodegradation being recorded for the samples with higher amount of 2FPBA and less intense in the case of those in which CI predominated. The investigation of the biocompatibility showed that the fiber mats presented fibroblasts viability higher than 80%, possibly due to the lack of toxicity of the two aldehydes and the presence of citril-imine units (Fig. 1a).Antimicrobial tests have shown antifungal activity against *C. albicans* and *A. brasiliensis*, especially for the samples with a high 2-FPBA content (Fig. 1b,c).

Figure 1. *a) Biocompatibility tests of the nanofibers with MTS assay presented as means ± S. E. M. (standard error of the mean), n = 9; Antifungal activity of the tested dressings against b) C. albicans ATCC10231 and c) A. brasiliensis*



All these findings confirmed that the double imination of chitosan nanofibers is an efficient method for obtaining biomaterials with suitable properties for wound healing.

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NEW HYBRID QUATERNARY SALTS WITH SULFANYLAMIDE/BENZIMIDAZOLE SKELETON

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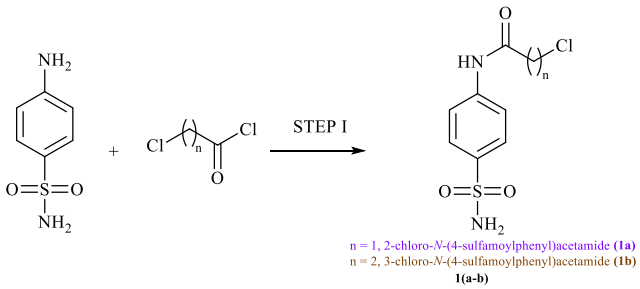
1. Introduction

Sulfanylamides and sulfanilamide derivatives are invaluable scaffolds in drug design and although they have been extensively studied over the years, they still remain of major interest in organic chemistry. On the other way, the chemistry of hybrid compounds containing both imidazole/benzimidazole and sulfanylamide fragments have attracted particular interest due to their biological profile.[1]

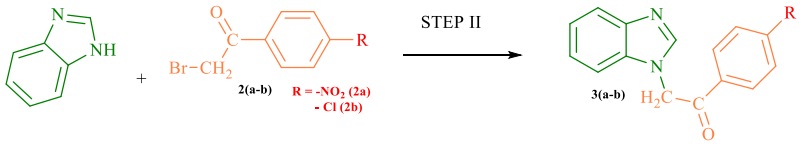
2. Results and discussion

Considering the above, our main objective was to synthesize and characterize novel hybrid quaternary salts with sulfanylamide/benzimidazole skeleton adopting a general and straightforward strategy, involving three steps:

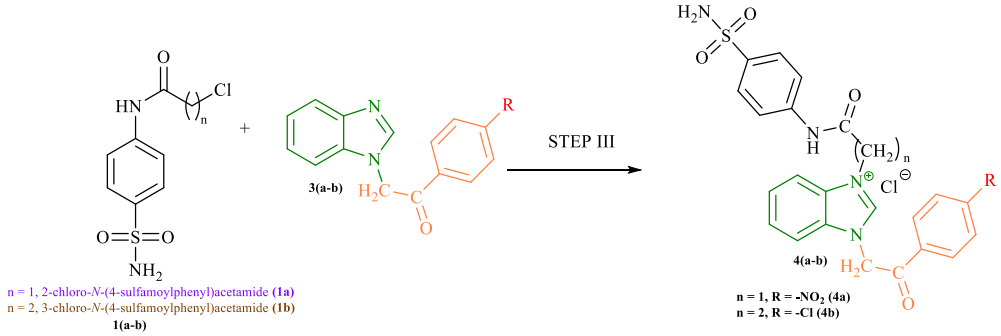
I) *N*-acylation of 4-aminobenzensulfonamide with α-chloroacetyl chloride or α-chloropropionyl chloride, giving the corresponding acylated compounds (1a-b):



II) *N*-alkylation of benzimidazole using K_2CO_3 or NaH as bases and bromoacetophenones differently substituted at the *para* position:



III) *N3*-quaternization of the benzimidazole derivatives (2a-b) previously obtained, using the acylated sulfonamides:



The obtained quaternary salts (1a-b) and some of the precursors (2b) are new compounds, which are not mentioned in the literature.[2-4]

The structure of newly compounds were proved using Nuclear Magnetic Resonance (NMR) experiments (^{1}H, ^{13}C, 2D-correlation). The NMR apparatus (Bruker Avance III 500 spectrometer) is equipped with a 5 mm PABBO detection probe, operating at 500.1 MHz for ^{1}H and 125 MHz for ^{13}C.

3. Conclusions

The hybrid sulfanylamide/benzimidazole quaternary salts (1a-b) were obtained using three steps procedure, by adapting the literature available protocols.[2,3] Quaternary salts were obtained in moderate to good yields (between 20% and 50%).

The newly synthesized quaternary salts are key intermediates that will be used in 3+2 dipolar cycloaddition reactions, using various dipolarophiles (symmetrically or asymmetrically substituted).

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SQUALENE FUNCTIONALIZED WITH COUMARINES OR BENZENESULFONAMIDES AS HYBRID INHIBITORS FOR CARBONIC ANHYDRASE

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1. Introduction

Squalene is a natural lipid widespread in nature in different plants as well as in living organisms. In the human body, squalene is the biochemical precursor for cholesterol and can be found in skin tissue and liver.[1] Due to its unique polyunsaturated structure containing six isoprene units, squalene has the ability to self-assemble under different conditions conducing to improved biological properties and makes it a potential biocompatible candidate for drug and genes delivery applications involving the inhibition of carbonic anhydrases (CAs).[2,3]

CAs are pervasive metalloenzymes in all the living organisms that have the property to catalyze the reverse hydration of carbon dioxide to generate the bicarbonate anion and the proton cation.[4,5] The human Carbonic Anhydrases (hCAs) are belonging to α-CA class, and can be found as 15 different isoforms which are distinct in terms of tissue distribution, cellular localization and kinetic characteristics.[6]

These enzymes' mediated processes contribute to different biological pathways including respiration, pH and bicarbonate homeostasis, bone metabolism and tumorigenesis.[7,8] Furthermore, aberrant levels and/or activities have frequently been linked to a variety of human pathologies. Lately, CAs have emerged as an attractive target for development of inhibitors or activators with unique, non-traditional medicinal uses.[9,10]

In this context, our studies were focused on the obtaining of new hybrid inhibitors for carbonic anhydrase isoforms based on squalene derivatives functionalized with zinc binding group such as the sulfonamide or coumarin moieties.[11] The addition of a sulfonamide moiety is thought to increase the selective inhibitory profile against the hCA II isoform, which is implicated in numerous diseases (i.e., glaucoma, epilepsy), meanwhile, the coumarines are highly efficient against tumor-associated hCA IX and XII isoforms.

2. Experimental

The synthesis of carbon anhydrase inhibitors (CAIs) was achieved by obtaining the active ester of the squalenic acid derivative which was further treated by nucleophilic attack with the desired benzensulfonamides or coumarines to afford squalene amide derivatives. All the obtained compounds were structurally characterized by ^{1}H-NMR and ^{13}C-NMR, ESI-MS and Elemental Analysis to confirm the obtaining of the desired CAIs.

3. Results and discussion

The obtained hybrid CAIs were tested *in vitro* for their inhibitory activity against the physiologically relevant hCA isoforms I, II, IX and XII by means of the stopped-flow carbon dioxide hydrationassay,[12] and their activities were compared to the standard CAI, acetazolamide.

The obtained results showed that the hybrid CAIs containing sulfonamide groups are very effective against the two cytosolic CAs (hCA I and hCA II), meanwhile the CAIs containing coumarines moieties did not inhibit the two cytosolic CAs, which is a desirable feature for compounds designed to target the tumor-associated enzymes.

Moreover, *in silico* studies were performed to correlate the structural features with the inhibition profiles

of the CAIs containing sulfonamides groups. The obtained results showed that the benzenesulfonamide moiety is accommodated deep within the active site region, with the positively charged nitrogen atom coordinating the zinc atom. Meanwhile, the squalene tail is reaching the region exposed to the solvent, interacting with the surficial residues of the hCA II isoform.

4. Conclusions

By combining squalenic acid derivative with various zinc binding groups such as sulfonamides or coumarine derivatives, a series of squalene-based CAIs were synthetized. All the obtained compounds were characterized to confirm their chemical structure. Among the obtained hybrid CAIs, the squalene derivatives with benzensulfonamide moieties showed high selectivity and excellent inhibition profile of hCA II over the tumor-associate enzyme hCA IX and hCA XII, making them suitable candidates for preclinical evaluation in glaucoma or related diseases in which the hCA II is involved.

Acknowledgements

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TOWARDS ROBUST METAL-ORGANIC FRAMEWORKS BASED ON FLUORINATED LINKERS FOR GAS STORAGE

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1. Introduction

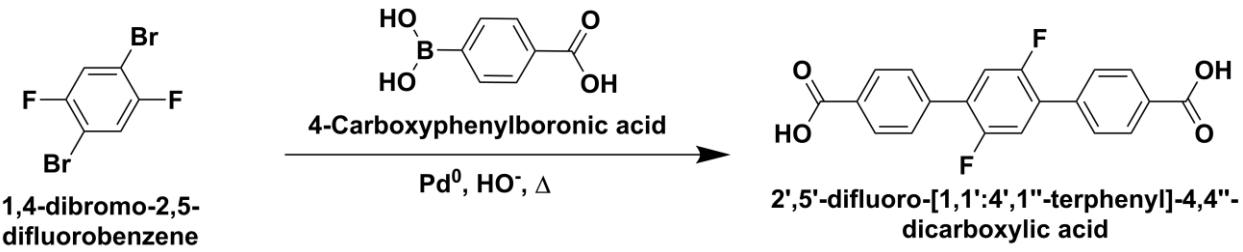
Metal-organic frameworks MOF are an intensely studied class of materials owing to their porous nature that have found use in applications such as gas storage and separation,[1] catalysis,[2] water adsorption,[3] etc. These compounds are three dimensional networks comprised of metal nodes interconnected by rigid organic molecules called linkers.[4]

The developments of a new MOF for a specific application, apart from selecting the coordinating metal, involves the selection of the linker features such as size, shape, number and nature of coordinating groups or the presence of specific functional groups.

2. Results and discussion

This report describes the development of a fluorous zirconium MOF starting with the preparation of the ligand 2',5'-difluoro-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid through a one-step reaction (Figure 1).

Figure 1. *Schematic representation of the synthesis procedure of the ligand 2',5'-difluoro-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid*



Despite the solubility issues associated with fluorinated linkers an adequate synthesis and isolation protocol was identified leading up to the characterization of this compound by single crystal X- ray diffraction. The structure and purity of the compound was further confirmed by ^{1}H, ^{13}C and ^{19}F NMR.

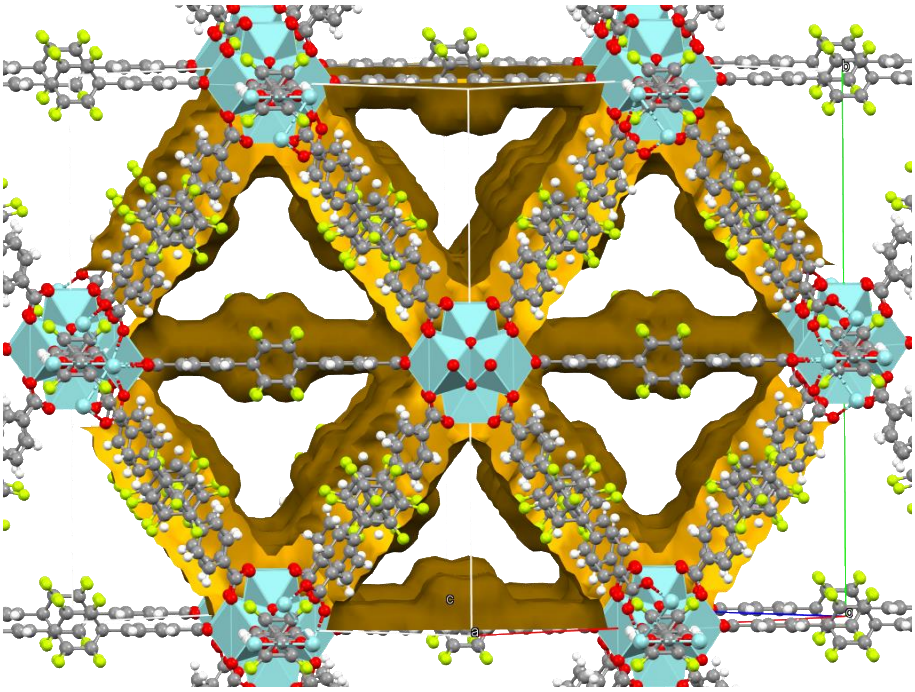
In the next step, the solvothermal reaction between the zirconium tetrachloride and the linker in dimethylformamide yielded a partially fluorinated UiO-68 analogue (Figure 2).[5]

The reaction was modulated by acetic acid which proved to be more effective than the other tested modulators (benzoic or trifluoroacetic acid). The structure was identified by single crystal X-ray diffraction and phase purity was confirmed by powder XRD.

Thermogravimetric analysis was used to demonstrate the high thermal stability (up to 400 °C) of the 3D network and a safe temperature threshold up to which the thermal activation of the MOF can be achieved.

Nitrogen adsorption/desorption measurements revealed that the BET surface area of the MOF was approximately 1500 m^2/g.

Figure 2. *The crystal packing diagram of the MOF composed of Zr and the ligand 2',5'-difluoro-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid*



3. Conclusions

The synthesis and purification procedure for a therphenylic linear dicarboxylic acid has been achieved. The partially fluorinated linker was successfully used in the preparation of a robust zirconium metal organic framework. The detailed structure and phase purity of the 3D network was demonstrated by single crystal and powder X-ray diffraction. The obtained MOF demonstrated high thermal stability and a BET surface area of approximately 1500 m^2/g. This design strategy will be exploited in MOF synthesis experiments with linkers functionalized with a various number of fluorine atoms.

Acknowledgements

This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PN-III-P1-1.1-PD-2019-1303, within PNCDI III.

The financial support of European Social Fund for Regional Development, Competitiveness Operational Programme Axis 1 - POCPOLIG (ID P_37_707, Contract 67/08.09.2016, cod MySMIS: 104810) is gratefully acknowledged.

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IDENTIFICATION OF BIO-CHEMICAL CONTAMINANTS IN COMPOSITE MATERIALS BASED ON RECYCLED PET USING TERAHERTZ SPECTROSCOPY

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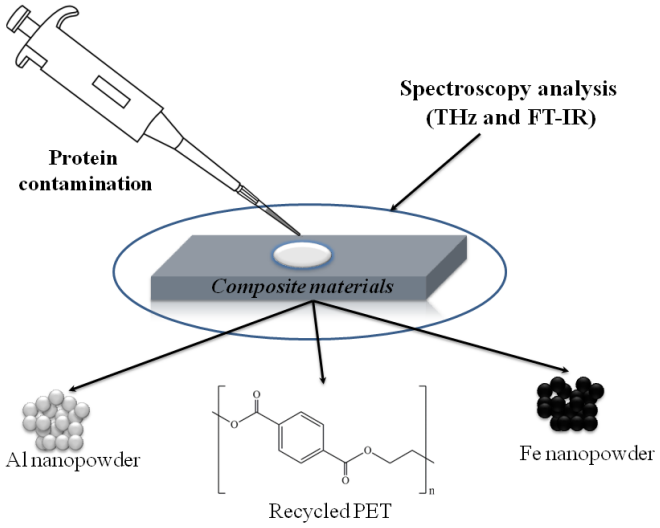
Nowadays, polyethylene terephthalic acid (PET), the main component of plastic packaging materials with around 70 million tons being manufactured every year, is intensely used in a lot of applications, such as textiles, food and pharmaceutical industries. PET materials are single-used and are not degraded by microorganism, being estimated that from 359 million tons of plastics produced globally per year, 150–200 million tons accumulate in natural habitats.[1,2] As a solution for this important issue, in some packaging technologies, secondary recycled PET is used. Unfortunately, since there is no control over the waste PET source, and are often collected from some common city or industrial garbage dumps, secondary recycled PET can contain chemical and/or biological contaminants[3,4] According to the literature data, there are over 175 potentially hazardous substances (alone or mixtures) legally used in the production of food/pharmaceutics contact materials that can be transferred towards packing, a high risk factor for public health.[4] The responsible authorities monitor the types of residues present in foods and drugs, but there is no actual laboratory methodology focused on chemical and biological contaminants in packaging.

Terahertz (THz) spectroscopy is an emerging technology that brings a number of technical breakthroughs in several scientific applications.[5] This new technique has gained considerable attention as a method for studying properties of various materials, based on its key features, such as: non-invasive and non-ionizing properties, phase-sensitive to polar compounds, selectivity to numerous organic molecules through particular absorption and dispersion, unique spectral feature used to recognize molecules in the THz range by assessing their specific spectral signatures, high spatial resolution capabilities, coherent detection and ability to penetrate nonpolar molecules.[6] Due to these unique properties, THz can be seen as a valuable technique in a variety of fields: chemistry, materials sciences, engineering and medicine.[7] But, compared with Raman and Infrared spectroscopy, the development of approaches for generating, manipulating, and detecting terahertz radiation are insufficiently studied.[8]

Considering all the aspects mentioned above, the aim of this study was to detect potential biochemical contaminates based on proteins on recycled PET using THz waves spectroscopy as an innovative and promising technique and compared with already available infrared spectroscopy (Figure 1).

An injection-molding machine has been used to obtain various composite materials based on recycled PET in different amounts of aluminum and iron nano-powders, as part of the components. The contamination was performed using quantified protein solution added in droplets on the clean, decontaminated PET samples, oven dried and kept in protective environment until the analysis. THz (using Terapulse 4000 Pulsed Portable Terahertz Spectrometer) and IR (using Spectrometer FT-IT Nicolet Summit Pro equipped with Everest attenuated total reflectance accessory) spectroscopy have been used to analyze the bare composite materials and the protein solution contaminated samples. The workflow of the study is schematically represented in Figure 1.

Figure 1. *Workflow of the study*



The preliminary results of THz spectrometry obtained at 4 THz showed consistent modifications between bare and contaminated materials. Also, when comparing the THz and IR spectra obtain for bare materials and contaminated ones, significant differences have been observed, meaning that THz is a promising technique for the identification of potential biochemical contaminates on recycled PET.

Acknowledgement

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LIGNIN AS SOURCE OF NEW HYBRID MATERIALS

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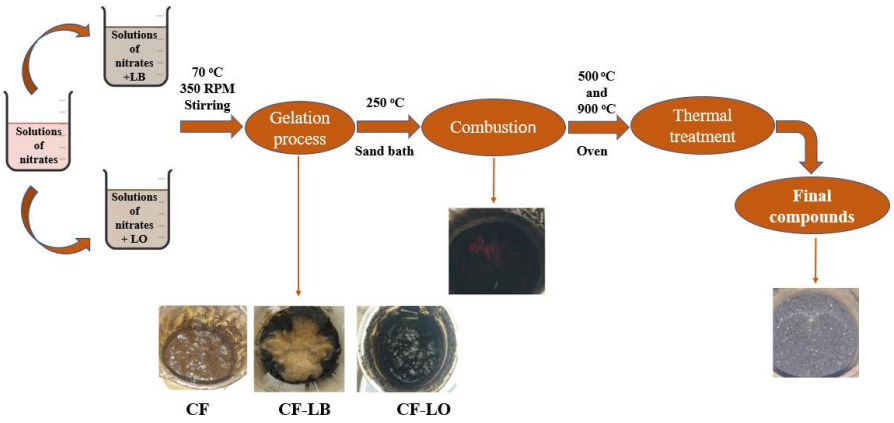
1. Introduction

Lignin represents a major constituent of lignocellulosic biomass. It consists of three phenylpropanoid units named p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), linked by different carbon-carbon and/or carbon-oxygen bonds.[1] The proportion of these monomers varies as a function of the biomass source.[1] In the last years, the interest in lignin has increased due to the environmental needs to replace pollutant materials. Thus, lignin is already being used in different materials for biomedical applications,[2] photocatalysis[3] or dye removal.[4] Cobalt ferrite ($CoFe_2O_4$) is one of the most studied spinel materials due to its properties (magnetism, chemical stability or electrical insulation) and it can be used to synthetize new hybrid/composite materials.[5] In this work, we have used Organosolv lignin (LO) and Lignoboost® lignin (LB) to prepare new cobalt ferrite-lignin hybrids.

2. Experimental

The hybrids materials were synthetized by sol-gel auto-combustion method. All the components of reaction system were dissolved in distilled water. The atomic ratio of the metal cation Co^{2+}: Fe^{3+} was 1:2 and the mass ratio for ferrite:lignin was 1:3, according to Scheme 1.

Scheme 1. *Schematic illustration of the $CoFe_2O_4$-lignin hybrids' obtainment*



The samples were named according to the chelating/combustion agents used and the treatment temperatures, as follows: CF-LB500, CF-LB900, CF-LO500, and CF-LO900.
The present paper contains information about partial characterization of materials by X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS)

3. Results and discussion

The crystalline structure of synthesized and thermally treated $CoFe_2O_4$-lignin hybrid particles was evaluated by XRD (Figure 1). The two-theta values corresponding to the characteristic reflections planes, confirm the formation of $CoFe_2O_4$-based materials with a spinel structure.

The data from Table 1 evidence that the crystallite size increased with the calcination temperature due to the variation in microstructure during thermal treatment, as well as to the ordering or reordering of cations in the cubic spinel structure.

XPS measurements were performed to provide chemical state information on the materials/electronic state. In the spectra of all materials (Figure 2), the binding energies (780.1 eV, 710.7 eV, 529.8 eV, and 284.7

eV) are attributed to the core photoionization peaks of Co 2p, Fe 2p, O 1s, and C 1s, respectively, which represents a clear proof of successful synthesis of ferrite-lignin hybrids. The relative height of the C 1s peak at 284.7 eV confirms that carbon is present in all the materials.

Figure 1. *XRD spectra of lignin hybrids*

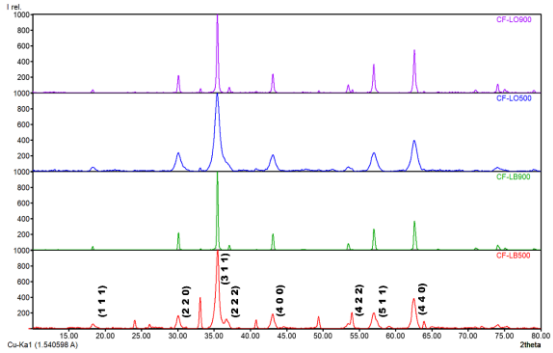
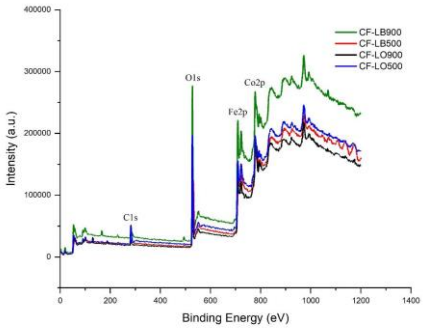


Table 1. *Statistical numeric indicators of the wppf (Rwp, S and χ^2) and the calculated lattice parameter (a) and unit cell volume (V)*

Sample	Rwp (%)	S	χ^2	a (Å)	V (Å^3)	Crystallite size (Å)
CF-LB500	4.96	2.044	4.178	8.4104 ± 0.0018	594.914	119
CF-LB900	2.66	1.0920	1.1924	8.38490 ± 0.00017	589.514	615
CF-LO500	1.92	0.8064	0.6503	8.3816 ± 0.00010	588.827	76
CF-LO900	3.22	1.1147	1.2425	8.3858 ± 0.0003	589.708	332

Figure 2. *XPS spectra of $CoFe_2O_4$-lignin hybrids*



4. Conclusions

New $CoFe_2O_4$-lignin hybrids were synthetized by sol-gel combustion method, using lignin as chelating/combustion agent. The evaluation of the developed materials by XRD and XPS has evidenced the formation of hybrids with a spinel structure. The lignin needed for the designed hybrids is a by-product of the paper and pulp industry, which means that ferrite-lignin hybrids could be produced at a low cost, as compared with other synthesis routes.

Acknowledgements

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MODIFICATION OF THE POLYURETHANE FILM SURFACE PROPERTIES AFTER AIR-PLASMA TREATMENT

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1. Introduction

One of the most powerful methods to modify the polymeric proprieties is plasma treatment, because the changes are made only at the surface, without altering their bulk characteristics. The plasma treatments are used to modify surface hydrophobicity/hydrophilicity so that cells adhere to the surface of the polymer.[1] In this work, the influence of the air plasma treatment on the hydrophilicity and surface roughness of a polyurethane film with siloxane sequences was studied.

2. Experimental

The polyurethane film is based on polycaprolactone (PCL), polybutylenadipate diol (PBA),4,4`-diphenylmethane diisocyanate (MDI), 1,4-butane diol (BD) and polydimethylsiloxane diol (PDMS). Briefly, the plasma treatments were performed in air with an EMITECH RF plasma device at 5 min and 5Wwithout affecting the polymer bulk. Films roughness were determined using a Tencor Alpha-Step D-500 stylus profiler (KLA Tencor Corporation, Milpitas, CA, USA) both before and the treated sample with air plasma (Figure 1). Images were recorded using a confocal Raman microscope spectrometer (Renishaw plc, Gloucestershire, UK) inVia, equipped with a Leica DM2700 microscope with 5x, 20x and 100x lenses (Figure 2).

3. Results and discussion

Several studies have indicated that the surface wettability and roughness proprieties of the polymers are key factors in cell adhesion.[2,3] Due to the complex factors, such as different surfaces properties like roughness, wettability, charge, the mechanism of cell–biomaterial interaction is not very understood. For example, the hydrophilic character of the biomaterial surfaces can improve the cell interaction. On the contrary, other authors have shown that very hydrophobic surfaces determine a good proliferation or adhesion of some cells, but the adapting to the surface requires more time. Generally, a moderate wettability is more able to bind cells in comparison with very hydrophilic or hydrophobic surfaces.[4]

The reported contact angle measurements of our samples showed a contact angle of 81.71 for neat PU and 74.71 for PU treated (Table 1). Hence, the PU treated with plasma showed an improvement in the hydrophilic character than the neat polyurethane. The decrease of the contact angle value is in accordance with the slight increase of the cell viability, as was observed in biological test. Regarding the roughness parameters measured with profiler it was revealed that the increase of treatment time causes an increase of the surface roughness parameters (Table 1, Fig.2), values found by other authors in the literature for the polyurethane membranes[5].

Raman images were taken from different parts of the surfaces in order to see the differences of the samples roughness. After the plasma treatment the surface morphology has a rougher appearance than before (Figure 1).

Table 1. *Surface roughness and wettability results*

Samples	Roughness, R_a (nm)	Contact Angle Parameters, Θ_W
PU neat	388.72±0.10	81.17±0.12
PU treated	436.38±0.15	70.71±0.17

Figure 1. *Raman image at 20x μm for neat (left), and treated in air plasma polyurethane (right)*

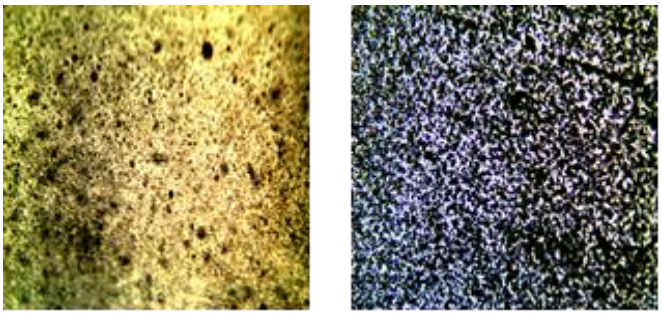
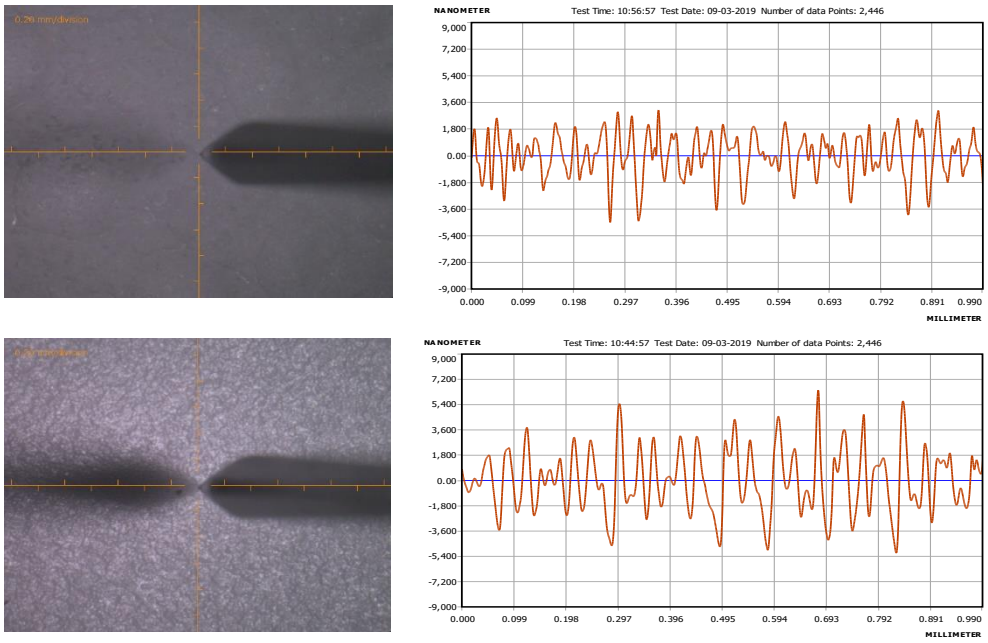


Figure 2. *Profiler of the roughness measurements profiles for neat (left), and treated in air plasma polyurethane samples (right)*



4. Conclusions

The surface wettability and roughness play an important role in cell adhesion and proliferation. Hence, the polyurethane sample after the air plasma treatment showed an increased in hydrophilic character than the neat polyurethane. The roughness morphology of the treated polyurethane sample is changed and the values parameters of the average square roughness are increased.

Acknowledgements

The authors acknowledge the financial support of this research through the Project "Partnerships for knowledge transfer in the field of polymer materials used in biomedical engineering" ID P_40_443, Contract no. 86/8.09.2016, SMIS 105689, co-financed by the European Regional Development Fund by the Competitiveness Operational Programme 2014–2020, Axis 1 Research, Technological Development and Innovation in support of economic competitiveness and business development, Action 1.2.3 Knowledge Transfer Partnerships.

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HYOSCINE EXTRACTION FROM *DATURA INNOXIA* BIOMASS AND ANALYSIS BY SPECTROPHOTOMETRIC AND FLUORESCENCE METHODS

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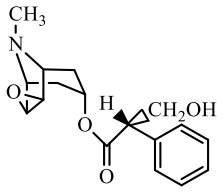
1. Introduction

Nowadays, the literature presents studies on investigation for route of a specific drug carrier system, by combining pharmaceutical drug design, nanotechnology and the principles of biomedical technology.[1] Novel technologies have been used to extract bioactive compounds from natural biomass. *Datura* species (*Datura innoxia* (Figure 1), *Datura ceratocaula*, *Datura discolor*, *Datura ferox*, *Datura leichhardtii*, *Datura metel*, *Datura quercifolia*, *Datura stramonium* and *Datura wrightii*), belongs to the Solanaceae family and have become important, especially for medicine due to their rich content of tropane alkaloids, mainly for hyoscine.[2] Hyoscine, (Figure 2) is an important tropane alkaloid with wide applications in the pharmaceutical industry mainly due to its antimuscarinic, antispasmodic, anticholinergic activity.[3]

Figure 1. *Datura innoxia from Romania*

Figure 2. *Chemical structure of Hyoscine*



Ultrasound-assisted extraction (UAE) application has been considered by researchers an alternative or auxiliary method for extraction of biocompounds from plant. Moreover, application of ultrasound in extraction of different vegetable biomass is considered a clean and green technology.[4] Taking into account the information rewired, the main objective of this work was the extraction of the hyoscine using ultrasound-assisted extraction from different organs of *Datura innoxia* dry biomass (leaves, flowers, seeds, stem and root) from Romania. The quantitative analysis of hyoscine was performed using UV-VIS and fluorescence methods.

2. Experimental

Ultrasound-assisted extraction was investigated with dried biomass from *Datura innoxia* in the presence of ethanol or 1-butanol. Powders of each matrix (~0.2 g) were weighed and solubilized in 2 mL ethanol and 1-butanol and left to macerate for 24 h. After maceration, the samples were subjected for 45 minutes to the ultrasonic process at a room temperature, followed by centrifugation. For each individual matrix 3 samples were processed to highlight the repeatability and reproducibility of the method. Before UV-VIS and fluorescence analysis, the samples were filtered. All absorption spectra of the standard and samples of the compound of interest (hyoscine) were recorded on a UV-Vis spectrophotometer V-550 (JASCO, Japan) and fluorescence spectra were measured using Perkin Elmer LS50B Luminescence Spectrometer.

3. Results and discussion

Hyoscine standard solutions and samples of the matrices were scanned by UV–VIS and fluorescence spectroscopic methods to determine the maximum absorbance and excitation. The absorbance of hyoscine was obtained at 203 nm and for maximum excitation was 345 nm. The UV–VIS spectra and fluorescence emission spectra in ethanol and 1-butanol of the tropane alkaloid (hyoscine) are shown in Figure 3 (ethanol), Figure 4 (1-butanol) and Figure 5 (ethanol), Figure 6 (1-butanol) respectively.

To conduct quantitative determination of the hyoscine in the ethanol and 1-butanol extracts of *Datura*

innoxia dry biomass, the spectrophotometric and fluorescence excitation spectral acquisition mode was used. Hence, the calibration curves for the determination of the amount of hyoscine in the solvents extracts of *Daura innoxia* dry biomass using the calibration equation were constructed. The standard and sample solutions were scanned in 4 replicate in the spectrophotometric and fluorescence excitation spectral acquisition mode. The calibration curves of hyosciamine for the developed method were linear with calibration equations of y = 0.0310x + 0.0474 (R^2 = 0.993) for spectrophotometric measurements and y = 14.136x + 29.863 (R^2 = 0.919) for fluorescence excitation intensity.

Figure 3. *UV-VIS total spectra of Datura innoxia leaves, flowers, seeds, stem and root matrix extracts in ethanol revealing the absorption peak for hyoscine*

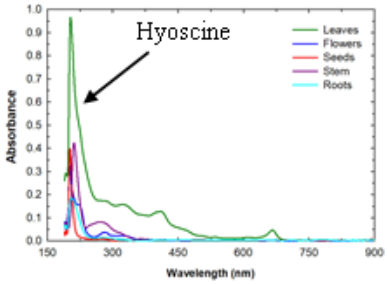


Figure 4. *UV-VIS total spectra of Datura innoxia leaves, flowers, seeds, stem and root matrix extracts in 1-butanol revealing the absorption peak for hyoscine*

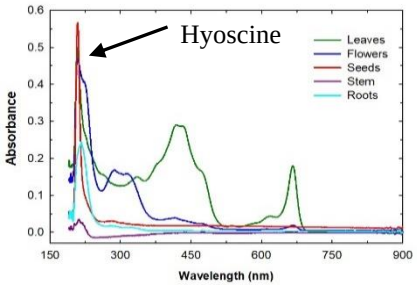


Figure 5. *Fluorescence spectra of hyoscine from Datura innoxia leaves, flowers, seeds, stem and root matrix extracts in ethanol using deconvolution to identify the best Gaussian peaks for matching experimental data*

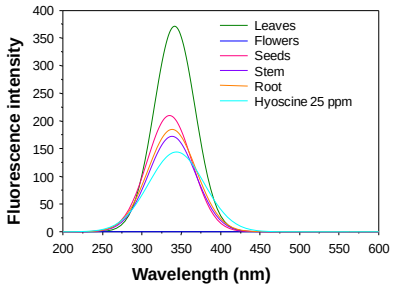
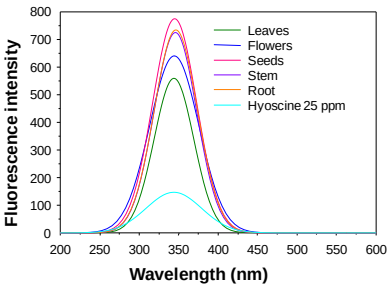


Figure 6. *Fluorescence spectra of hyoscine from Datura innoxia leaves, flowers, seeds, stem and root matrix extracts in 1-butanol using deconvolution to identify the best Gaussian peaks for matching experimental data*



The amount of hyoscine in *Datura innoxia* dry biomass ethanol extracts in various parts of the plant obtained by spectrophotometric method showed the highest content in leaves (297,19 ± 0,01 mg/kg) and lowest content in root (45,89 ± 0,01 mg/kg), and for 1-butanol extracts (173,33 ± 0,02 mg/kg) in seeds and (12,08 ± 0,01 mg/kg) in stem, respectively. Regarding fluorescence method, the highest content of hyoscine in ethanol extracts was found in leaves (244,56 ± 2,99 mg/kg) and lowest content in root (101,01 ± 0,57 mg/kg), and for 1-butanol extracts (524,59 ± 2,81 mg/kg) in seeds and (370,09 ± 6,01 mg/kg) in leaves, respectively.

4. Conclusions

Hyoscine was identified in all vegetative organs of *Datura innoxia* dry biomass using ultrasound-assisted extraction with the highest efficiency extraction in 1-butanol. Quantitative analysis of hyoscine using spectrophotometric and fluorescence methods revealed potential tools that can be used as an acceptable and validated methods for the analysis of this tropane alkaloid. The results obtained are in accordance with the degree of lipophilicity of hyoscine, so a higher efficiency is achieved using the less polar, in this study, 1-butanol.

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MORPHOLOGICAL STUDY OF SOME EPOXY RESIN WITH DOPO – BASED OLIGOPHOSPHONATE S-IPNs

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1. Introduction

The study describes the obtaining and morphology of three flame retardant semi–interpenetrating polymer networks (S–IPNs) from an aromatic oligophosphonate (OP) and an epoxy resin cured with aromatic, cycloaliphatic and aliphatic crosslinkers. The morphologies of the structures were investigated by scanning electron microscopy (SEM).

2. Experimental

The semi–interpenetrating polymer networks (S–IPNs) were obtained by mixing epoxy resin based on bisphenol A diglycidyl ether (EP) with different masses of oligophosphonate (OP) under heating and stirring, followed by the crosslinking in the presence of three crosslinkers: aromatic (4,4'–diaminodiphenylsulfone) (DDS), cycloaliphatic (1,3–bis(aminomethyl)cyclohexane) (CYDM) and fully aliphatic (octamethylenediamine) (8CH_2DA). The quantities of the compounds in the S–IPNs were calculated to obtain final products with 2 wt% phosphorus each.

The S–IPNs were obtained under mixing EP with OP and stirring at 130 ºC. Then the mixtures were cooled to 80 ºC when the curing agents were added. All mixtures were crosslinked for 4 h at 70 ºC, 2 h at 130 ºC and 1 h and 150 ºC and cooled to room temperature. Only the mixture containing DDS was crosslinked 2 h at 150 ºC and 3 h at 180 ºC.

The morphologies of the samples were investigated with the aid of a scanning electron microscope (SEM) SEM Quanta 200 (USA), operating at 30 kV with secondary and backscattering electrons in high vacuum mode. The SEM studies were performed on uncoated samples fixed on aluminum supports.

3. Results and discussion

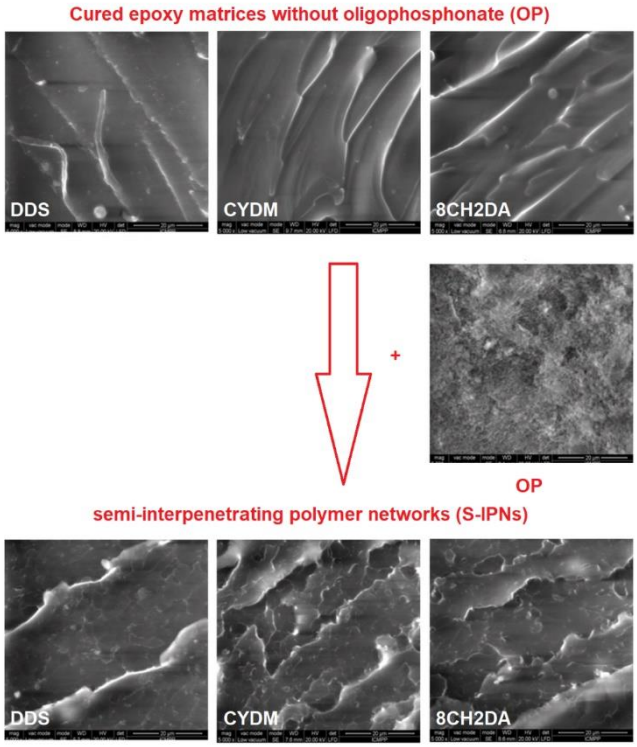
3.1. Morphological study

Scanning electron microscopy (SEM) was used to investigate morphology–phase correlations in the multicomponent polymer systems. Figure 1 shows the SEM images of the studied structures. The networks exhibited smooth parallel cracks with fracture lines. This is due to the presence of the curing agents generating different crosslinking degrees with increase in aromatic character.[1]

Although the S–IPNs present relatively similar uniform fracture lines, they exhibited more cracks, due to the higher rigidity imposed by the curing process in the presence of OP.[2]

These fracture lines occurred during thermal treatment by OP, acting like stress centres,[3] and showing a homogeneous dispersion of the OP in the crosslinked epoxy matrices.[4] Furthermore, the highly reactive oxirane rings of the resin are cured to generate longer chains, owed to a good distribution of the hardeners within the matrices.[1]

Figure 1. *SEM images of the samples (5000x magnification)*



4. Conclusions

Flame resistant S–IPNs were synthesized from an aromatic oligophosphonate and an epoxy resin based on bisphenol A diglycidyl ether crosslinked with three curing agents: 4,4'–diaminodiphenylsulfone, 1,3–bis(aminomethyl)cyclohexane and octamethylenediamine. SEM technique showed a good miscibility of the oligophoshonate in the cured epoxy resin. SEM demonstrated that S–IPNs were highly compact networks.

Acknowledgements

This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PN-III-P1-1.1-TE-2019-0604, within PNCDI III and sustained by the project "Petru Poni Institute of Macromolecular Chemistry-Interdisciplinary Pol for Smart Specialization through Research and Innovation and Technology Transfer in Bio(nano)polymeric Materials and (Eco)Technology", InoMatPol (ID P_36_570, Contract142/10.10.2016, cod MySMIS: 107464).

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SYNTHESIS AND CHARACTERIZATION OF ACRYLIC ION EXCHANGE RESINS AND THEIR ENVIRONMENTAL APPLICATIONS AS SORBENTS

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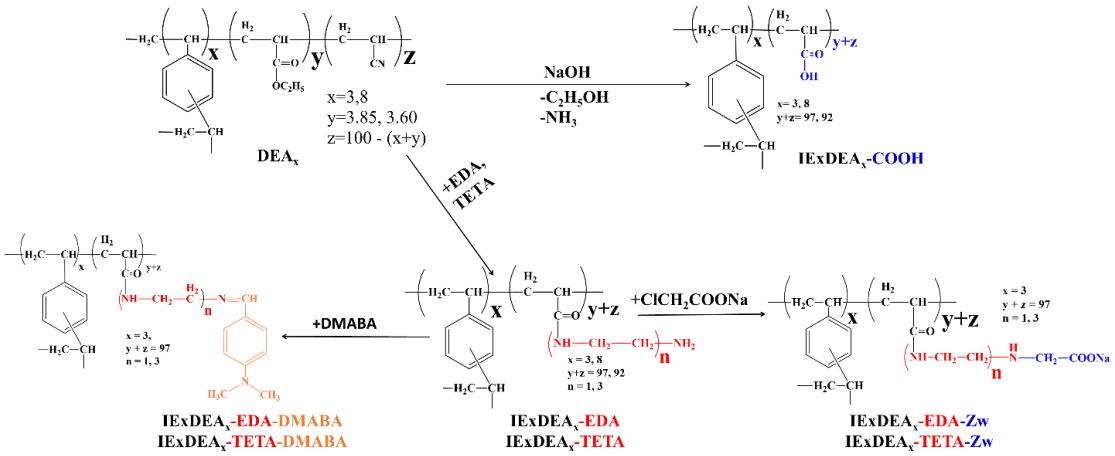
1. Introduction

The anthropic activity led to the environmental contamination, being one of the most important ecological disasters in the world, with a major and continuous impact on the local communities. All these practices have generated various pollutants (heavy metal ions, dyes, residual drug etc.) and altered the environmental cycle causing a global concern linked to their eventual impact on wild life and human health.[1] The ecological rehabilitation measures undertaken so far in order to mitigate the effects of anthropic activities cover just a small part of the affected environment and are not necessarily economically efficient.[2] Various methods are currently proposed to remove pollutants which are efficient but expensive.[3] Some polymeric materials have the ability to retain/remove this compounds. For this purpose, ion exchange resins are widely used in addition to other usual separation techniques, such as membrane processes. Therefore, the synthesis of inexpensive and reusable ion exchange resins based on acrylic copolymers (DEA_x), as beads, with different cross-linking degree, can be a solution for decontamination. Thus, the ionic exchange resins (IEx) can be synthesized: the anionic IEx can be obtained by basic hydrolysis of acrylic copolymers with sodium hydroxide. The cationic IEx with amino groups can be obtained by aminolysis with ethylenediamine (EDA) and triethylenetetramine (TETA). The weak cationic ion exchangers obtained with EDA and TETA can be further transformed by adding 4-dimethylaminobenzaldehyde (DMABA). The zwitterionic IEx can be obtained by carboxymethylation reaction with sodium chloroacetate of weak cationic ion exchangers.[4] The functionalization pathway for obtaining the all the ion exchangers is summarized in Figure 1.

Figure 1. *Synthesis scheme of the ion exchangers*



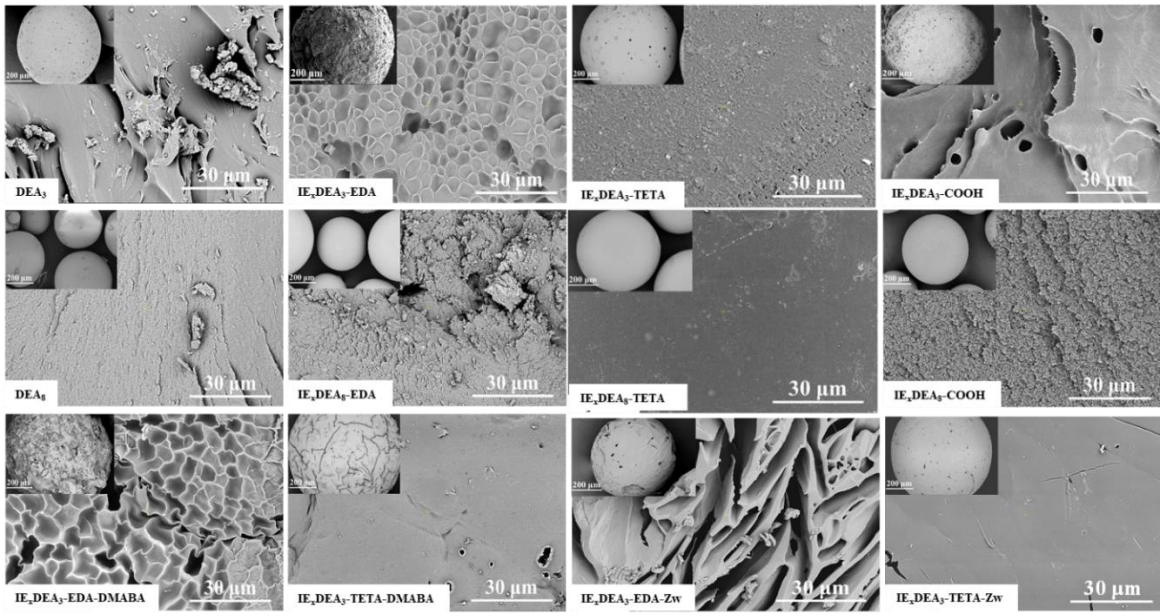
Although the ion-exchangers synthesis method is already well known, the aim of this study represents the first integrated work (synthesis – characterization – application). The main objective of this research is a study on the synthesis and characterization of some ion exchange resins based on acrylic copolymers and their applications as sorbents for inorganic (heavy metal ions) and organic compounds (dyes and residual drugs).

2. Results and discussion

First of all, the obtained acrylic ionic exchangers were deeply characterized by the specific volume and mass exchange capacity and volume weight. Using the equations was determined water swelling capacity, charge density, and also size of beads was measured. The qualitative evaluation of the chemical

modifications has been performed by FTIR-ATR spectroscopy, to get information about the structure of obtained ion exchange resins. The surface morphology of the ion exchange resins based on acrylic copolymer has been evidenced by SEM. The amount of the crosslinker influences the structure of the microparticles, increasing the amount of the crosslinking agent leading to more dense structures (Figure 2).

Figure 2. *SEM images of ion exchange resins based on acrylic copolymers (200 µm scale bar). Insets (30 µm scale bar)*



The capacity of the synthesized resins to interact with different toxic environmental compounds (heavy metal ions, dyes and residual drugs) was also investigated in static condition. As expected, the high sorption capacity was obtained in the case of zwitterionic exchange resins due to the presence of both anionic and cationic functional groups. The samples with 8% crosslinked had a lower sorption comparatively with similar sample with 3% crosslinking degree.

3. Conclusions

In this study, was obtained by water suspensions radical polymerization of divinylbenzene, acrylonitrile and ethyl acrylate, with 3% and 8% cross-linking density. Next step was obtained of a library of ion exchange resins as beads with multi-channelled, having weak acid, basic and amphoteric functional groups with high affinity to different pollutants. The beads obtained were thoroughly characterized by specific characteristics (ion-exchange capacity, volume variation, swelling degree- and charge density), structure (FT-IR) and morphology (SEM, EDX). The FTIR-ATR analysis demonstrated the formation of ionic exchange resins starting from acrylic copolymers. The obtained acrylic ion exchange resins were tested toward various pollutants (heavy metal ions, dyes, residual drugs, etc.), under static conditions (in batch).

Acknowledgements

This work was supported by grants of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P1-1.1-PD-2019-0286 and project number PN-III-P4-ID-PCE-2020-1541, within PNCDI III, and by the project InoMatPol (ID P_36_570, Contract 142/10.10.2016, cod MySMIS: 107464).

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POLYSACCHARIDES-BASED MATERIALS AS DRUG DELIVERY SYSTEMS

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1. Introduction

Alginate and xanthan are well-known polymers that have been used for developing drug delivery systems with adequate properties for biomedicine.[1] Alginate (Alg) is a polysaccharide comprising mannuronic acid and guluronic acid residues, obtained either from brown algae or bacterial sources. It is widely used in drug delivery[2] and tissue engineering.[3] Xanthan (Xa) is an anionic, high molecular weight polysaccharide produced by the *Xanthomonas campestris* bacterium. It has the ability to form very stiff double-stranded structures.[4] In this work, novel drug delivery systems have been developed based on xanthan, and xanthan esterified with oleic acid and alginate. Piroxicam (P) has been selected as a model drug and added into the polysaccharide matrix as anti-inflammatory agent, considering that it is recommended in chronic inflammatory diseases and controlling postoperative pain.

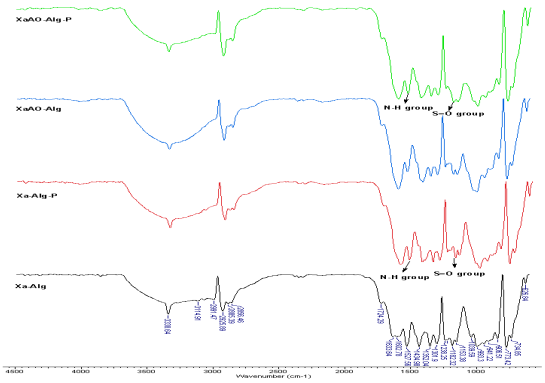
2. Experimental

Esterification of xanthan with oleic acid was performed at room temperature. The reaction product (XaAO) was separated by filtration and dried at room temperature. FTIR and ^{1}H-NMR spectra evidenced that the esterification reaction of xanthan took place. New materials comprising equal amounts of polysaccharides (named Xa-Alg and XaAO-Alg) and 0.05 g of piroxicam (Xa-Alg-P, XaAO-Alg-P) were obtained by freeze-thawing cycles, followed by lyophilization.

3. Results and discussion

The peaks at 1180 and 1529 cm^{-1} (Figure 1) confirm the presence of piroxicam in the obtained materials.[5] The compressive strength of the material based on modified xanthan was reduced when compared with that of the sample comprising unmodified xanthan (Table 1).

***Figure 1**. FTIR spectra of materials based on polysaccharides and piroxicam*



Tako *et al*. proposed that intramolecular associations within the xanthan molecule, involving an interaction between an alternate hydroxyl group at C-3 and the adjacent hemiacetal oxygen atom of the D-glucosyl residues with hydrogen bonding, as in cellulose, and between the methyl group of the acetyl residue and the adjacent hemiacetal oxygen atom of the D-glucosyl residue, with van der Waals interaction, are formed.[6] It is possible that the chemical reaction with oleic acid influenced the xanthan capacity to maintain these inter- and intra- molecular associations. When piroxicam was added into the Xa-Alg matrix, the resulted films recorded lower compressive strength (47.16%), with diminished elongation at the break point.

Table 1. *Mechanical properties of materials*

Sample	Elastic Modulus*, kPa	R^2	Compressive nominal stress**, kPa	Strain%
Xa-Alg	86.81	0.975	52.47	40.59
Xa-Alg-P	20.21	0.974	27.72	72.51
XaAO-Alg	1.30	0.997	22.40	79.14
XaAO-Alg-P	9.28	0.998	37.83	68.39

It seems that the interactions between the piroxicam and the polysaccharide matrix, at the concentration included into the formed gel network, reduced the intramolecular space inside the backbone, increasing the elasticity of the material. An increment of 68.88% in the compressive strength of the formulation comprising XaAO was recorded. SEM images (Figure 2) evidence the presence of pores in all materials (studies related to the average pore size are in progress). The release of active principles from materials is best described by the Korsmeyer-Peppas model.[7] P is released at a slightly faster rate from the material based on Xa (Figure 3), compared with that comprising XaAO (due to the different interaction of the active principle with the polymer matrix).

Figure 2. *SEM images for Xa-Alg (a), Xa-Alg-P (b), XaAO-Alg (c) and XaAO-Alg-P (d)*

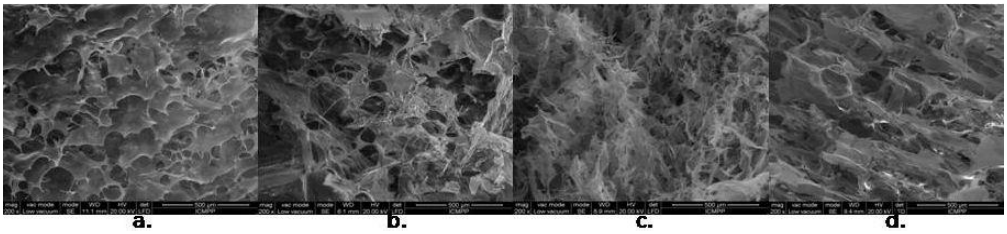
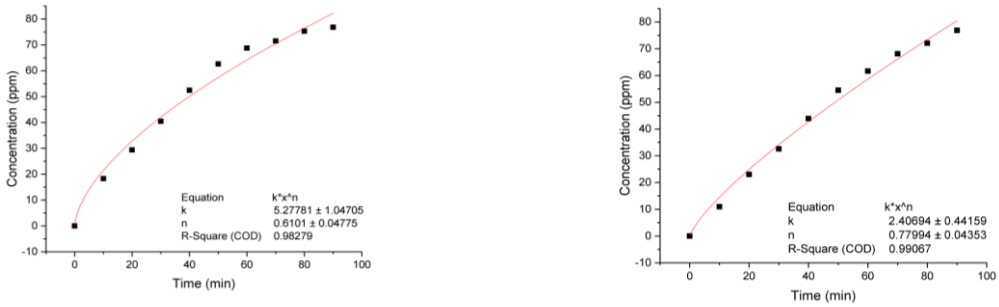


Figure 3. *The release of piroxicam from Xa-Alg and XaAO-Alg*



4. Conclusions

New drug delivery systems based on xanthan and alginate, and containing piroxicam, have been developed. The properties of the materials are dependent on the composition of the formulations. When piroxicam was added into the Xa-Alg matrix, a lower compressive strength (47.16%) of the material, along with a decline in elongation at the break, was recorded. An increment of 68.88% in the compressive strength of the formulation comprising XaAO was observed. The strain values decreased after piroxicam was loaded into the polysaccharide matrix. The release kinetics of piroxicam through the matrix components was explained by the Korsmeyer-Peppas model, with non-Fickian diffusion.

Acknowledgements. This work was supported by the project InoMatPol (ID P_36_570, Contract 142/10.10.2016, cod MySMIS: 107464).

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CHITOSAN-PVA COMPOSITE HYDROGELS: SYNTHESIS, CHARACTERIZATION AND THEIR ANTIBACTERIAL PROPERTIES

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1. Introduction

Hydrogels are usually polymeric networks, extensively developed as appropriate materials for biomedical and pharmaceutical applications. Due to their hydrophilic properties, they are capable of retaining large amounts of water yet remaining insoluble and maintaining the three-dimensional structure. Natural and synthetic polymers offer many possibilities for the design and development of hydrogels that can be used in biomedical applications. Natural polymers, as polysaccharides, are frequently used in the manufacture of hydrogels, due to their non-toxic, biocompatible, and biodegradable properties.

Chitosan (CS) is a cationic polysaccharide widely used in pharmaceutical formulations or for other biomedical applications. Many researchers have highlighted its attractive properties such as biodegradability, biocompatibility, cellular binding capability, antimicrobial, antifungal, antioxidant, and wound healing property.[1] Poly(vinyl alcohol) (PVA) is the most used synthetic polymer for the synthesis of hydrogels with biomedical/pharmaceutical applications due to its high biocompatibility, non-toxicity, and non-carcinogenicity.[2] Several recent investigations have focused on the combination of CS with PVA in order to obtain soft, flexible, and swellable hydrogels by different methods for medical applications.[3,4]

The paper presents original results regarding a novel method for the synthesis of stable CS/PVA-based hydrogels by double cross-linking procedure: physically by freeze-thawing method and covalently using an epoxy cross-linking agent. The morphology of new CS/PVA hydrogels was analyzed by scanning electron microscopy (SEM) and their chemical structure was confirmed by FTIR spectroscopy. The main characteristics of these hydrogels were studied, such as the gel fraction (GF), the swelling degree (SD) in pure water, as well as the mechanical behaviour. Then, the native antimicrobial activity of chitosan was enhanced by the *in situ* generation of silver nanoparticles (AgNPs) under UV irradiation. The total amount of Ag from CS/PVA-based hydrogel was determined by elemental analyses and the crystalline form of Ag was confirmed by X-ray diffraction (XRD). The cytotoxicity and *in vitro* antibacterial activity of the hydrogels with or without AgNPs were also investigated.

2. Experimental

CS/PVA hydrogels were prepared by mixing CS solutions (1 or 2%, w/v, in 0.1 M HCl) and PVA solutions (1 or 2%, w/v) in different weight ratios. Then, the 1,4-butanediol diglycidyl ether (BDDE) was slowly added, thus to obtain a 1:1 or 1:2 stoichiometric ratio between the amine groups of CS and the epoxy groups of the cross-linking agent. The mixtures were stored for 24 h at room temperature (RT), until the chemical cross-linking reaction of the polymer chains occurred. Then, the samples were subjected to a freezing process for 24 h at -20 °C until the physical cross-linking of the PVA chains took place. The freeze-thaw (F-T) process was repeated for 3 and 6 cycles in order to establish the optimum conditions for the synthesis of the highest performing hydrogel. AgNPs were generated *in situ* by immersing hydrogel in silver nitrate solutions with various concentrations (1 - 10 mM). The silver ion-loaded discs were rinsed with distilled water in order to remove the excess of silver ions, then were exposed for 15 min to ultraviolet light using a UV lamp (365 nm; 9 W) for reducing the Ag^+ to Ag^0.

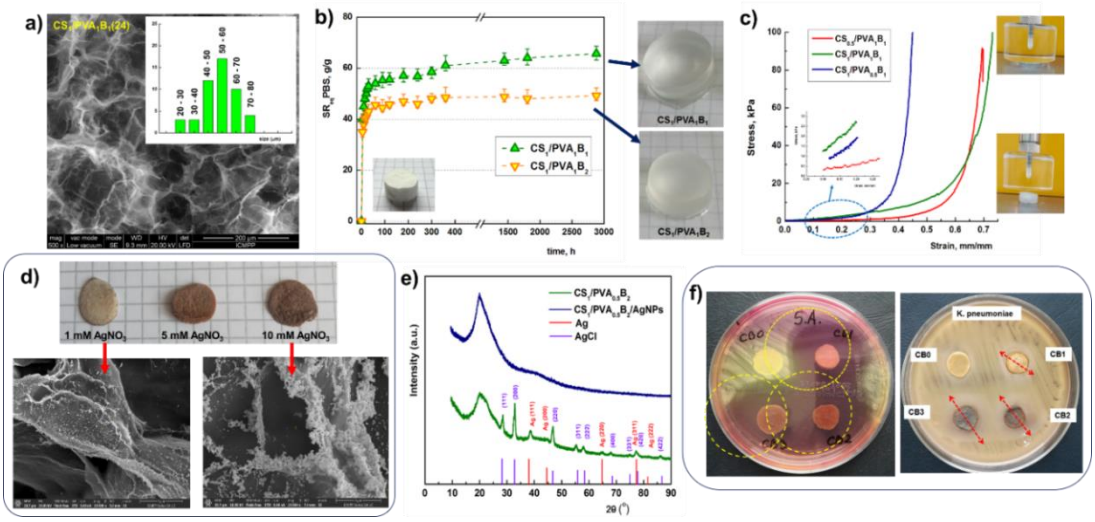
3. Results and discussion

GF of hydrogels between 38 and 76% were obtained, values that were deeply influenced by the synthesis conditions. SEM micrographs of the hydrogels (Fig. 1a) in cross-section show a three-dimensional network with well-defined pores with a diameter ranging between 40 and 60 μm. Hydrogels showed relatively high water swelling rates of about 60% and reached the swelling equilibrium in the first hour (Fig. 1b). The

compression tests of hydrogels showed an elastic behavior with value of elastic modulus of 2.6 – 14.6 kPa (Fig. 1c). These values are ideal for future medical applications, as wound or oral dressing that must be strong, soft and flexible materials. The native antimicrobial activity of chitosan was enhanced by the *in situ* generation of AgNPs under UV irradiation (an ecological method). The SEM images showed that the size of Ag particles increases from 88 nm to 400 nm ($p << 0.05$) with the increase of $AgNO_3$ concentration from 1 mM to 10 mM (Fig. 1d). The spectrum of CS/PVA hydrogel with AgNPs shows the diffraction peaks at around 38.1°, 44.3°, 64.4°, 77.3°, and 81.5° which were associated to the (111), (200), (220), (311), and (222) crystalline planes of face-centered cubic crystal of metallic Ag structure in hydrogel, that confirms the successful synthesis of crystalline AgNPs (Fig. 1e).

The antibacterial testes of CS/PVA hydrogels loaded with AgNPs were performed by disk diffusion method. The hydrogels presented a high inhibitory activity against *S. aureus* (Gram positive) and *K. pneumonia* (Gram-negative) bacteria (Fig. 1f).

Figure 1. *CS/PVA hydrogels cross-linked with BDDE: (a) Scanning electron micrographs in cross-section; (b) Swelling kinetics in water; (c) Stress-strain curve for CS/PVA hydrogel under compressive loading; (d) Optical and SEM microphotographs of hydrogels in situ loaded with silver nanoparticles; (e) XRD patterns of hydrogel without and with AgNPs; (f) Antibacterial activity*



4. Conclusions

New CS/PVA-based hydrogels were obtained by combining chemical and physical cross-linking methods. The morphology was analysed by SEM when well-defined pores having dimensions of 40-60 μm were observed. Hydrogels with highest gel fractions were obtained at six F-T cycles and a CS/PVA ratio of 1:0.5 (w/w). CS/PVA cryogels showed a fast swelling capacity when the equilibrium was reached in the first hour. The mechanical tests have shown an elastic behaviour of hydrogels with low elastic modulus values and without cracking up to 70% compression. The native antimicrobial activity of CS was enhanced by the *in-situ* AgNPs generations under UV irradiation. SEM micrograph highlighted AgNPs with size of 88 nm and cubic shape, and XRD analysis confirmed the face-centered cubic crystal of the Ag metal structure. The loaded hydrogels with AgNPs present a high inhibitory activity against *S. aureus* (gram-positive bacteria) and *K. pneumonia*.

Acknowledgements

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ANTIBACTERIAL CELLULOSE HYDROGELS WITH NOBLE METALS NANOPARTICLES: SYNTHESIS, MECHANISM, AND PROPERTIES

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1. Introduction

Natural polymers, such as cellulose, starch and chitosan, polylactic acid, and others provide promising properties to composite materials. That is why composites based on natural polymers with metal nanophase have been used to develop environmentally friendly materials for various applications. Cellulose has been already used in numerous scopes and some routes for the preparation of novel functional cellulose composites for chemical and industrial applications. One of the most elaborated directions is to make biobased, biodegradable, and low-cost natural polymers also antimicrobial. Nevertheless, this is still a complex problem and an important issue nowadays. And metals, such as gold, silver, and copper in nanosized or colloid states reveal antimicrobial properties.

In this study, the results on the chemical aspects of a modification of cellulose by chemical reduction of the noble metals, namely silver and gold, have been represented.

2. Experimental

We used two types of cellulose: powder celluloses (PC) obtained from hardwood pulp and flax fiber wastes and super-swollen hydrogels (HG) as matrices to produce cellulose-metal composites. PC was a porous system of conjugate fibres available for absorption processes. The HGs were prepared via spontaneous self-assembly and aggregation of cellulose chains from N,N-dimethylacetamide/LiCl solutions. In the HGs which contained 3 wt.% or less of cellulose, up to 2500 wt.% of water was trapped. The material demonstrated high porosity and specific surface areas that was necessary to fix the reduced metal NPs in the cellulose matrix. The pores performed a barrier function, preventing the agglomeration of NPs.

Synthesis of silver and gold nanoparticles was carried out directly in the matrices of the PCs and HGs. We applied Turkevich method of reduction gold ions from trisodium tetrachloroaurat (III) $Na[AuCl_4]$ solution and silver ions from $AgNO_3$ solution with trisodium citrate as a reducer. The diffusion-reduction process of nanoparticle synthesis in the powders and hydrogels consisted of two stages. The first stage was diffusion of the metal ions into the cellulose matrix. The solutions of the salts containing added cellulose samples were heated for 70 degrees for 30 minutes. On the second reduction stage, the trisodium citrate with low concentration was quickly added under constant stirring. Aspect ratio of trisodium citrate to metal ions was 1:1.5. After a few minutes, the colloidal suspensions of different colors were obtained. Finally, the cellulose samples were washed with distilled water to remove unfixed metal particles. So, the reduction proceeded to zero-valent NPs of metals directly in the cellulose matrix.

3. Results and discussion

In the given method, trisodium citrate was used as both reducing and stabilizing agent. The cellulose fibres and the HGs played the dual roles – as matrices for the obtained nanoparticles and they were also responsible for stabilization of the metal nanoparticles.

The mechanism of metal reduction consisted of the coordination of metal ions with hydroxyl groups in the cellulose chain. During absorption-diffusion processes, some OH groups were oxidized to carboxyl groups, which led to further binding of metal ions and their reduction to zero-valent metals with the help of a reducing agent. The initial step of AuNPs formation using trisodium citrate was the oxidation of citrate that yields dicarboxy acetone. Then, the auric salt was reduced to aurous salt and to Au^0, and the aurous salt was assembled on the Au^0 atoms to form the AuNP. Therefore, in the Turkevich method, trisodium citrate was not the only stabilizer of NP, also dicarboxy acetone resulting from the oxidation of citrate contributed to the stabilization of the particles. The color of the obtained composites depended on the aspect ratio

between cellulose and silver ions. The less was the aspect ratio, the less was the share of cellulose and respectively higher the amount of silver in the solutions. Correspondingly, the darker was the color of the composite.

A blank experiment was carried out to demonstrate that the end (reducing) aldehyde groups in cellulose chains allowed the reduction without a reducing agent. It was the same procedure of diffusion of metal ions from their salts to the matrix but without adding trisodium citrate. The composites of the hydrogels and Au resulted from the blank experiment were colored in purple when the cellulose/metal aspect ratio was 60:1. In this case, the reduction process was successful. However, the more Au-ions were introduced in the solution, the slighter was the color of the composite. That might be explained by the fact that cellulose has not enough end reducing groups capable to interact with all Au ions. As a result, not all of them were involved into the redox process. So, the quantity did not matter in this case.

Color of the solution provides information about the size of Au particles that have been obtained, since the absorbance of colloidal gold is a function of the particle size. The solutions were colored in dark yellow-brown or from light to dark purple. That was evidence that coagulation occurred during the reaction. The composites obtained with trisodium citrate were colored in purple and the color became darker when aspect ratio cellulose/Au was lower, which means that the amount of Au-ions in the solution was the biggest in the row. The same trend we observed in all the composites. Obviously, the color of samples depended directly on the aspect ratio of cellulose to metal.

The content of the reduced metal, in the case of the blank experiment, was low; however, in the presence of the trisodium citrate, the reduction proceeded at a high rate and resulted in a larger content of reduced metal in the samples. Thus, the composites HG-Ag and HG-Au contained the low amount of metals(0) (up to 0.9 wt. % of Ag and up to 1.5 wt.% of Au), the metal content in the PC was much higher (to 4.8 wt.%). The NPs of both metals intercalated to cellulose samples had various shapes (spherical or rectangular) and different sizes. The gold NPs mostly ranged 40-120 nm, some of them formed huge agglomerates with sizes of dozen μm. A high concentration of citrate more rapidly stabilized AuNPs of smaller sizes, whereas a low concentration of citrate led to large-size AuNPs and even to the aggregation of them. Since we used rather low concentrations, the sizes of particles were comparatively big. The size of the silver NPs varied between 20-260 nm. The size distribution of the gold NPs was more uniform than that one of the silver NPs.

X-ray diffraction analysis of the PC samples revealed the structure of cellulose modification I. The introduction of silver did not change the supramolecular structure of composites. In the case of the embedding of the silver NPs to the hydrogel matrix, the structure of cellulose modification II did not change also. However, the structure of cellulose II in the matrix of the hydrogel slightly changed via intercalation of the gold NPs. The presence of silver moderately affected the crystallinity of the PC in the composites. Thus, with an increase in the silver content in the composite by 32 times, the crystallinity increased by 8.1%. However, the transverse dimensions of PC crystallites were significantly reduced. With the increase in the content of silver in the HG, the crystallinity of the composite also slightly increased and there was no noticeable change in the crystallite size also. Note in general that the crystallite size in PC composites was much larger than in HG composites.

The composites containing Ag and Au exhibited the antibacterial properties against gram-positive (*Staphylococcus aureus*) and gram-negative (*Escherichia coli*) bacteria. It was almost the same for all contents of silver except for the highest one.

4. Conclusions

We have successfully trailed a synthetic method to embed the Ag and Au NPs in cellulose fibres and hydrogels and have obtained the hybrid nanocomposites using cellulose matrix as the depot. The method is "green" since we used the matrix based on renewable natural polymer cellulose and the process was performed at normal conditions and very low concentrations of chemicals. Composites cellulose-Au and Ag contained low amount of reduced metals and demonstrated antimicrobial properties. Due to this fact, the composite materials have promising properties for application in biomedicine and beauty industry.

NEW ZWITTERIONIC COPOLYMER WITH CARBOXYBETAINE MOIETIES AS POSSIBLE DRUG DELIVERY SYSTEM

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1. Introduction

Polybetaines, that have moieties bearing both cationic (quaternary ammonium group) and anionic groups (carboxylate, sulfonate, phosphate/phosphinate/phosphonate groups) situated in the same structural unit represent an important class of zwitterionic polymers with unique and specific properties. The structural diversity of polybetaines and their special properties such as antifouling, antimicrobial, strong hydration properties and good biocompatibility lead to their use in nanotechnology, biological and medical fields, water remediation, hydrometallurgy and the oil industry.[1-3]

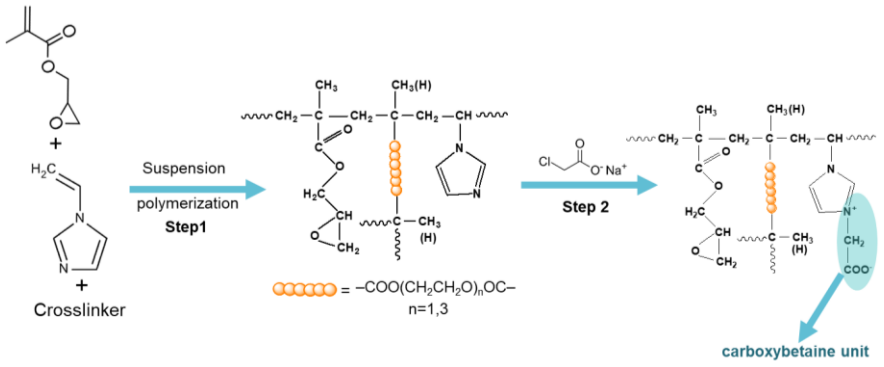
In recent years, researchers in the medical and pharmaceutical fields have generally focused on the following findings: (a) the discovery of new drug delivery based on micro and nano-sized particles that have the ability to respond to stimuli, to carry biologically active targeting principles, to treat cancer or have a multifunctional role in the delivery of therapeutic genes; (b) the use of polymeric materials for diagnosis, therapeutic and biomedical applications, particularly in tissue engineering.[4]

In this context, the purpose of this study is to investigate several aspects: (a) synthesis of porous crosslinking microparticles starting from methacrylic monomers and N-vinylimidazole; (2) chemical modification of porous microparticles containing an imidazole ring by polymer analogous reactions in order to obtain new zwitterionic copolymers with carboxybetaine moieties; (3) immobilization and drug release studies of an antibiotic drug (tetracycline).

2. Results and discussion

The porous crosslinking copolymers were synthesized by aqueous suspension copolymerization of glycidyl methacrylate (GMA), N-vinylimidazole (NVI) and dimethacrylic monomers such as: ethylene glycol dimethacrylate (EGDMA), diethylene glycol dimethacrylate (DEGDMA) and triethylene glycol dimethacrylate (TEGDMA) using 2wt.% of benzoyl peroxide as initiator and toluene as porogenic agent. The preparation of zwitterionic porous microparticles with carboxybetaine moieties took place in two steps as shown in Figure 1.

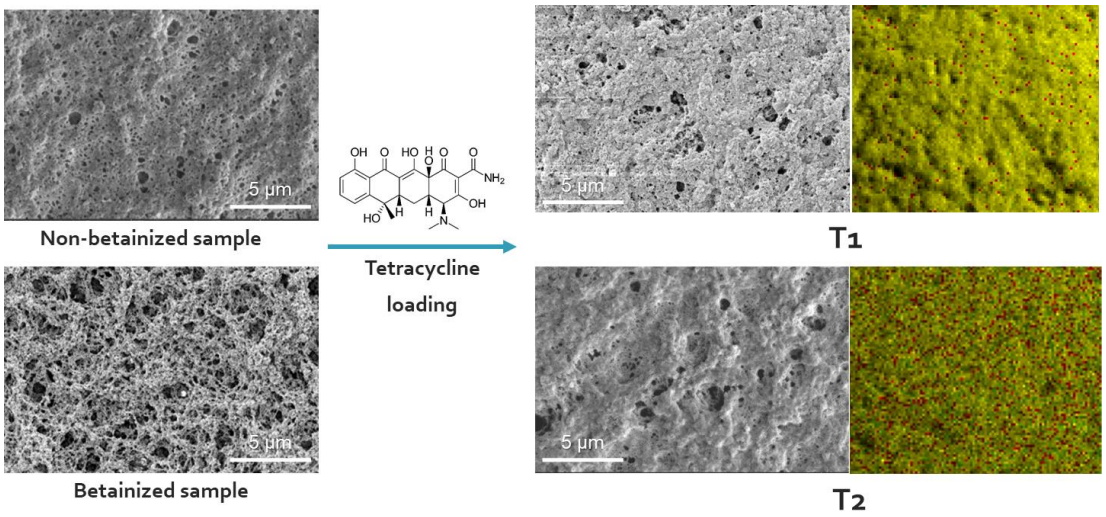
Figure 1. *Synthesis reaction of zwitterionic porous microparticles*



The influence of different parameters (monomer ratio, nature and amount of crosslinkers) on the copolymerization yield, surface morphology as well as on the swelling capacity of the porous microparticles has been investigated. Also, the betainization of porous microparticles was highlighted by FTIR and SEM analyses indicating the presence of COO^- and quaternary nitrogen atom, thus demonstrating the successful preparation of zwitterionic microparticles.

At the same time the possibility to use the microparticles as drug delivery systems has been evaluated. The tetracycline loading into zwitterionic porous microparticles (Figure 2) was performed in a batch system and the concentration of the drug in the supernatant solution before and after adsorption were determined using UV-VIS Spectrophotometer.

Figure 2. *SEM images of non-betainized and betainized samples before and after tetracycline loading*



To elucidate the drug transport mechanism involved in the release of tetracycline from zwitterion porous microparticles three models were considered: Higuchi model, Korsmeyer-Peppas model and Baker-Lonsdale model. The release exponents "n" from Korsmeyer-Peppas are 0.609 (T_1 microparticles) and 0.644 (T_2 microparticles), respectively. These results suggest that the release mechanism corresponds to anomalous transport or non-Fickian transport mechanism indicating that the drug release was controlled by more than one process (diffusion, swelling). The values of n which are less than 0.85 indicate that although the microparticles swelled they did not undergo erosion or disintegration.

4. Conclusions

Porous zwitterionic microparticles based on glycidyl methacrylate, N-vinylimidazole and dimethacrylic monomers (EGDMA, DEGDMA and TEGDMA) were obtained by suspension polymerization method followed by the polymer-analogous reactions in the presence of sodium chloroacetate as betainization agent. Some conclusions can be drawn as follows: (1) porous zwitterionic with diameters between 200 and 400 µm were obtained; (2) tetracycline can be loaded on the zwitterionic beads due to both physical and chemical interactions; (3) Korsmeyer-Peppas diffusion coefficient is aprox. 0.6 suggesting a non-Fickian transport mechanism; (4) zwitterionic microparticles can be suitable for drug delivery applications.

Acknowledgement

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SYNTHESIS OF SILICA PARTICLES LOADED WITH CURCUMIN AND COATED WITH PEG$_{750}$

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1. Introduction

Mesoporous silica nanoparticles (MSN) have been the centre of studies in different scientific areas nowadays. One of the most promising domains for the study of MSN applications is nanomedicine. They have gained significant advantages over other types of nanoparticles used as transport vectors for drugs. These advantages are primarily due to the adaptable structure depending on the synthesis conditions, high specific surface area and a large pore volume. Also, the manufacture of mesoporous silica nanoparticles is simple, scalable, cost-effective and controllable. The biocompatibility character of MSN depends on several factors, such as size, shape, whether or not the particles are functionalized.[1]

One of the major problems with MSN used as drug nanocarriers is the unwanted interactions with the immune system, which cause allergic or rejection reactions. These problems can be avoided, for example, by functionalization with polyethyleneglicols (PEG).[2] Moreover, PEG is an effective steric stabilizer, capable of reducing the coagulation rate of nanoparticles. As a result, PEG-functionalized silica nanoparticles produced by the sol-gel method have received special attention in recent years.[3] In this study we obtained mesoporous silica nanoparticles functionalized with PEG via a sol-gel process as transport vectors for curcumin, which are intended to be applied in treatment of Alzheimer's disease by preventing fibrillation of β amyloid peptides.

2. Experimental

In this study, we chose PEG$_{750}$ as a functionalization agent for the silica nanoparticles. In order to have a fine control over MSNs size, we used different silica co-precursors, namely aminopropyl-triethoxysilane (APTES) and vinyl-triethoxysilane (VTES), while Tween 80 was used as a template agent for silica matrix. Curcumin was solubilized in dimethyl sulfoxide (DMSO).

In order to remove the excess of Tween 80 and DMSO, a purification process through dialysis was performed, using a membrane with MWCO of 6-8 kDa. Size and zeta potential measurements were performed using the Dynamic Light Scattering (DLS) technique.

3. Results and discussion

Before PEG functionalization, our group obtained in preliminary tests four different series of samples in which we varied different synthesis parameters such as nature and amount of silica co-precursor or amount of ammonia.

After DLS analyses it was observed that the most stable compositions were the ones in series B and D (Fig. 1-a), therefore, these series were functionalized with PEG$_{750}$, obtaining VB and VD series (Table 1).

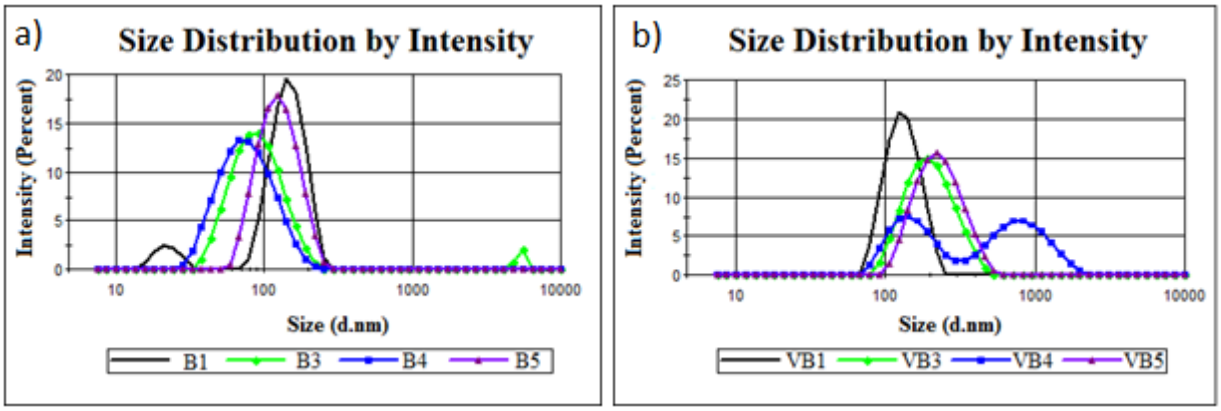
The particle size distributions of series B, D, VB and VD show that NP of silica synthesized in the presence of APTES and VTES and without ammonia (B5, D5, VB5 and VD5) are uniform, stable and, after coating with PEG$_{750}$, their size increases. For the samples coated with PEG$_{750}$ (Fig. 1-b), there is an increase in the particle diameters synthesized with VTES (VB3 and VB5, respectively VD3 and VD5), compared to those obtained in the absence of this silica derivative (VB1 and VB4 respectively VD1 and VD4). An explanation can be given by the fact that the presence of vinyl functions at the surface of the particles allows a better orientation of the PEG chains towards the aqueous environment, which can adopt a more extensive

conformation.

Table 1. *Composition of silica particles loaded with curcumin*

Sample	Tween 80 (mL)	H_2O (mL)	Curcumin in DMSO (µL)	Ammonia (µL)	ODTES (µL)	OTES (µL)	Buthanol (µL)	PEG_{750}-Si (µL)	Co-precursor (µL)	
									VTES	APTES
B1	0.22	10	50	100	50	-	600	-	-	10
B3	0.22	10	50	100	50	-	600	-	50	10
B4	0.22	10	50	-	50	-	600	-	-	10
B5	0.22	10	50	-	50	-	600	-	50	10
D1	0.22	10	50	100	-	50	600	-	-	10
D3	0.22	10	50	100	-	50	600	-	50	10
D4	0.22	10	50	-	-	50	600	-	-	10
D5	0.22	10	50	-	-	50	600	-	50	10
VB1	0.22	10	50	100	50	-	600	40	-	10
VB3	0.22	10	50	100	50	-	600	40	50	10
VB4	0.22	10	50	-	50	-	600	40	-	10
VB5	0.22	10	50	-	50	-	600	40	50	10
VD1	0.22	10	50	100	-	50	600	40	-	10
VD3	0.22	10	50	100	-	50	600	40	50	10
VD4	0.22	10	50	-	-	50	600	40	-	10
VD5	0.22	10	50	-	-	50	600	40	50	10

Figure 1. *Size distribution for particles in: a) B (without PEG_{750}) and b) VB series (coated with PEG_{750})*



4. Conclusions

In conclusion, our group successfully managed to obtain mesoporous silica nanoparticles functionalized with PEG_{750} via a sol-gel process. Our aim is to use these nanoparticles as transport vectors for active compounds such as curcumin in various biomedical applications.

Acknowledgements

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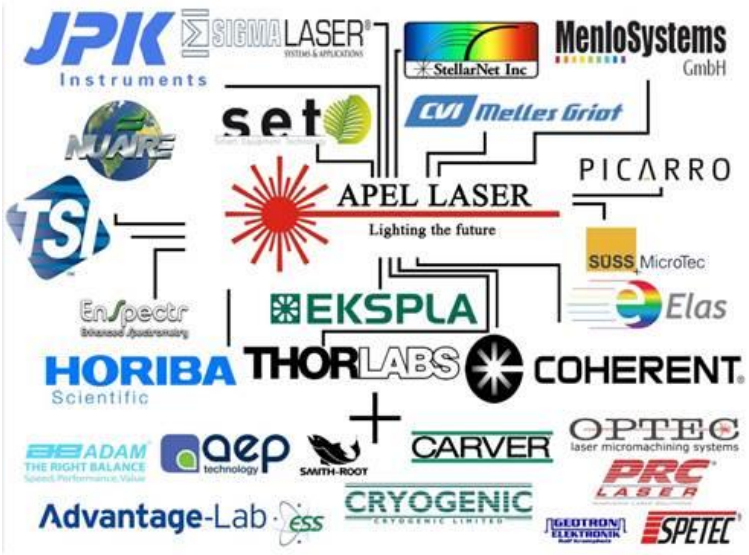

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BYPASSING LC SYSTEM PASSIVATION REQUIREMENTS USING ACQUITY PREMIER WITH MAXPEAK HPS TECHNOLOGY

Laboratorium – Waters Corporation

Chemical passivation is a common technique used to enhance chromatographic performance in sensitive applications. Without passivation, analytes that are particularly susceptible to surface adsorption have been shown to suffer from peak tailing and poor recovery or reproducibility when using conventional LC systems and columns. Waters ACQUITY PREMIER with MaxPeak HPS technology can provide an off the shelf solution, bypassing the need for system passivation as required by conventional LC technology.

1. Introduction

The ACQUITY Premier System is the next evolution of the ACQUITY UPLC platform of liquid chromatography systems, which includes the ACQUITY UPLC H-Class PLUS and I-Class PLUS. Along with the reliability, ruggedness, high quality, and configuration flexibility you expect from the ACQUITY UPLC PLUS Series, the ACQUITY Premier System delivers a step change in chromatographic performance, lab efficiency, and risk control.

The ACQUITY Premier System features novel MaxPeak High Performance Surfaces (HPS) technology, which effectively reduces non-specific adsorption losses due to metal interactions and provides:

- ✓ Reduced analysis times
- ✓ Improved peak shapes
- ✓ Decreased reagent costs
- ✓ Improved LODs and RSDs
- ✓ Reliable quantitation
- ✓ Lower system downtime

Non-specific adsorption of metal sensitive compounds is an unpredictable challenge, leading to long system passivation times, chromatography with large RSDs, and broad peaks that can be a challenge to detect. The ACQUITY Premier System is built with proven ACQUITY technology, which offers true UPLC performance, ultra-low dispersion, and high resolution.

Designed with MaxPeak HPS Technology, the ACQUITY Premier System improves peak shape and reproducibility for even the most challenging metal-sensitive compounds

MaxPeak Premier Columns are designed to be the most universal column platform for chromatographers who need to reduce variability risks and save time, while increasing recovery and sensitivity. Non-specific adsorption (NSA) of metal sensitive compounds is an unpredictable challenge, leading to long column passivation times, chromatography with large RSDs, and broad peaks that can be a challenge to detect.

MaxPeak Premier Columns feature MaxPeak High Performance Surfaces (HPS) which effectively reduce NSA losses due to metal interactions and provide:

- ✓ Reduced column passivation
- ✓ Increased reproducibility
- ✓ Enhanced sensitivity
- ✓ Improved peak shapes

Features and Benefits:

Maxpeak high performance surface technology increases analyte recovery, sensitivity, and reproducibility by minimizing analyte/surface interactions that can lead to sample losses.

Get the flexibility of multi-solvent blending with the Quaternary Solvent Manager (QSM), and blend four solvents in any combination or proportion. Expand to up to nine solvents with the optional and integrated solvent-select valve for even greater flexibility. Automated solvent compressibility allows you to run any solvent in any combination without loss in accuracy or precision.

Deliver precise and accurate binary solvent blending with the Binary Solvent Manager (BSM) at pressures up to 15,000 psi. Two integrated solvent-select valves provide access to a total of four solvents. Automated solvent compressibility, integrated solvent degassing, and programmable seal wash maximize flow accuracy, precision, and reliability.

High-precision injections with direct inject sampling. The needle-in-flow path design ensures an accurate needle seal at high pressure. Injection volumes from 0.1 µL up to 1 mL are supported. Ultra-low carryover is managed through programmable method settings to ensure compatibility even with the most sensitive mass spectrometers.

Accurate temperature control across the entire column. Configurable for one to six columns, each housed in individual temperature-controlled zones with active pre-heating and a temperature range of 4 to 90 °C.

Low-dispersion detection capabilities. Minimizing dispersion and optimizing the electronics and optical paths for the narrow UPLC peaks yields the highest sensitivity and repeatability with the most accurate quantification.

Significantly reduce the time you spend in the prep lab by automating the formulation of mobile phases at specific pH and ionic strength from reservoirs of pure solvents or concentrated stock solutions using Auto•Blend Plus Technology, available with the ACQUITY Premier Quaternary System.

Automatically manage gradient start time and pre-injection steps in parallel with SmartStart technology. This allows you to compensate for system volume differences when transferring methods between different LC systems or to minimize inject-to-inject cycle times for high-throughput applications.

Gradient SmartStart easily adjusts for system volume differences when transferring methods from an alternative LC system without alteration to the method table.

Supported in Empower, Masslynx, and UNIFI softwares.

In this study, a peptide mixture containing a phosphorylated peptide is used to highlight performance differences observed between conventional LC technology and ACQUITY PREMIER with MaxPeak High Performance Surfaces (HPS) technology. Analyte recovery using a conventional LC system and column is only achievable through system passivation using phosphoric acid. MaxPeak HPS technology offers confidence in chromatographic performance through improved recovery, allowing laboratories to run more efficiently by bypassing the need for system passivation.

2. Experimental

A RPLC gradient using water and acetonitrile with formic acid was used to separate a four-component mixture containing insulin receptor (a doubly phosphorylated peptide having the sequence TRDIpYETDpYYRK), angiotensin I, enolase T37, and bradykinin using a conventional LC system and column.

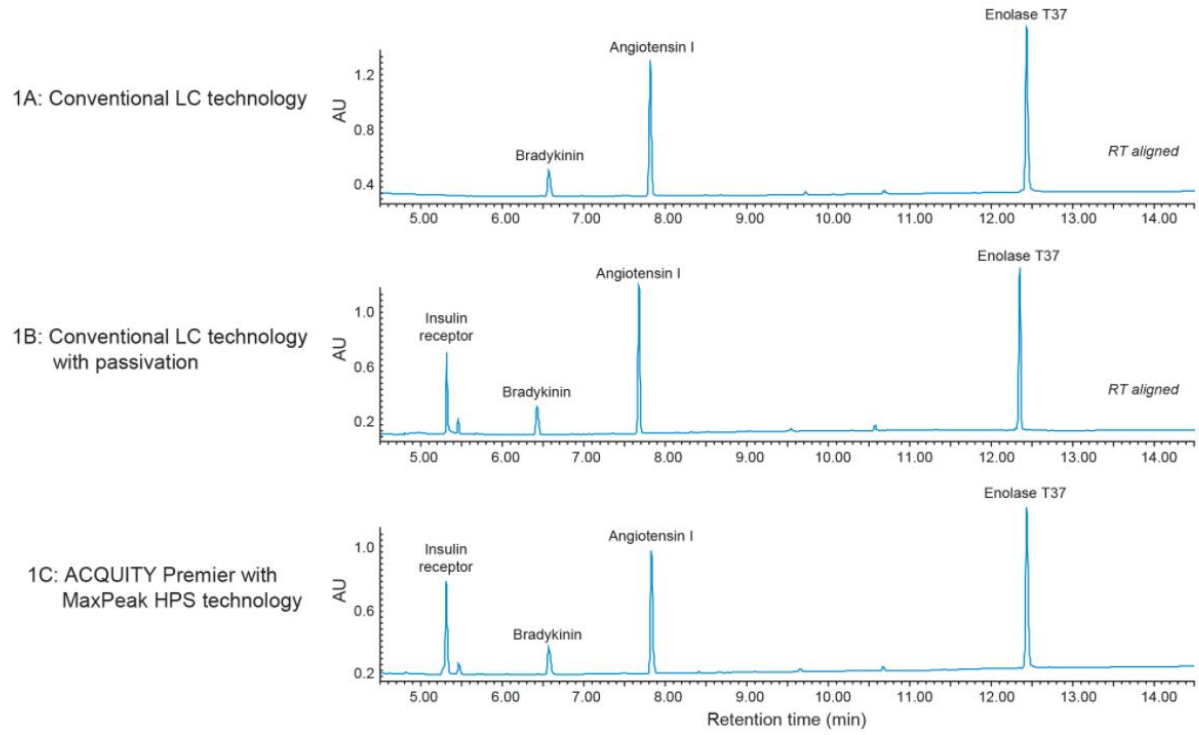
This well-conditioned LC system was a dedicated system for RPLC analysis of proteins and peptides and had performed numerous routine assays meeting various system suitability requirements for retention time repeatability, peak tailing, and analyte recovery.

3. Results and discussion

From Figure 1A, only three components of this mixture could be detected. Because insulin receptor is a phosphorylated analyte with a high affinity for metal surfaces, it was completely adsorbed by the wetted flow path. Only after the system was passivated with phosphoric acid could the peptide be recovered (Figure 1B).

This same separation was then performed using an ACQUITY PREMIER Peptide CSH C18 Column (130Å 1.7 µm 2.1 x 100 mm) and an ACQUITY PREMIER System, and all components of the mixture could be recovered without passivation, as was required by the conventional LC technology (Figure 1C). This demonstrates the ability of the ACQUITY PREMIER technology to provide reliable performance without the need for time consuming system passivation using harsh chemicals.

Figure 1. *Recovery of insulin receptor, a doubly phosphorylated peptide (TRDIpYETDpYYRK).*
1A: Insulin receptor cannot be recovered using "well-seasoned" conventional LC technology.
1B: Adsorption is greatly reduced after system passivation, leading to recovery of insulin receptor.
1C: ACQUITY PREMIER with MaxPeak HPS technology offers superior chromatographic performance off the shelf, bypassing the need for system passivation required by conventional LC technology



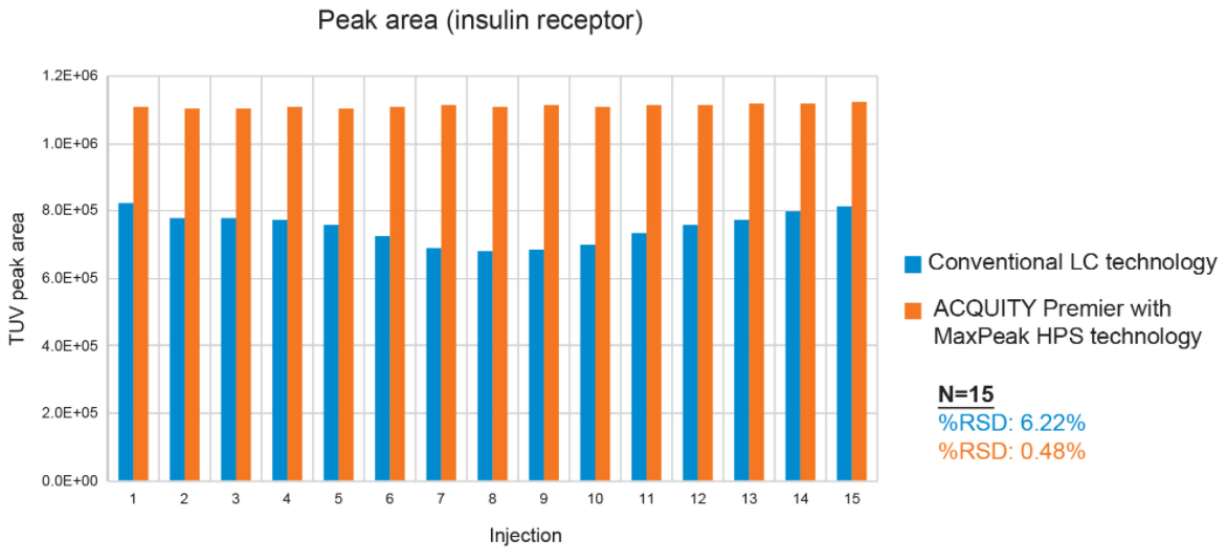
Method conditions: MPA: 0.1% formic acid in water; MPB: 0.1% formic acid in acetonitrile; gradient conditions: 0.5% to 40% MPB over 12 minutes. A 30% phosphoric acid wash was used for system passivation (Figure 1B only) followed by equilibration at initial gradient conditions.

Furthermore, assay repeatability was also observed to improve using the ACQUITY PREMIER with MaxPeak HPS technology. Peak area repeatability, which reflects analyte recovery, was compared using conventional technology and MaxPeak HPS technology after system passivation (Figure 2). The %RSD was calculated as 6.22% and 0.48% over 15 injections for conventional technology and MaxPeak HPS technology, respectively.

Not only does the MaxPeak HPS technology offer more stable performance over the injection series, but the average peak area is approximately 1.5 times greater than that reported with conventional technology.

Improved analyte recovery and repeatability further demonstrate the advantages of MaxPeak HPS technology for the development of robust methods with enhanced detection of sensitive analytes.

***Figure 2**. Recovery and peak area repeatability of insulin receptor, a doubly phosphorylated peptide (TRDIpYETDpYYRK). The %RSD across 15 injections was calculated as 6.22% and 0.48% for conventional LC technology and ACQUITY PREMIER with MaxPeak HPS technology, respectively.*



Method conditions: A 30% phosphoric acid wash was used for system passivation followed by equilibration at initial gradient conditions. MPA: 0.1% formic acid in water; MPB: 0.1% formic acid in acetonitrile; gradient conditions: 0.5% to 40% MPB over 12 minutes.

4. Conclusions

System passivation has become a common practice for analysis of sensitive biopharmaceutical analytes which exhibit surface adsorption artifacts as a means to improve recovery, and assay reproducibility. In this work, a well-conditioned LC system dedicated to RPLC analysis of proteins and peptides was shown to effectively recover a phosphorylated peptide only after surface passivation with an acid treatment. Waters ACQUITY PREMIER with MaxPeak HPS technology offers an off the shelf solution for enhanced chromatographic performance through improved analyte recovery and repeatability compared to more conventional LC technology.

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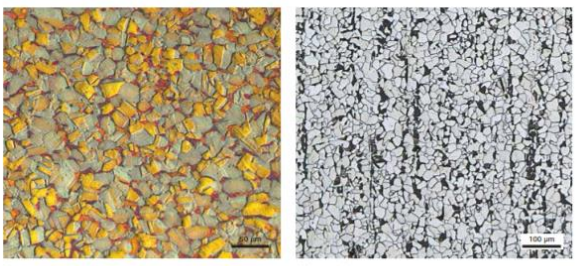

Brass structure
Objective: EC-Epiplan NEOFLUAR 20×/0.50, brightfield
Courtesy of: the Materials Research Institute at Aalen University

Steel, tempered structure
Objective: EC-Epiplan NEOFLUAR 50×/0.80, bright field
Courtesy of: the Materials Research Institute at Aalen University

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CELLULOSE CHEMISTRY AND TECHNOLOGY

In the academic year 1949/1950, the Cellulose department, established a year earlier in Bucharest, was transferred to Iasi, and the responsibility for coordinating it lay with Academician Cristofor Simionescu, then associate professor. The core of the department was formed by Assoc. Prof. Eng. Vasile Diaconescu (later professor) and Profs.-to-be Elena Calistru and Emanuel Poppel. The team was then completed by Dorel Feldman, Grigore Stejar, Elena Corlățeanu and Gheorghe Rozmarin, who along the years brought their contribution to the formation of specialists in the fields of cellulose, paper and synthetic fibres, and to the development of a number of research directions.

From the very start, the teaching staff became actively engaged in a prolific research activity, which was recognised both nationally and internationally. As a result, the first success was recorded in 1961, when the **First International Symposium of Cellulose Chemistry and Technology** was held in Iași, under Prof. Cristofor Simionescu's coordination. The event became a tradition, and 13 editions were further organised under Prof. Cristofor Simionescu's leadership. The 14th edition paid homage to Prof. Simionescu's lifelong scientific activity, celebrating his 90th birth anniversary. Over the years, the international symposia have enjoyed the participation of renowned experts in the field from around the world.

On the occasion of the 2nd Symposium (1965), Z. A. Rogovin, former professor at the Institute of Textiles in Moscow, well-known for his valuable contribution to the field of cellulose chemistry, along with other foreign specialists, proposed to launch a journal entitled *Cellulose Chemistry and Technology*, to be edited in Iași under the auspices of the Romanian Academy, and to entrust Acad. Cristofor Simionescu with this mission. Pointing out the steadfast climate favourable for the progress of research in this area, the great hospitality of the Romanian people, the spiritual youth and the excellent organisation of the symposia, in association with a few foreign participants, whose names are still listed on the frontispiece of the journal, even though they have passed away, he addressed Acad. I. G. Murgulescu, asking him to embrace and support this proposal.

Further results confirmed that, although it appeared spontaneous, his suggestion was well thought out and had chances of long-term success. The meetings of the members of an international editorial board would create occasions for more and more specialists, both experienced and younger ones, to come to know each other, build communication bridges and boost creation. The city of Iași was entrusted with a research centre, which, at the crossroads of civilisations and responsive to cultural acts, would prove capable of standing up to the scientists' expectations.

In September 1968, the first meeting of the editorial board was organized (at that moment, formed by 53 members), which drew together the most brilliant representatives of the cellulose schools from around the world at that time: M. Chêne (France), P. Cremonesi (Italy), K. Dimov (Bulgaria), H. Dolmetsch (Germany), E. Giese (Germany), R. Husemann (Germany), A. I. Kalninsh (USSR), H. Sihtola (Finland), T. E. Timell (USA), V. Diaconescu (Romania). The meeting was held on the occasion of the 3rd International Symposium of Cellulose Chemistry and Technology, organised on 18-22 September, 1968, in Iași. The editor-in-chief Cristofor Simionescu's report highlighted the wide geographical coverage of the journal, ensured by scientific contributions submitted for publication by authors virtually from all over the world: Austria, Bulgaria, Canada, Czechoslovakia, Egypt, France, the split Germany at the time, India, Italy, Japan, Poland, Romania, USA and USSR.

The second editorial meeting was held in September 1971, and again enjoyed remarkable international participation: F. Bertran (Cuba), E. Correns (GDR), E. Daruwalla (India), Y. Fahmy (Egypt), A. Frey-Wyssling (Switzerland), E. Garnum (FAO), M. Lewin (Israel), H. P. Naveau (Belgium), Z. A. Rogovin (USSR), I. Sakurada (Japan), J. Schurz (Austria), L. Stockman (Sweden), V. Diaconescu, E. Poppel and D. Feldman (Romania). The participants emphasised the echo of the *Cellulose Chemistry and Technology* journal abroad and expressed their appreciation of its steady progress, achieved by raising the scientific quality and the degree of originality of the contributions published – the result of a collective effort, of the perseverance and enthusiasm of all those involved in the magazine. In his report, Prof. Simionescu underscored the contribution of the 58 members of the editorial board (from 27 countries), who engaged in reviewing the manuscripts to ensure the publication of high-quality scientific content.

In the opening conference of the 4th International Symposium (Iași-Suceava, 28 September-2 October 1971), Prof. Simionescu addressed issues of pressing actuality in the field of cellulose and paper chemistry and technology of the time, which, despite the time elapsed, are still as current and have even turned into priorities. Defying the idea brought out the same year (1971) by *Angewandte Chemie*, which announced that "natural sciences were approaching their endpoint", Prof. Simionescu expressed his belief that, in order to maintain the status of science in progress, cellulose chemistry and technology needed to join biology, physics and mathematics in an interdisciplinary relation (a very bold idea!). In his view, the so-called crisis in the theoretical chemical sciences emerged from the lack of understanding that in the near future the various branches of the natural sciences would interact and join in the common effort to decipher the secrets of nature.

Thus, considering that the chemistry of cellulose, hemicelluloses, lignin and their derivatives was only a Cinderella of modern chemistry, it would be imperative to intensify research in the field of wood to find solutions to pressing issues:

- ✓ the alarming increase in the degree of irrational forest exploitation, as a result of expanding industrialization and continual population growth
- ✓ a more efficient use of the wood, possible by deeper research on its biological, physical and chemical structure
- ✓ processing wood in a way that would diminish the quantity of waste and unusable by-products, and thus, would reduce environmental pollution
- ✓ preventing global crisis in the cellulose and paper industry, which was going to affect mainly Europe – said Prof. Simionescu in 1971! – by planting new forests, along with using alternative raw materials, provided by, for example, annual plants, gramineae straws, reed, kenaf or fast-growing species, especially willow, poplar and eucalyptus, and other tropical species that can be grown on lands unsuitable for agriculture.

However, all these objectives require not only theoretical studies in plant physiology, anatomy and molecular biology (and other sciences), but also the fast application of the results in practice, developing chemical technologies and biotechnologies for valorising vegetal biomass. In this context, since its founding, the journal has published numerous papers on fundamental and applicative issues regarding regenerative and recyclable resources, which make this field the only one that belongs under sustainable development, thus embodying the hope to provide, besides conventional products, bioproducts with the most diverse applications. In this way, the biorefinery concept was coined, which refers to a facility that can lead to increasing the efficiency of the cellulose and paper industry, integrating the possibilities to obtain products of chemical and energetic value. Thus, contributions to the biorefinery field have also found a place in the contents of the journal in recent years.

The journal joined an already existing publication in Romania – Cellulose and Paper (1951), and allowed the exchange with journals and books published abroad, thus offering Romanian scientists the possibility to keep a permanent contact with similar research centres from around the world, even during the harsh period preceding 1989.

In its 55 years of existence, the journal has proven its real importance in ensuring the participation of Romanian scientists to the exchange of information, to make their contribution known, as well as in bringing numerous journals and books into the country annually.

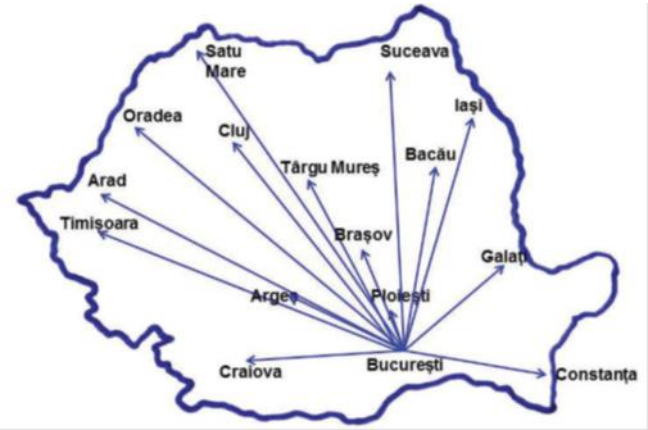
At present, when we are witnessing a real informational tsunami, the *Cellulose Chemistry and Technology* journal, indexed ISI since 1992 (IF 1.467 in 2020), is published in both online (www.cellulosechemtechnol.ro) and print forms, and successfully continues its activity, hosting papers from all over the world. On this anniversary, we hope that both the editorial board and our steadfast collaborators will continue to contribute to increasing the quality and prestige of the journal.

Valentin I. Popa, Editor in chief
Iuliana Spiridon, Associate Editor

ROMANIAN CHEMICAL SOCIETY
SOCIETATEA DE CHIMIE DIN ROMANIA, SChR

"Chemistry is not everything, but anything is nothing without chemistry"

SChR Objective: "*Attracting young people towards chemistry as study field and profession* "



Sections and Local Branches

21 Local branches

7 Sections

3000 Members
(including honorary and affiliated members – students and pupils)

The activity of organizing scientific meetings is continued and developed:

- ✓ *ICOSECS, The International Conference of the Chemical Societies of the South Eastern European Countries* is organized by regional cooperation with the chemical societies from Albania, Bulgaria, Cyprus, Greece, Macedonia, Montenegro and Serbia
- ✓ *COFrRoCA, The Franco-Romanian Colloquia of Applied Chemistry* is organized in cooperation with the universities of Bacău (Romania) and Orleans (France)
- ✓ Periodically international conferences with a high scientific level are organized in cooperation with the University Politechnica Bucharest, Ovidius University Constanta, Petru Poni Institute Iasi.

The present publications of SChR include the ***Bulletin of the Romanian Chemical Society*** (an information journal on the activity in chemistry in Romania), ***Revista de Chimie*** (a scientific journal publishing original results, with a constantly rising ISI impact factor), ***Chimia*** (a publication for undergraduates), as well as a series of publications of the local sections of SChR: *ProChimia*, *Universul Chimiei*, *ChimMax*.

The ***Bulletin of the Romanian Chemical Society*** founded in 1919, since the very beginning of SChR, aims to periodically present the life and activity of SChR, the actions of the Society for the promotion of chemistry and its position on the chemistry policy.

Among the modern numbers is the one from 2009 where one can find detailed information about the SChR history as well as about some outstanding personalities of the Romanian chemistry.

For high school students, the journal ***Chimia*** was launched in the early 2000s. It included comprehensive articles on the topics of contemporary chemistry (sometimes written by eminent students), exciting problems and experiments, curiosities and biographical notes of the great Romanian or universal chemists.

"SChR grants medals, prizes and awards as recognition of scientific and/or professional activities of the chemists, located in the country or abroad" – SChR Rules

Petru Poni – first SChR medal

...in Pre-university Education

....in Inorganic Chemistry

... in Organic Chemistry

... in Chemical Engineering

Many important figures of the chemical world are honorary members of SChR and visited Romania on various occasions. SChR signed bilateral agreement papers with several societies within Europe.

SChR - Member of EUChemS

EuChemS, the European Chemical Society, is an umbrella organisation representing national Chemical Societies and other chemistry-related organisations in Europe. EuChemS aims to nurture a platform for scientific discussion and to provide a single, unbiased European voice on key policy issues in chemistry and related fields. Contact: www.euchems.org

EuChemS
European Chemical Society

The local sections of SChR together with the universities have as an important activity to attract young people in the study of chemistry. The constant orientation to increase weight of the experimental activity is not aleatory, nor is it isolated. It comes from the tendency to fill, even partially, the gaps in experimental instruction of the undergraduate studies and it follows the recommendations of SChR. Many of the activities promoted by the local sections and the sections of the society belong to this line of action.

STC – "Secția Tinerilor Chimiști" - the Youth Division of SChR is an active and dynamic group.

The STC SChR members were part of the initiative group that sign the formation of EYCN in 2007 in Berlin. Since then, members of STC were part of the EYCN board and in 2011-2013 chaired EYCN/

Contact: Romanian Chemical Society, Str. Gheorghe POLIZU, nr. 1-3, sector 1, BUCURESTI, ROMANIA, Phone: +4 021 402 3962; +4 021 402 3912, Email: secretargenschr@icmpp.ro

DIGITALIZATION CHALLENGE FOR THE BIONANOTECH PROJECT SUPPORT CENTRE

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[1]*Petru Poni Institute of Macromolecular Chemistry, Romanian Academy, Iasi, Romania*
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1. BioNanoTech Project - objectives and activities

The BioNanoTech project was submitted several years ago to a competition within the Structural Funds Program, competition dedicated to offer financial support in synergy with the Horizon 2020 program. One of the tasks of this call was to support the establishment of Support Centers able to provide information and consultancy for European and international projects. In this framework the BioNanoTech Project was submitted, accepted and started in April 2020. Within this competition a total of eleven projects were selected[1].

The aim of the BioNanoTech-Support Center is to improve Romania's participation in the Horizon 2020 and other European and international projects (ie. Horizon Europe program) in the fields: advanced ecomaterials, nanomaterials and biotechnologies - beneficiary focus in the NE region of Romania (research institutes, universities, innovative enterprises etc.).

To address its ambitious goal, the BioNanoTech Support project contains several specific objectives:

O1. The administrative organization of a BioNanoTech-Support Centre for European projects.

O2. To set up a national and international cooperation network that will improve the participation of institutions from the NE region of Romania in the European Union Research Framework Program (Horizon 2020 / Horizon Europe);

O3. To develop a web platform and a dedicated database to provide on-line support for beneficiaries from the NE region to design and implementation of research projects within the European Framework Program

O4. Consultancy and support in making proposals and managing projects within the European Framework Program.

These objectives are to be archived through a specific set of activities:

- ✓ Documentary and informational activities
- ✓ Support for proposals for RDI projects submitted to EU programs: (a) appropriated calls for specific ideas, (b) search for partners in the country and abroad, (c) eligibility verification, (d) proposal verification; (e) proposal submission in ECAS
- ✓ Dissemination of information for EU projects proposals ***including the development of a dedicated web portal[2] able to become a long-lasting working tool for the Center***
- ✓ Administrative support for the management of financed projects.

2. Digitalization challenge in Horizon Europe

As shown in the *2030 Digital Compass*[3] Strategy, "one of the key lessons of the pandemic is that digitalisation can bring people together independently of where they are physically located. Digital infrastructure and rapid fast connectivity bring people new opportunities. Digitalisation can become a decisive enabler of rights and freedoms, allowing people to reach out beyond specific territories, social positions or community groups, and opening new possibilities to learn, have fun, work, explore and fulfil one's ambitions.

This will enable a society where geographical distance matters less, because people can work, learn, interact with public administrations, manage their finance and payments, make use of health care systems, automated transport systems, participate to democratic life, be entertained or meet and discuss with people anywhere in the EU, including in rural and remote areas."

The Commission proposes setting up a Digital Compass to translate the EU's digital ambitions for 2030 into concrete targets and to ensure that these objectives will be met. The first two cardinal points are focused on digital capacities in infrastructures and education & skills, and the other two are focused on digital transformation of business and public services.

The BioNanoTech portal addresses these goals directly and its Center is moving as much as possible to the online structure. Even if initially the development of the portal wasn't the core of the project, pandemic experience has changed our perspective.

The transformation of BioNanoTech activities will depend on the ability to adopt new digital technologies rapidly and across the board. However, even if the team members have understood the need of digitalization of part of the Center activities, the end users are still distrustful of this change. Thus, the BioNanoTech has to face a new and unexpected challenge: to train the NE Romanian region end users (and not only) to face the digital challenges in Horizon Europe program.

3. BioNanoTech digitalization challenge

One of the main tasks included in the work plan of the BioNanoTech project was the development of a web portal that can offer all services provided by the Centre in an on-line environment. The initial idea for this portal was that sometimes end users would prefer on-line contact to face to face contact. As such, the BioNanoTech team came up with this tool as a modality to attract more end users. The unexpected Coronavirus crisis has change the importance of this tool in the BioNanoTech project implementation and we are currently working to develop it as a central element of the project.

Aware of the role and importance of digitalization, the BioNanoTech team, in collaboration with the company S.C. Click Net Solutions S.R.L designed and created the project website and portal.

The specialized company's contribution was of a great importance in:

- ✓ setting and configuring the database;
- ✓ the graphic development of the web interface (html, css, php, javascript)
- ✓ menu implementation.
- ✓ adding and formatting content to the section "General information," Expertise offer "," Information about competitions "," News and events "," Procurement "+ administration panel available to the procurement department," Contact ";
- ✓ creating a customized interface.
- ✓ the technical maintenance of the website.

Among the services offered through the portal we list:

- ✓ Consulting services in identification of funding sources,
- ✓ Consulting services in drafting project proposals,
- ✓ Consulting services in project management,
- ✓ Partner search services.

With a single click, online, beneficiaries can access updated information about open competitions, as well as useful documents in drafting a project proposal: (a) O2020 COMPENDIUM – that contains a summary of main technical questions (financial, legal and HR related) received from our users and the reply offered by our team, (b) Horizon-europe-strategic-plan-2021-2024, (c) Horizon Europe Work Programs with short resume and open calls; (d) Romanian National Contact Points for Horizon Europe Program; (e) links to several partner search facilities; (f) links to several tools useful for project management etc.

The portal interface has also a private section where:

- ✓ The BioNanoTech team can access their mail and also modify/update content of several sections of the portal (ie Open Calls, New, Events etc.)
- ✓ end users can register and directly contact our team in private chat room where they can directly discuss their project ideas – section under development

Finally, throughout development, the design of our portal should build on and seek collaboration with existing project related webpages and develop synergies with other relevant European, national or regional initiatives and platforms.

All participants in European projects will need to adapt to the new trends in project management and will need to relay on digitalized solutions so it is vital de develop such tools that can provide working interfaces for collaboration. For instance: an important part of Horizon Europe is channelled through collaborative projects; it's very important to provide a guidance around the current ways available for participants to look for partners for their proposals.

Although in the current social media & digital era, there are many channels available where suitable partners can be found to start research collaborations, the official support structures of Horizon Europe do also continue to provide this type of support to the special needs of Horizon Europe consortia.

The members of the BioNanoTech team are available to offer help in finding partners on official platforms (such as ECAS Funding and Tenders Portal[4] or Enterprise Europe Network partner search tool[5]) and from other sources (brokerage events, training sessions, workshops, and periodic newsletters) and to support applicants in the preparation of their partner profiles. The BioNanoTech portal offer links to several partner search facilities and also a section (section under development) were user can register and post their partners search profiles.

4. Conclusions

It has been widely recognized that the availability and fast upgrade of digital skills in Europe is vital for the future of the European economy. The EU's Recovery and Resilience Facility (RRF) aims to finance projects that directly tackle the economic and social impact of the Coronavirus crisis and support the green and digital transition.

Thus the development of IT solutions is vital for companies/projects and other initiatives that need to update their digital skills in order to be able to fully take stock of future opportunities arising from advancements in fields such as artificial intelligence, future networks and mixed reality nor will they resist on a market.

For us, the BioNanoTech portal now represents the first step to the future shape of the Center that needs to become more and more digitalized to coop with the European development trends.

Acknowledgements

We would like to thank to the BioNanoTech Project supported by European Regional Development Fund through the Operational Program Competitiveness 2014-2020; Contract no. 241/27.04.2020; My SMIS: 107524.

We look forward to having your questions and to guide you with proposal writing.

Reach out to us at: e-mail: bionanotech_suport@icmpp.ro

Website: https://www.bionanotech.ro/

[1] https://www.research.gov.ro/uploads/comunicare/comunicate/analiza-centre-suport2.pdf
[2] www.bionanotech.ro
[3] 2030 Digital Compass: the European way for the Digital Decade; COMMUNICATION FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT, THE COUNCIL, THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE COMMITTEE OF THE REGIONS; COM(2021) 118; Brussels, 9.3.2021
[4] https://ec.europa.eu/info/funding-tenders/opportunities/portal/screen/how-to-participate/partner-search
[5] https://een.ec.europa.eu/partners

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Instrumente Structurale 2014-2020

PETRU PONI INSTITUTE OF MACROMOLECULAR CHEMISTRY - INTERDISCIPLINARY POLE FOR SMART SPECIALIZATION THROUGH RESEARCH-INNOVATION AND TECHNOLOGY FOR POLYMERIC (BIO/NANO)MATERIALS AND (ECO)TECHNOLOGIES

- INOMATPOL –

1. General information

- ✓ Beneficiary: Petru Poni Institute of Macromolecular Chemistry Iasi (PPIMC)
- ✓ Project co-financed by European Regional Development Fund under the Competitiveness Operational Program 2014-2020
- ✓ Priority Axis 1 – Research, Technological Development and Innovation to Support Economic Competitiveness and Business Development
- ✓ Action 1.1.1 Large R&D Infrastructure, tip "Investment projects for public R & D institutions/universities"
- ✓ Period: 10.10.2016 – 09.07.2020
- ✓ MySMIS: 107464

2. Management team

- ✓ Project director – Dr. Narcisa Laura MARANGOCI
- ✓ Technic Coordinator – Dr. Anton AIRINEI
- ✓ Technical Expert (I) – Dr. Marcela MIHAI
- ✓ Technical Expert (II) – Dr. Ion BUNIA
- ✓ Acquisition Coordinator – Daniel CONDREA
- ✓ Legal Responsible – Jr. Dr. Raluca ANDONE
- ✓ Financial Responsible – Roxana MATACHE
- ✓ Manager Assistant – Diana ENCIU

3. General objective

Enhancing the capacity, quality and efficiency of the RDI activity be opening new research directions and by diversifying the range of research services targeted for industry – in accordance with the particular innovation needs of economic agents belonging to cluster-type organisations, with the purpose of stimulating the competitiveness of the Romanian scientific research at European level and enhancing the national/regional economic competitiveness of the Institute and its industrial partners in the field of smart specialisation in eco-nano-technologies and advanced materials.

4. Specific objectives / expected results

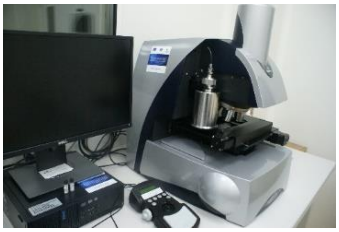
OS 1 – Reorganization and upgrading of the PPIMC RDI areas, in order to increase the capacity for innovative research services, by

- ✓ creating new RDI laboratories: 20 synthesis laboratories and 1 support laboratory
- ✓ upgrading of existing RDI laboratories: 10 synthesis laboratories and 5 support laboratories




OS 2 – Development and upgrading the PPIMC RDI infrastructure to the EU advanced standards by purchasing 62 RDI equipments (including pilot ones), of which 18 with value above 100.000 euro, 87 chemical niches, 87 special laboratory tables, 23 IT equipment and 4 intangible assets

1. Combined system NMR liquid 600 MHz - LC – MS, Bruker MaXis II
2. MALDI TOF Mass spectrometer, Bruker – Rapiflex
3. Lasers for Raman spectroscopy, Renishaw
4. Analysis system for determining the shape, concentration and size of the particles, Malvern Instruments Ltd UK Morphology G3 series
5. Microbalance with quartz crystal (QCM-D), Biolin Scienti Cryo-ultramicrotome fic Suedia Q-SENSE
6. Equipment for mechanical analysis in dynamic regime – DMA
7. Spin electronic resonance spectrometer
8. Atomic absorption spectrometer
9. Multifunctional plant for complex exploitation of plant biomass type microscale
10. Real-time spectrometry system with pulsed laser photolysis
11. Real Time PCR
12. GPC / SEC multidetector system
13. Flow cytometry system for immunophenotypic analysis of cells
14. Vibrating sample magnetometer (VSM) with temperature chamber
15. Thermoanalysis sytem with ATG and DSC
16. Extruder for elastomers
17. UHR-SEM-STEM high resolution scanning electron microscope
18. Cryo-ultramicrotome



OS 3 – Improving the quality and diversifying the offer of RDI services especially for the business media and the cluster structures, during the project and within a minimum of 5 years from the completion of its implementation

OS 4 – Development of eco-nano-technologies and industrial production of (bio-nano) polimer materials in Romania and in N-E Region by creating minimum 10 technologies or new products and publication of minimum 70 scientific papers with authors from public and private sector, based on the protocols of collaboration with the economic agents, during the project duration and at least 5 years after its completion

OS 5 – Increasing the competiveness of the cluster members and internationalization of their activity/performance by answering to the request of innovation, ensuring the transfer of knowledge and innovative services for the private companies from clusters or innovative parks, upon request and based on public-private contracts, for traditional and new economic partners, members of the technological clusters / parks at least 5 years after the comple.tion of the project

OS 6 – Increasing the human resources quality by creating optimum conditions for the RDI activities and a number of 30 new jobs created by the end of the project implementation period

OS 7 –Increasing the international visibility and PPIMC involvement in the European projects - at least 35 project proposals for Horizon 2020 will be submitted within 5 years from the completion of the project implementation

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Instrumente Structurale 2014-2020

PARTNERSHIPS FOR KNOWLEDGE TRANSFER IN THE FIELD OF POLYMER MATERIALS USED IN BIOMEDICAL ENGINEERING

- POINGBIO -

Petru Poni Institute of Macromolecular Chemistry Iasi is implementing the project "Partnerships for knowledge transfer in the field of polymer materials used in biomedical engineering", Contract no.86/08.09.2016, ID P_40_443, SMIS 105689. The project is cofinanced by the European Regional Development (ERDF) Fund by the Competitiveness Operational Programme (OCP) 2014-2020, Axis 1 Research, Technological Development and Innovation (RDI) in support of economic competitiveness and business development, Action 1.2.3 Knowledge Transfer Partnerships. The project duration is 69 months.

The project aims to enhance the economic competitiveness of small and medium enterprises, which are partners in the project during 2016-2020, following the transfer of knowledge aimed at scientific and technological expertise in the design and development of multifunctional polymer systems that can stimulate a specific biological response and allow adherence and proliferation of a particular type of cell, depending on the tissue to be treated.

The eligible activities of the project are:

- ✓ the access of the companies to the facilities, installations, equipment of the research organizations in order to realize the analysis, tests, experiments, characteristics, quality labeling and the certification and to develop new products / technologies/ methods improved through:
- ✓ the transfer of the activities skills/competencies for research-development and for innovation support from research organization to industrial partner;
- ✓ industrial research activities and / or experimental development executed for and on behalf of the organization;
- ✓ the detachment of highly qualified personal who perform the research activities, development and innovation, from research organization to enterprises, in a newly function created within the enterprise, without replacing other personnel;
- ✓ the market research realized by the research organization for companies;

Knowledge transfer Contracts with SMEs between 2016 and 2021:

- ✓ 2 contracts type B. Access of SMEs to facilities, installations, equipment;
- ✓ 1 contract type C. Activities of skills transfer/ competencies and innovation support RD;
- ✓ 8 contracts type D. Research and Development in effective collaboration with:

S.C. Centrul Medical Domenico S.R.L. Iasi

S.C. Sanimed International Impex S.R.L. Bucharest

S.C. Polymer Adhesive Tapes S.R.L. Bucharest

S.C. Intelectro Iasi S.R.L.

S.C. All Green S.R.L. Iasi

S.C. Apel Laser S.R.L Bucharest

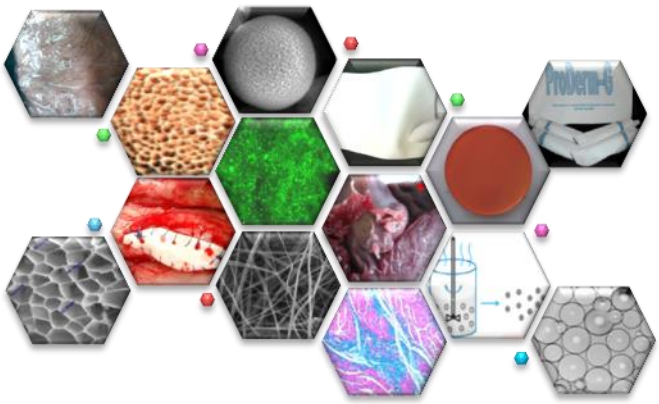
S.C. Innovative Green Power S.R.L Iasi

POINGBIO project contributes significantly to the objectives undertaken by Romania in 2014-2020 POC program, facilitating the use of eco - nano- technology economy by transfer of scientific knowledge and technical means to top fields in biomedical science, so that interested economic partners with the POINGBIO team can conceive or improve technologies for high performance, non-polluting, long-lived, with scientific and economic importance for the production of advanced materials

Other expected results: 40 papers published in collaboration with SMEs; 4 patents in collaboration with SMEs; 1 new research position in the project

The scientific subjects of the contracts are:

- ✓ Polymeric materials for transepidermal therapy
- ✓ Bioactive multilayer hemostatic polymer membranes
- ✓ Collagen-based micro- and nano-fibrillar structures with biomaterial characteristics for biomedical applications
- ✓ Protocols and framework technologies for obtaining innovative biomaterials based on (bio) macromolecular compounds
- ✓ Printable nano-sensors on biocompatible flexible support for medical applications
- ✓ Polymeric materials containing phytotherapeutic extract for biomedical applications
- ✓ The microwave devices utilization for the improvement of polymeric materials with applications in biomedical engineering
- ✓ Polymeric materials obtained by conventional and unconventional methods for biomedical applications
- ✓ Flexible biocompatible nano-conductive composite materials, with pre-defined multilayer architecture for increasing the quality, sensitivity and selectivity of images obtained by magnetic resonance



poingbio@icmpp.ro

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Instrumente Structurale 2014-2020

INFRA SUPRACHEM LAB ADVANCED RESEARCH CENTER IN THE FIELD OF SUPRAMOLECULAR CHEMISTRY

- Infra SupraChem Lab –

1. General information

- ✓ Beneficiary: Petru Poni Institute of Macromolecular Chemistry Iasi
- ✓ Project co-financed by European Regional Development Fund under the Competitiveness Operational Program 2014-2020
- ✓ Priority Axis 1 – Research, Technological Development and Innovation to Support Economic Competitiveness and Business Development
- ✓ Investment priority 1a – Improving research and innovation infrastructures and capacities to develop excellence in RDI and promoting centers of expertise, especially those of European interest
- ✓ Action 1.1.3 Creating synergies with the RDI actions of the European Union's HORIZON 2020 framework program and other international RDI programs
- ✓ Period: 25.02.2021 – 24.06.2023.
- ✓ MySMIS: 108983

2. General objective

The overall objective of the Infra SupraChem Lab project is to create an advanced infrastructure that deserves the supramolecular chemistry working group SupraChem Lab, a group created within the Horizon 2020 Project WIDESPREAD 2-2014: ERA Chairs (667387) - SupraChem Lab Laboratory of Supramolecular Chemistry for Adaptive Delivery Systems ERA Chair initiative.

3. Specific objectives / Expected results

O1. Realization of the design component for the Infra SupraChem Lab project - objective already in implementation
O2. Realization of the infrastructure of the SupraChem Lab center
O3. Equipping and launching the SupraChem Lab center
O4. Dissemination and publicity
O5. Project management

The implementation of the Infra SupraChem Lab project represents the creation of an adequate structure for the activity of the SupraChem Lab group, a group created through a Horizon 2020 ERA CHAIR project (Horizon 2020 WIDESPREAD 2-2014: ERA Chairs Project no 667387). The project aims to carry out advanced research activities in the field of supramolecular chemistry with predominant applications to medicine and the pharmaceutical industry.

The implementation of the Infra SupraChem Lab infrastructure is a step forward to create the premises for applied research as a natural continuation of the application of the results of fundamental research obtained by the newly created group. Within IntelCentru and ICMPP as a whole, numerous research projects financed from structural funds have been implemented or are being implemented (eg POS-CCE, POC E, POC F, POC G), EU funds (FP5, FP6, FP7, Horizon 2020, ERA-IB, etc.) as well as from national funds (eg MATNANTECH, CERES, CEEX, PNII, PNIII), materialized in well-defined innovative directions, and the research results are capitalized in numerous publications and patents.

Over the last ten years, ICMPP's research directions have clearly evolved into interdisciplinary fields and have adapted to global research trends, while also presenting their own original directions, based on

knowledge and experience gained over time. If the current development of ICMPP is extrapolated for the next ten years, surprising new findings can be made in already existing research areas.

The implementation of the Infra SupraChem Lab project would contribute on the one hand to the improvement of the existing research within the SupraChem Lab team and on the other hand to the development besides the fundamental research directions and of some applied research directions for new top products. An important part in the development of new directions is based on a modern infrastructure, aimed at interdisciplinary research. An infrastructure based on the synthesis and complete characterization of new materials presents a real support for the development of application fields.

The implementation of the Horizon 2020 ERA CHAIR SupraChem Lab project started in 2015 and with the support of a community investment of 2.5 MEuro, the foundations of a young team of researchers with knowledge focused on the principles of supramolecular chemistry were laid. The team's research areas range from the creation of dynamic systems for targeted biomedical applications to the dynamic molecular modeling of the interaction of complex supramolecular systems. This human resource presents a secure core for the training of new generations of specialists, able to continue and develop new fields with great applicative impact. The creation of a modern infrastructure would allow the even more accentuated development of supramolecular materials focused on applications in various fields.

Infra SupraChem Lab will be set up in spaces owned by the "Petru Poni" Institute of Macromolecular Chemistry - in buildings currently unused, under conservation. The new center will also benefit from the arrangement of auxiliary spaces, for the storage of chemicals, glassware and laboratory materials as well as the related access ways to facilitate the access to the research infrastructure.

The structure of Infra SupraChem Lab will include the following departments:

A. **Operating department** consisting of:

A1 Chemical and biochemical synthesis laboratory

In the synthesis lab, supramolecular compound synthesis will be performed for special applications such as biomedical, membranes, biosensors and bioelectronics.

A2. Laboratory for the study of special properties and possible applications

In this laboratory will be tested the properties of materials for possible applications (e.g., electrochemical biosensors, gas absorption, ion transport through membranes, drug release, etc.)

A3. Physical and chemical characterization laboratory

In this laboratory the characterization of the newly created compounds will be performed

The laboratories are provided with chemical ventilation niche and specific laboratory equipment for chemical syntheses (eg: magnetic stirrers, inert gas purification installations, vacuum pumps, electric ovens, etc.), study of properties and material characterization.

B. **Data processing department**

Within this department, the data will be processed and structural optimization studies will be performed.

C. **Department of projects and technology transfer**

All departments are provided with computers connected to the Internet and implicitly to the internal network of the center.

The project has as **direct beneficiaries** the SupraChem Lab team, a group created by implementing the Horizon 2020 WIDESPREAD 2-2014 project: ERA Chairs, no. 667387 SupraChem Lab.

In addition to these direct beneficiaries, the project is addressed to other **interest groups** as follows:

- ✓ graduates of the universities of Iasi and not only who in time could join the SupraChem Lab ERA CHAIR team or could benefit from training within the newly created Center
- ✓ teachers from universities in Iasi and not only, who will be able to carry out educational activities within the center
- ✓ various researchers from ICMPP or other collaborating research institutions, who will be able to perform tests or determinations on the equipment within the center within the collaborations that will be developed in the center.
- ✓ various SMEs that will be able to benefit from technology transfer facilities of the patented results that will be obtained within the center

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MACRO Iași 2021