

**PETRU PONI  
INSTITUTE OF  
MACROMOLECULAR  
CHEMISTRY**



**ICMPP  
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**SCIENTIFIC  
COMMUNICATIONS OF  
YOUNG  
RESEARCHERS**  
3<sup>rd</sup> Edition



Marking the Romanian Researcher's

November 18, 2022 • Iasi, Romania



**ICMPP – OPEN DOOR TO THE FUTURE  
SCIENTIFIC COMMUNICATIONS OF  
YOUNG RESEARCHERS**

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*Marking the Romanian Researcher's Day*

**Organizer**



**Petru Poni Institute of Macromolecular Chemistry – ICMPP**





The scientific communications event is organized by Petru Poni Institute of Macromolecular Chemistry - ICMPP, to mark the Romanian Researcher's Day and offers the opportunity to young researchers (doctoral and postdoctoral students) to present the results of their studies.



The scientific program includes oral presentations (15 minutes, Q & A included) and the conference language will be English.



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## **SCIENTIFIC PROGRAM**





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**CONFERENCE OPENING**

**9.00-9.15**

<https://us06web.zoom.us/j/81845419251?pwd=bG15NjZjMk11bjh0WmlBMStPOTJKUT09>  
Meeting ID: 818 4541 9251  
Passcode: 528250

Dr. Valeria Harabagiu, Welcome to MacroYouth

Dr. Marcela Mihai, Introduction to SChR and EUChemS

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**9.15-10.00**

**INVITED LECTURE**

**An interdisciplinary approach on coordination chemistry**

Acad. Marius ANDRUH  
Vice President of Romanian Academy  
Director of C. D. Nenitzescu Institute of Organic and Supramolecular Chemistry of the Romanian Academy, Bucharest, Romania

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**10.00-11.15**

**SESSION 1 – Oral Communications**

Chair: Dr. Marcela Mihai

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**10.00-10.15**

**Conformational effects and electronic structure of some azobenzene derivatives in the ground state**

Page 7

Dragos-Lucian Isac, Anton Airinei, Emilian Rosca

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**10.15-10.30**

**Merging hydrophobic moieties within five-membered heterocycles. Mighty approaches toward achieving some spectacular phenomena**

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Madalin Damoc, Alexandru-Constantin Stoica, Maria Cazacu

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**10.30-10.45**

**Studies on hydrogels based on periodate-oxidized pullulan for potential biomedical applications**

Page 11

Ioana A. Duceac, Raluca Ioana Baron, Gabriela Biliuta, Sergiu Coseri

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**10.45-11.00**

**Zwitterionic grafted gellan: synthesis, solution and gel properties**

Page 13

Marin-Aurel Trofin, Maria Karayianni, Silvia Vasiliu, Ștefania Racoviță, Marcela Mihai, Stergios Pispas

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**11.00-11.15**

**A one-pot approach to prepare elastic, but robust macroporous chitosan hydrogels functionalized with thiourea**

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Ioana-Victoria Platon, Claudiu-Augustin Ghiorghita, Maria Marinela Lazar, Maria Valentina Dinu

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**11.15-11.35**

**Cofee break**

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**11.35-13.05**

**SESSION 2 – Oral Communications**

**Chair: Dr. Corneliu Cojocaru**

<b>11.35-11.50</b>	<b>Binuclear complexes bearing paramagnetic compartmental ligands synthesized from 2,6-bis(hydroxymethyl)-p-cresol</b>	Page 17
	<u>Mihai Răducă</u> , Marius Andruh	
<b>11.50-12.05</b>	<b>The effectiveness of walnut shell eco-friendly modification in wastewater treatment</b>	Page 19
	<u>Andra-Cristina Enache</u> , Petrisor Samoila, Corneliu Cojocaru, Mariana Cristea, Roxana Apolzan, Georgeta Predeanu, Valeria Harabagiu	
<b>12.05-12.20</b>	<b>Interaction of spin labelled-4-phenoxyaniline with BSA in water and trehalose solution</b>	Page 21
	<u>Alexandru Vincentiu Florian Neculae</u> , Iulia Matei, Aurica Precupas, Sorin Mocanu, Gabriela Ionita	
<b>12.20-12.35</b>	<b>Solution and solid-state white light emission from polyfluorene-based organic blends</b>	Page 23
	<u>Ioana-Alexandra Trofin</u> , Radu-Dan Rusu, Catalin-Paul Constantin	
<b>12.35-12.50</b>	<b>Innovative polymer fibrous biomaterials with imparted antifungal activity</b>	Page 25
	<u>Nasko Nachev</u> , Mariya Spasova, Nevena Manolova, Iliya Rashkov, Mladen Naydenov	
<b>12.50-13.05</b>	<b>Strategies to improve the hydrophobic properties of xylan hemicelluloses for food packaging applications</b>	Page 27
	<u>Mirela Roman</u> , Petronela Nechita	

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**Lunch break**

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**SESSION 3 – Oral Communications**

**Chair: Dr. Florin Bucătariu**

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	<u>Gabriela Toader</u> , Traian Rotariu, Florin Marian Dirloman, Edina Rusen, Aurel Diacon, Adrian Rotariu	
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	<u>Diana-Andreea Blaj</u> , Mihaela Balan-Porcarasu, Valeria Harabagiu, Cristian Peptu	
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	<u>Raluca-Marieta Visan</u> , Anca-Ruxandra Leonties, Mihai Anastasescu, Daniel-George Angelescu	

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	<u>Larisa-Maria Petrila</u> , Florin Bucatariu, Frank Simon, Marcela Mihai	
15.30-15.45	<b>NMR study of some <math>\beta</math>-cyclodextrin-oligocapro lactone derivatives</b>	Page 37
	<u>Mihaela Balan-Porcarasu</u> , Diana-Andreea Blaj, Cristian Peptu, Valeria Harabagiu	
15.45-16.00	<b>Insight into the complex relationship among filamentous fungi and cement mortar</b>	Page 39
	<u>Cristina Firincă</u> , Mariana Constantin, Iuliana Răut, Ana-Maria Gurban, Nicoleta Radu, Lucian Gabriel Zamfir, Mihaela Doni, Gelu Vasilescu, Luiza Jecu	
16.00-16.20	<b>Cofee break</b>	
<b>SESSION 4 – Oral Communications</b>		
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	<u>Bogdan Cosman</u> , Marieta Constantin, Sanda Bucatariu, Gheorghe Fundueanu	
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	<u>Alexandra-Diana Diaconu</u> , Maricel Danu, Mariana Cristea, Valeria Harabagiu, Cristian Peptu	
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	<u>Irina Apostol</u> , Narcis Anghel, Florica Doroftei, Iuliana Spiridon	
17.05-17.20	<b>Low temperature synthesis of doped and undoped manganese ferrite nanoparticles using the sol-gel auto-combustion route</b>	Page 47
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	<u>Ioana-Sabina Trifan</u> , Violeta Melinte, Andreea Chibac-Scutaru, Sergiu Coseri	
17.35-17.50	<b>Study of sunflower and corn stalk pith as raw materials in preparation of carbonaceous adsorbents</b>	Page 51
	<u>Elvira Turcu</u> , Maria Ignat, Petrișor Samoilă, Corneliu Cojocaru, Liviu Săcărescu, Niță Tudorachi, Georgeta Predeanu, Felicia Cosmulescu, Valeria Harabagiu	
17.50-18.00	<b>Awarding and closing ceremony</b>	



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## **BOOK OF ABSTRACTS**



## CONFORMATIONAL EFFECTS AND ELECTRONIC STRUCTURE OF SOME AZOBENZENE DERIVATIVES IN THE GROUND STATE

**Dragos-Lucian Isac<sup>1\*</sup>, Anton Airinei<sup>1</sup>, Emilian Rosca<sup>2</sup>**

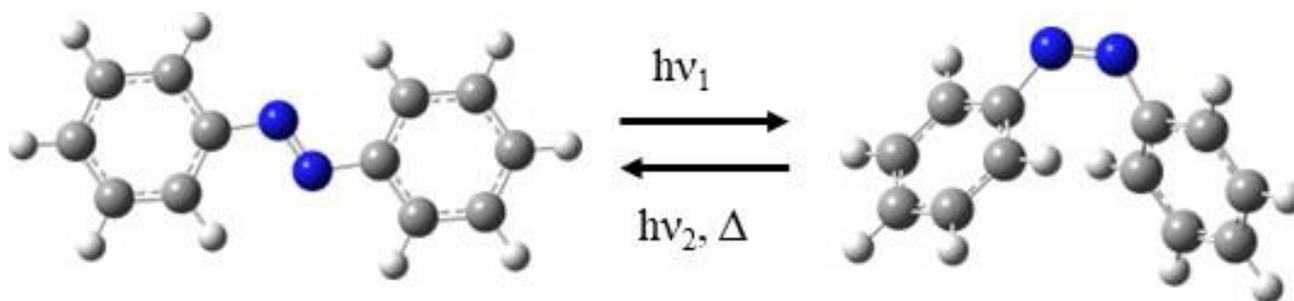
<sup>1</sup>*Petru Poni Institute of Macromolecular Chemistry, Iasi, Romania*

<sup>2</sup>*Alexandu Ioan Cuza University of Iasi, Faculty of Chemistry, Iasi, Romania*

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Azobenzene derivatives represent a class of organic compound where two phenyl rings are bridged by -N=N- atoms. Moreover, the presence of the double bond -N=N- in the azobenzene structural unit permits to this compound to adopt two antagonistic isomers. The first isomer has the most stable conformation because of its structural unit coplanarity, known as *trans* azobenzene. On the other hand, the second isomer (*cis* conformer) has got a twisted orientation. This twisted orientation as well as the steric repulsion between phenyl units make the *cis* azobenzene isomer to be metastable from the energetic point of view [1-3].

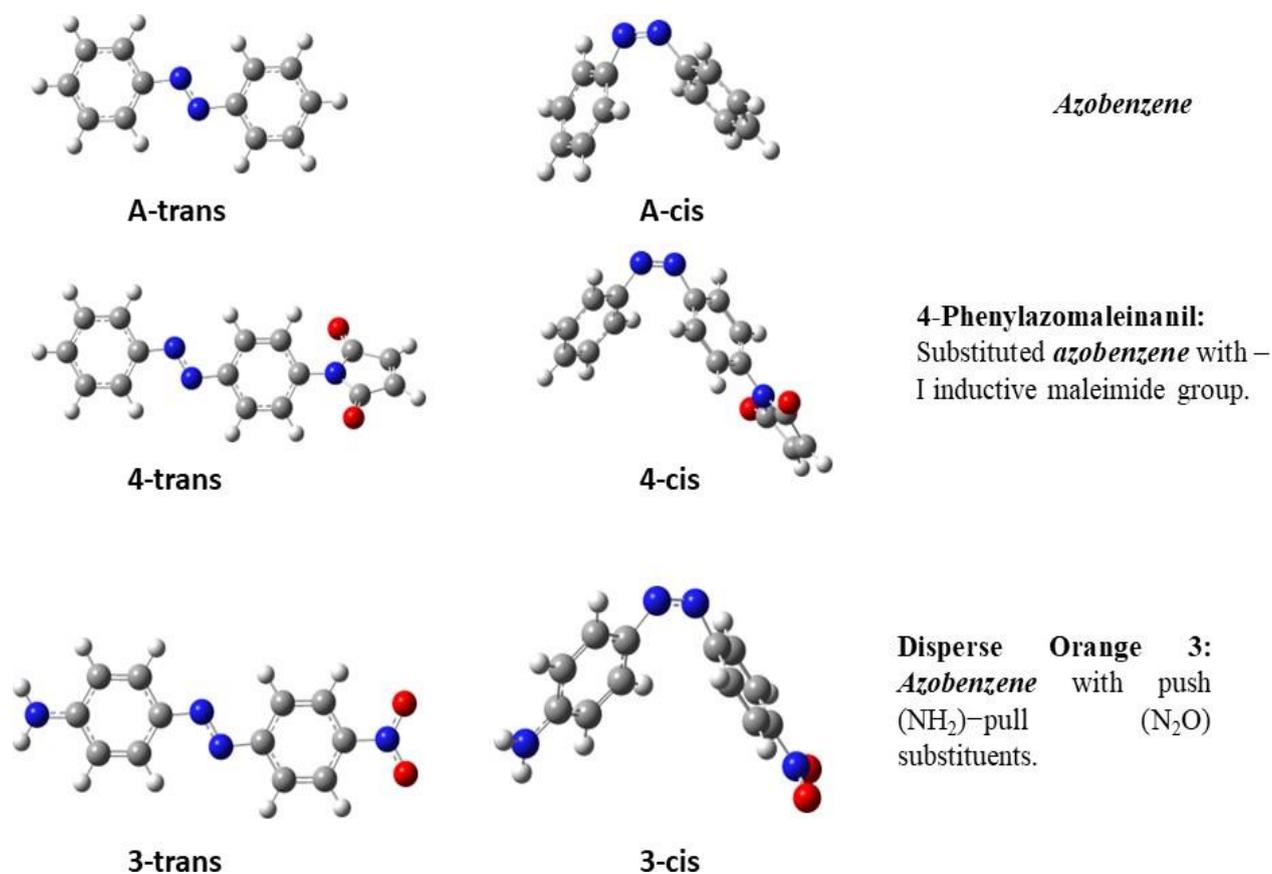
The isomerization in azobenzene occurs when the *trans* isomer is irradiated with UV ( $h\nu_1$ ) light giving the *cis* conformer. In this way, a reaction from *trans*, the reactant, to *cis* as a product can be occurred. While the *cis* isomer is metastable, an intramolecular back conversion can follow two channels. The first channel is the stimulated conversion using visible light ( $h\nu_2$ ) and this reaction takes place very fast. The second route is a slow process ( $\Delta$ ) and happened in the dark (Figure 1).



**Figure 1.** *Trans* ↔ *cis* isomerization reaction in azobenzene derivatives.

Applying an external source such as UV light, a photoisomerization reaction was obtained. Here, the reaction pathway follows the  $S_0 \rightarrow S_2$  ( $\pi \rightarrow \pi^*$ ) excitation route. Using visible light as external stimuli, a  $S_0 \rightarrow S_1$  ( $n \rightarrow \pi^*$ ) excitation appears. Into the ground state, the intramolecular conversion does not occur *via* the excited state, therefore the reaction follows one pathway. However, regardless of the reaction path either *via* the excited state or through the ground state, the isomerization mechanism for azobenzene derivatives is still unclear. The mechanism of azobenzene isomerization in excited state is more complicated, because the reaction does not follow a single pathway. In the excited state the reaction includes more pathways like a multidimensional conversion. Contrary, in ground state the reaction follows only one pathway, with the possibility to appear more transition state structures. In order to understand the mechanism of isomerization in excited state, firstly, we have to clarify the reaction mechanism into the ground state. The main goal of this study is to predict the mechanism of isomerization into the ground state based on theoretical approaches such as DFT method and *ab initio* molecular dynamics simulations.

Three azo derivatives in their *trans* and *cis* conformations have been selected for theoretical investigation (Figure 2). Computational results showed even in the ground state, the isomerization reaction occurs *via* multidimensional pathways.



**Figure 2.** The azobenzene derivatives selected for theoretical investigation.

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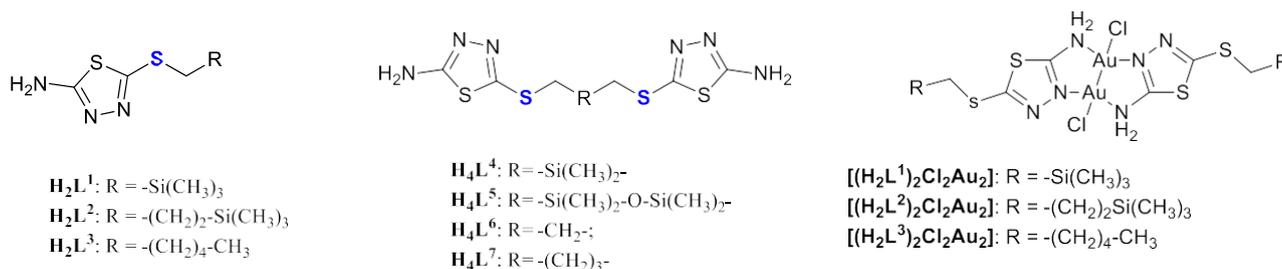
## MERGING HYDROPHOBIC MOIETIES WITHIN FIVE-MEMBERED HETEROCYCLES. MIGHTY APPROACHES TOWARD ACHIEVING SOME SPECTACULAR PHENOMENA

**Madalin Damoc\***, Alexandru-Constantin Stoica, Maria Cazacu

*Petru Poni Institute of Macromolecular Chemistry, Iasi, Romania*

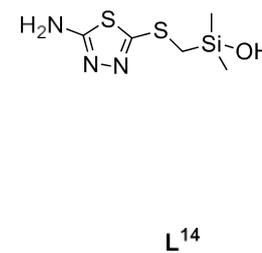
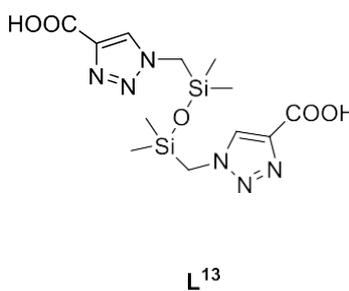
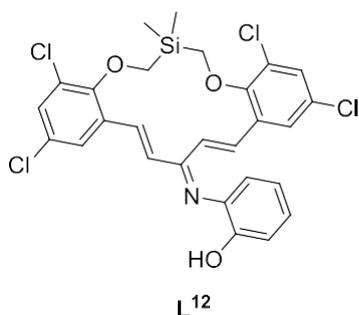
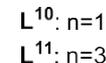
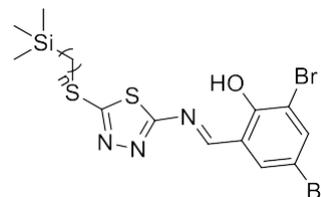
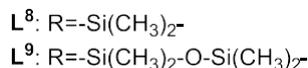
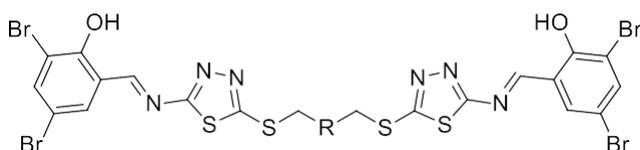
*\*damoc.madalin@icmpp.ro*

Achieving specific physical effects through chemical engineering always has aroused scientists' curiosity. Nowadays, taking into account the thriving technology, it is possible to overcome or smash each of the past impediments. Herein, we exhibit powerful synthetic routes toward branching the thiadiazole moiety and the molecular-physical effect approaches in achieving specific peculiarities of the new compounds. Starting from 5-amino-2-mercapto-1,3,4-thiadiazole, seven new amines were synthesized through S-alkylation with hydrocarbon and permethylated silicon fragments (Scheme 1, H<sub>2</sub>L<sup>1</sup>–H<sub>4</sub>L<sup>7</sup>). This strategy enabled light harvesting from the high-energy excited states by an intermolecular proton transfer, dual fluorescence, room temperature phosphorescence, and color tunability up to the excitation wavelength, all of them triggered by the aggregation process.



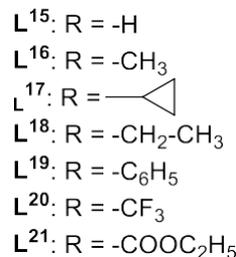
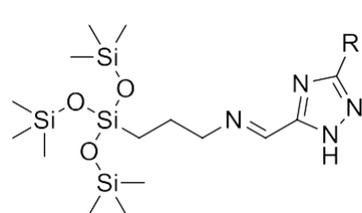
**Scheme 1.** Branching the 5-amino-2-mercapto-1,3,4-thiadiazole by S-alkylation (H<sub>2</sub>L<sup>1</sup>–H<sub>4</sub>L<sup>7</sup>) and further complexation with gold ions (right side).

We further reacted the thiadiazole derivatives with chloroauric acid in the second strategy, obtaining three new dinuclear gold complexes (Scheme 1, right side). An interesting master plan will be exposed toward photoactuation, relying on various features of them [1]. Furthermore, some of the S-alkylation products reacted with 3,5-dibromosalicylaldehyde, when four new imines were obtained (Scheme 2, L<sup>8</sup>–L<sup>11</sup>). Taking into account the possible 2D liquid crystal properties of the latter compounds and their special dielectric properties (i.e., permanent dipole moment) through the bromine atoms in some key positions, we propose a thermal actuation mechanism [2]. Ultimately, we engineered one of the biggest silacycles ever reported and one of the few molecules containing a Si-O-Si bond with an angle of 180° (Scheme 2, L<sup>12</sup> and L<sup>13</sup>, respectively). Studying the photobleaching resistance of H<sub>4</sub>L<sup>5</sup>, we broke the Si-O-Si bond through high-power excitation sources, resulting in silanol formation (Scheme 2, L<sup>14</sup>).



**Scheme 2.** Condensation of the S-alkylation products with 3,5-dibromosalicylaldehyde ( $L^8$ – $L^{11}$ ), silacycle ( $L^{12}$ ), dicarboxylic acid having a Si-O-Si bond with an angle of  $180^\circ$  ( $L^{13}$ ), and the silanol ( $L^{14}$ ).

Without limiting ourselves to the branching of the thiadiazole ring, we subsequently succeeded in inserting tris(trimethylsiloxy)silane moiety within 1,2,4 triazoles (Scheme 3). Our new design is expected to give rise to some special optical phenomena emerging at the supramolecular level, through the clusterization-induced emission effect and many other mechanisms [3]. Nonetheless, these strategies probably need enhancing and silver ions are envisaged to accomplish them.



**Scheme 3.** 1,2,4-Triazole derivatives containing tris(trimethylsiloxy)silane moiety.

These approaches, some already accomplished and others still developing, represent original ideas impacting fundamental and material research. This paper will reveal some interesting aspects, i.e., synthetic pathways, structure-properties relationship, and the resulting physical effects.

## References

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**Acknowledgment:** This work was supported by a grant from the Romanian Ministry of Research, Innovation, and Digitization, CNCS - UEFISCDI, project number PN-III-P4-ID-PCE-2020-2000, within PNCDI III, Contract 207/2021 (2D-PerMONSil).

## STUDIES ON HYDROGELS BASED ON PERIODATE-OXIDIZED PULLULAN FOR POTENTIAL BIOMEDICAL APPLICATIONS

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Hydrogels are crosslinked networks based on hydrophilic polymers that resemble native tissue due to their capacity to absorb and retain large volumes of fluid. The properties that they impart are varied since the matrix can be obtained from a plethora of polymers and types of crosslinks [1]. High flexibility, soft texture, excellent biocompatibility, self-healing, and injectability are some of the advantages that drive materials science research in this area.

Polysaccharides are the most abundant polymeric resource on the planet. The polyol nature of carbohydrates offers a significant opportunity for chemical functionalization. The reactions are those specific to the hydroxyl group. Among those that can be mentioned are etherification, esterification, silylation, grafting, copolymerization, crosslinking, and oxidation [2]. Within our group, selective oxidation reactions have been explored for the functionalization of various polysaccharides with novel functional groups [3]. Protocols based on the periodate oxidation reaction have been studied on cellulose, pullulan and starch [4–9]. The resulting derivative bears two new aldehyde groups at each anhydroglucose unit. Dialdehyde polysaccharides pose significant interest in preparing injectable and self-healing hydrogels with biomedical applications. In the past, synthesis and application of dialdehyde alginate, dialdehyde cellulose, dialdehyde dextran, dialdehyde carboxymethyl cellulose, and dialdehyde xanthan gum have been obtained to fabricate crosslinked films, fibers, and hydrogels [10].

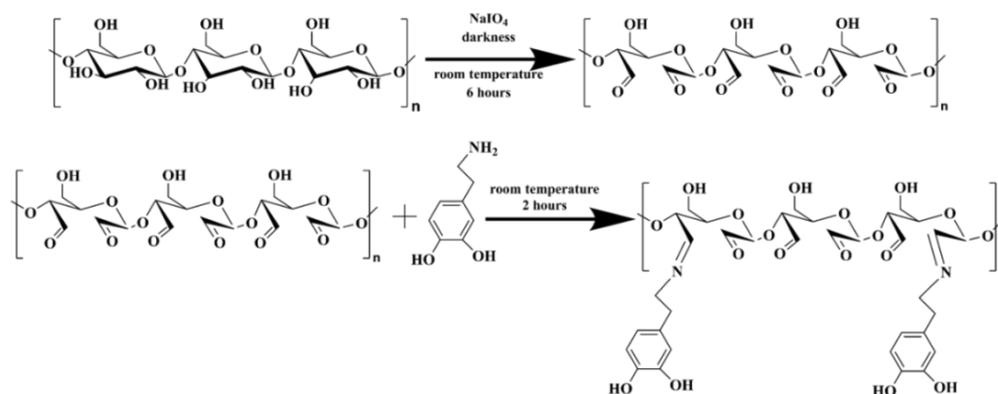
In this study, pullulan was chosen as the base material to prepare a series of hydrogels. This polysaccharide has a linear structure with glucose rings connected by  $\alpha$ -1,4 and  $\alpha$ -1,6 glycosidic bonds. Multiple species of the *Aureobasidium* bacterium produce pullulan from starch. The novel polymer possesses outstanding biological and physical features, including qualities such as non-toxic, edible, biocompatible, biodegradable, and water-soluble [11,12].

To create a crosslinked network, pullulan was oxidized in the presence of sodium periodate (Figure 1). The reaction undergoes the formation of two aldehyde groups at the C2 and C3 atoms in the anhydroglucose unit, simultaneous with breaking the C-C bond. The oxidized derivative was analysed in contrast to the initial polymer utilizing nuclear magnetic resonance and Fourier transform infrared spectroscopy. The changes observed in the spectra confirmed the intended chemical modifications.

The resulting derivative was used to prepare a hydrogel by freeze-drying, using a 5% polymer concentration. The dialdehyde pullulan can self-crosslink based on numerous acetal, hemiacetal and hydrogen bonds [13]. Aiming to enhance the stability of the network a low-molecular-weight compound was chosen to be introduced into the polysaccharide matrix. Dopamine is a neurotransmitter and hormone which plays an instrumental role in many body functions. Moreover, this compound was found to be the key element in the strong adhesion properties of specific mussel tissues [14]. The presence of the amine groups in the structure of dopamine is excellent for immobilizing the compound inside the dialdehyde pullulan matrix by the Schiff base reaction.

This interaction occurs readily and yields new imine bonds. Therefore, two methods were explored

to incorporate dopamine namely in solution and inside a previously lyophilized pullulan sponge. Finally, the samples were subjected to another freeze-drying process.



**Figure 1.** Schematic diagram of the reaction steps employed in functionalizing pullulan, first by periodate oxidation and then by Schiff base reaction with dopamine.

All samples were characterized using nuclear magnetic resonance and Fourier transform infrared spectroscopy, in addition to the UV-VIS measurements, to confirm the structural changes anticipated. Moreover, the internal morphology was investigated using scanning electron microscopy and the micrographs revealed a porous structure in all samples. Material aspect, however, varies greatly with the different compositions and preparation methods used. The swelling capacity and the stability of the networks were tested in distilled water and under compression loading. The experiments demonstrated that the polysaccharide materials have a good swelling performance and that they are stable and have a potential self-healing ability. Therefore, the viscoelastic properties were further investigated employing specific rheological measurements, *i.e.*, the frequency sweep test, continuous shear test and alternating strain test.

## References

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## ZWITTERIONIC GRAFTED GELLAN: SYNTHESIS, SOLUTION AND GEL PROPERTIES

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 Marcela Mihai<sup>1</sup>, Stergios Pispas<sup>2</sup>**

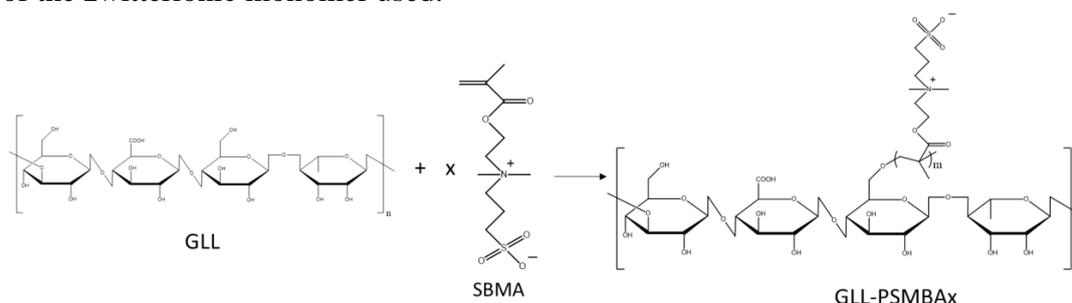
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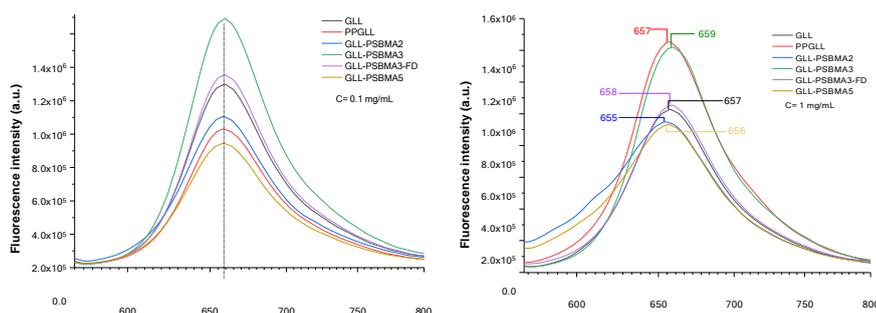
Gellan gum (GLL) which is an anionic extracellular bacterial polysaccharide has been an important ingredient in the food industry, while at the same time it has numerous attractive pharmaceutical and chemical applications. GLL is a relatively new gum produced by the Gram-negative bacterium *Sphingomonas paucimobilis* [1]. Regarding its structure, GLL is a charged tetrasaccharide containing two residues of D-glucose and one of each residues of L-rhamnose and D-glucuronic acid forming the repeating sequence: [D-Glc(β1→4)D-GlcA(β1→4)D-Glc(β1→4)L-Rha(α1→3)]<sub>n</sub> [2]. This polysaccharide can be chemically functionalized due to the presence of many hydroxyl groups that act as possible sites for grafting reactions [3].

In this work, the monomer sulfobetaine methacrylate (SBMA) was grafted onto GLL via free radical polymerization (Figure 1) using ammonium persulfate as initiator and N,N,N',N'-tetramethylethylenediamine as a catalyst. Three different grafted polymers were prepared varying the amount of the zwitterionic monomer used.



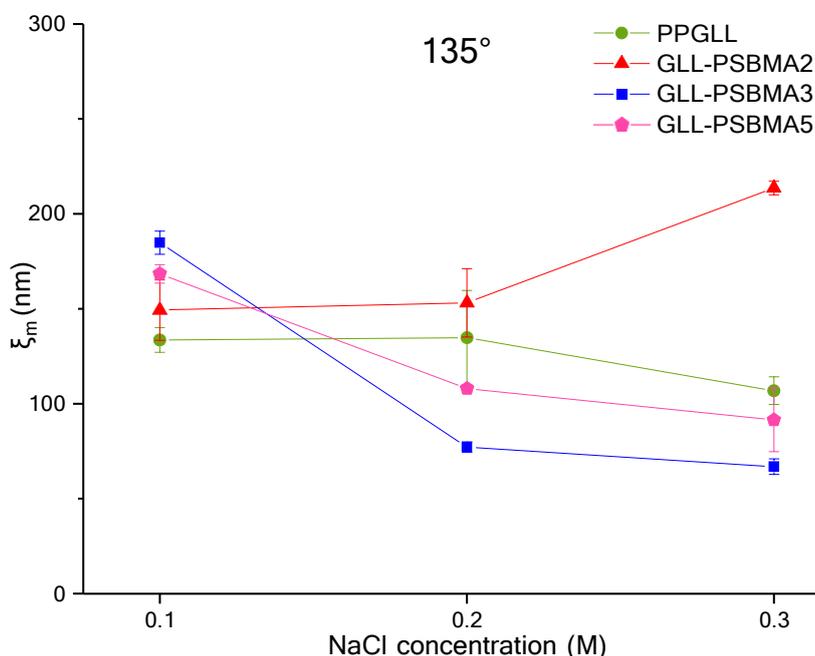
**Figure 1.** SBMA grafting reaction onto GLL.

Fluorescence spectroscopy technique was used to evaluate the polarity of the grafted polymers in solution using Nile Red as a probe in a final concentration of 0.01 mM. The emission intensity and the maxima wavelength showed a dependence on both functionalization degree and polymer concentration (Figure 2).



**Figure 2.** Fluorescence emission spectra for GLL and GLL-PSBMA at 0.1 mg/mL and 1 mg/mL polymer concentration, utilizing Nile Red as a probe.

Group I cations such as  $\text{Na}^+$  decrease the repulsion between GLL chains by interacting with the carboxylate groups thus promoting gel formation. Since gelation is a defining property of GLL, the impact of SMBA grafting onto GLL was followed by dynamic light scattering (DLS) at three different angles ( $60^\circ$ ,  $90^\circ$ ,  $135^\circ$ ) (Figure 3) [4].



**Figure 3.** Mesh size of GLL and GLL-PSBMA gels depending on the NaCl concentration, at  $135^\circ$ .

By correcting the DLS correlation function for non-ergodic systems, the polymer network mesh size can be calculated. The mesh size dependence on the NaCl concentration is dictated by both the screening of electrostatic repulsions between the anionic polymer backbone and also the anti-polyelectrolyte behaviour of the zwitterionic side chains. The polymer GLL-PSBMA3 showed the highest mesh size decrease suggesting a stronger gel formation.

Overall, the functionalization reaction of gellan has a significant effect on the properties of the grafted polysaccharide. More specifically, the amount of zwitterionic monomer used, seems to greatly influence the polarity and the gelation behaviour of the resulting polymer.

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## A ONE-POT APPROACH TO PREPARE ELASTIC, BUT ROBUST MACROPOROUS CHITOSAN HYDROGELS FUNCTIONALIZED WITH THIOUREA

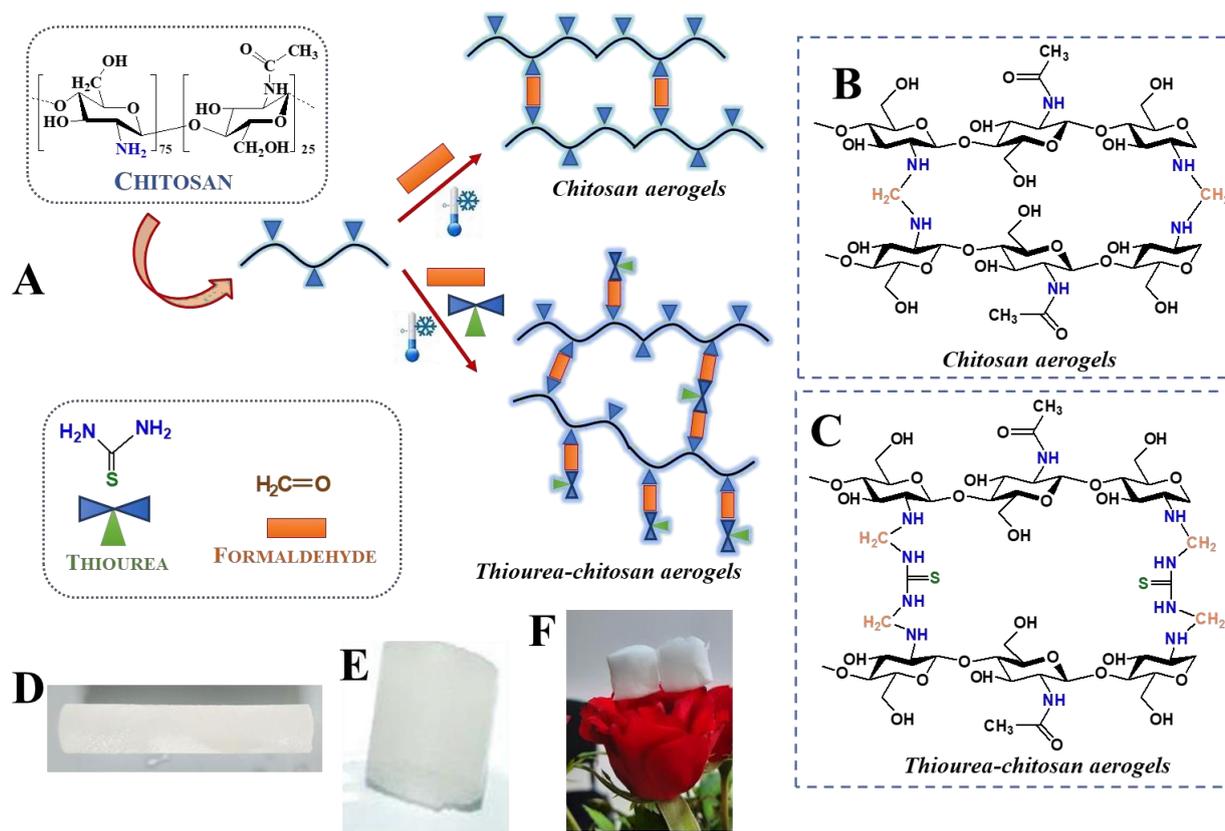
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Hydrogels are three-dimensional polymeric systems characterized by high-water absorbency and structural similarity to biological tissues that are constructed using synthetic or natural polymers and stabilized through chemical and/or physical cross-links. Chitosan (CS), the only cationic biopolymer, has received extensive attention lately as building-block for the design of multifunctional hydrogels because of its high number of functional groups, pH-responsiveness and biocompatibility. Consequently, CS-based hydrogels have been deeply investigated as potential drug delivery devices, actuators, insulators or as sorbents for water purification [1-4]. Formaldehyde is an accessible cross-linker that has been used to engineer CS aerogels via Schiff base chemistry [5]. It could also allow the grafting of different ligands bearing amino groups, such as thiourea, on CS backbone [6].

In this work, a one-pot approach to prepare CS and thiourea-functionalized CS (CSTU) hydrogels, as monoliths, by simply freezing aqueous solutions of CS, or CS and thiourea, at -20 °C in presence of formaldehyde as cross-linker (Figure 1) is presented. In the frozen system, the confined environment created by the growing ice crystals promotes the concentration of all molecules into small volume voids and ultimately their reaction to produce the cross-linked hydrogels. Optimization of hydrogels properties was achieved by changing the composition (concentration of CS solution, absence/presence of thiourea and  $-NH_2:CH_2O$  molar ratio) of feed reaction mixtures.

Structural characterization was performed by comparing FTIR spectra of pristine chitosan with that of CS and CSTU hydrogels. The density and porosity were determined to assess their ultralight weight characteristics, similar to aerogels. The swelling behaviour of the hydrogels was studied at different pH values. SEM micrographs showed that the hydrogels were macroporous, with a complex framework of honeycomb-like interconnected pores. The uniaxial compression measurements performed on selected swollen aerogels revealed typical compressive stress-strain profiles characteristic for macroporous materials. The CS2.10 and CSTU2.10 aerogels did not present failures at a deformation force of 50 N and could be compressed to over 80% strain, without any fracture development, which is attributed to the complete release of solvent (water) from their macroporous structures upon compression. To evaluate the resilience and robustness of the interconnected macroporous aerogels, their dynamic stress-strain behaviour was investigated up to 12 cycles by applying a strain of 90%. A remarkable elasticity and toughness with no obvious recovery loss was recorded for the aerogels prepared at an amine/aldehyde molar ratio of 1:10.



**Figure 1.** Graphic illustration with the preparation principle of formaldehyde cross-linked CS and CSTU hydrogels (A). Schematic representation with the chemical structures of CS (B) and CSTU (C) aerogels. Optical images of CS hydrogel, as monolith (D), in wet state (E) and as freeze-dried pieces placed on top of a rose flower (F) demonstrating its ultra-lightweight characteristics.

To conclude, the preparation method used yielded hydrogels with remarkable properties in terms of structural, morphological and mechanical features, being also a low-cost and facile strategy. The prepared hydrogels could be used in a variety of fields including as antibacterial materials or in wastewater treatment.

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## BINUCLEAR COMPLEXES BEARING PARAMAGNETIC COMPARTMENTAL LIGANDS SYNTHESIZED FROM 2,6-BIS(HYDROXYMETHYL)-*P*-CRESOL

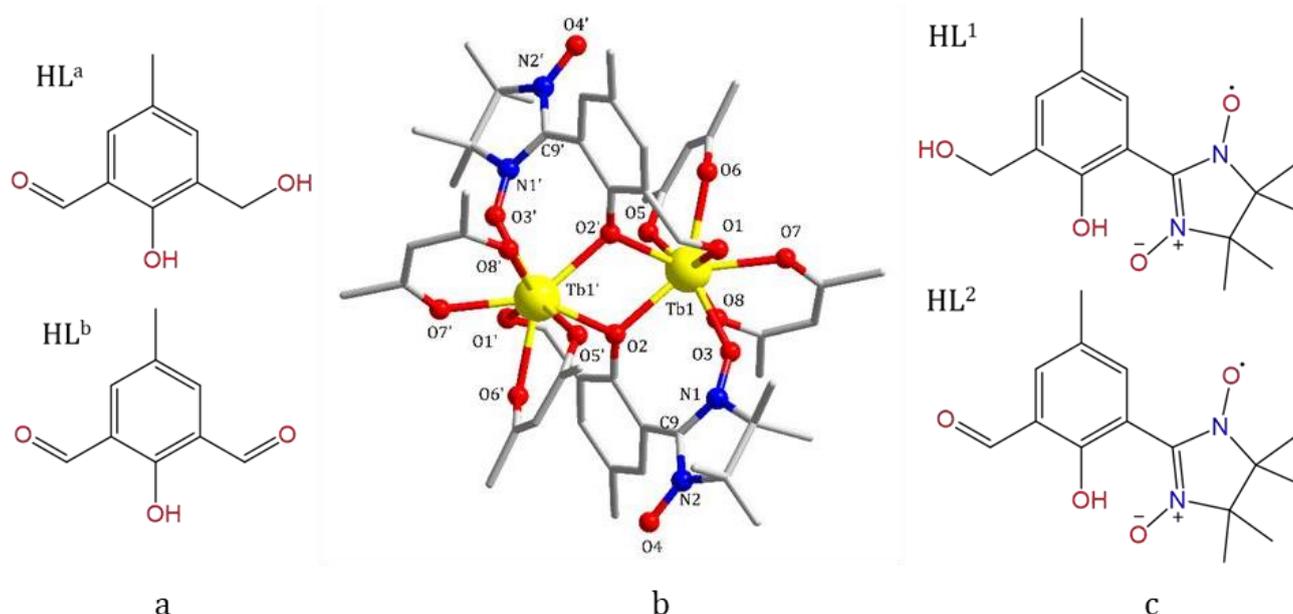
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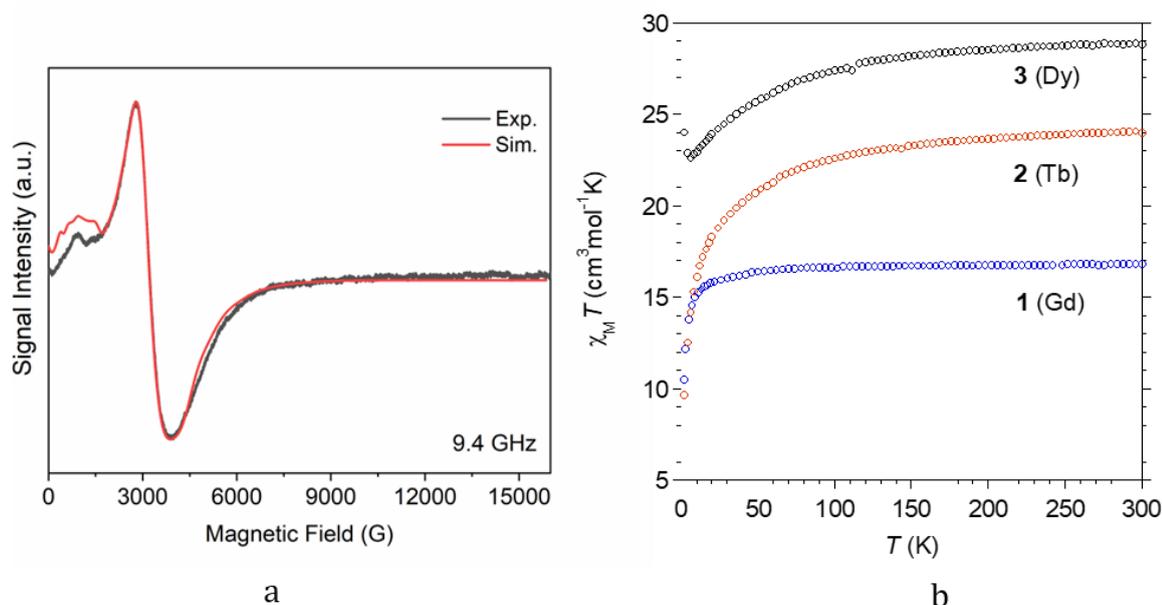
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Novel nitronyl nitroxid ligands, HL<sup>1</sup> and HL<sup>2</sup>, have been synthesized [1] starting from 2-hydroxy-3-(hydroxymethyl)-5-methylbenzaldehyde (HL<sup>a</sup>) and 2,6-diformyl-*p*-cresol (HL<sup>b</sup>), respectively, [2] (Figure 1) following the synthetic protocol reported in the literature [3]. Using the ligand HL<sup>1</sup>, three 2p-4f binuclear complexes have been obtained and crystallographically characterized: [Ln<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>(hfac)<sub>4</sub>], where Ln = Gd **1**, Tb **2**, Dy **3** and hfac = hexafluoroacetylacetonate anion (Figure 1b).



**Figure 1.** (a) Structures of HL<sup>a</sup> and HL<sup>b</sup> aldehydes. (b) Perspective view of the molecular structure of [Tb<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>(hfac)<sub>4</sub>] (**2**). Fluorine and hydrogen atoms have been omitted for clarity. Symmetry operation: ' = -x, 1-y, -z. (c) Structures of HL<sup>1</sup> and HL<sup>2</sup> nitronyl nitroxide monoradicals.

During the synthesis of the compounds **1-3**, three other complexes have been obtained as byproducts and subsequently characterized. The synthetic procedure was optimized in order to obtain pure dinuclear complexes. At the same time, the compounds obtained as byproducts have been systematically resynthesized. The cryomagnetic properties of compounds **1-3** have been investigated (Figure 2). Continuous-wave (CW) electron paramagnetic resonance (EPR) measurements were carried out at X- and Q-band for compound **1**. Time-dependent experiments were performed at three magnetic fields. Phase memory times, T<sub>m</sub>, were found to be about 1000 ns at 6 K.



**Figure 2.** (a) Powder EPR spectrum for **1** at X-band (9.4 GHz) and 30 K (black) and its simulated version (red). (b) Temperature dependence of the  $\chi_{MT}$  product for **1**, **2**, and **3**.

Apart from the desired compounds, during the synthetic steps two by-products have been isolated as a molecular alloy containing an intermediate bearing hydroxylamino and N-oxide groups, [4] namely 1-hydroxy-2-(2-hydroxy-3-(hydroxymethyl)-5-methylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole 3-oxide (**B**), and the imino nitroxide radical (**C**) equivalent with HL<sup>1</sup>. [5] This system was characterized by single crystal X-ray diffraction, UV-VIS and EPR spectroscopy. The compound **B** was also crystallized solely from chloroform. Similarly, the asymmetric paramagnetic ligand, HL<sup>2</sup>, [6] has been used for obtaining dinuclear complexes with 3d or 4f metal ions which were characterized by X-ray diffraction on single crystal bearing similar features as the case for HL<sup>1</sup>.

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## THE EFFECTIVENESS OF WALNUT SHELL ECO-FRIENDLY MODIFICATION IN WASTEWATER TREATMENT

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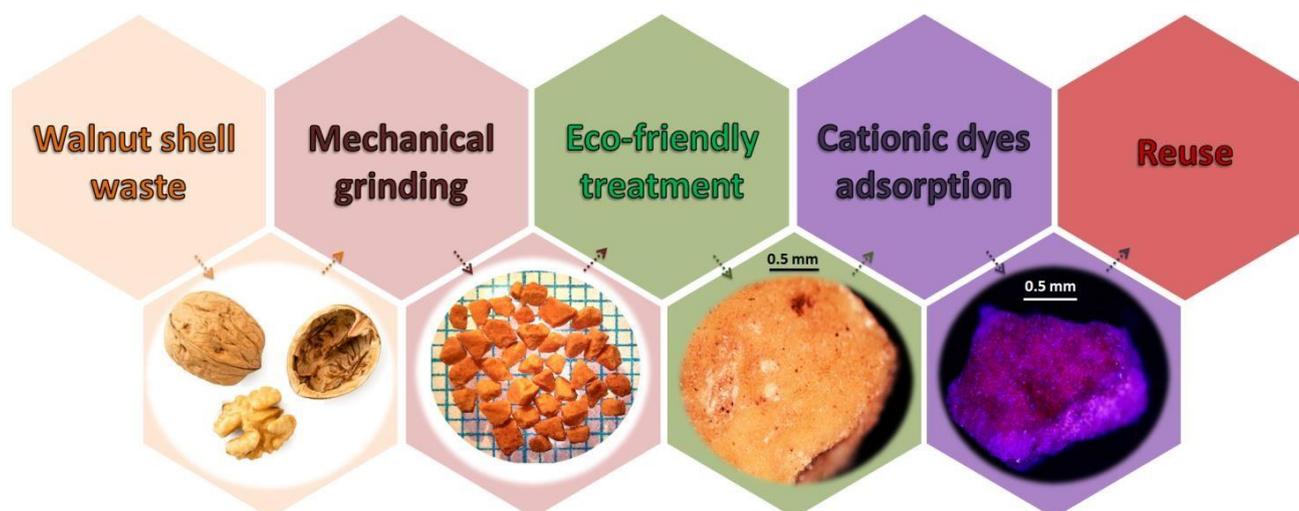
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To promote a sustainable development and encourage the transition to a circular economy, wastewater management creates opportunities for pollution reduction and also for enhancing freshwater availability. Globally, 52% of the total volume of produced wastewater is estimated to be treated, from which, only 11% is intended to be reused [1]. Therefore, a challenge in promoting wastewater reuse is to ensure an eco-friendly, reliable and cost-effective treatment method.

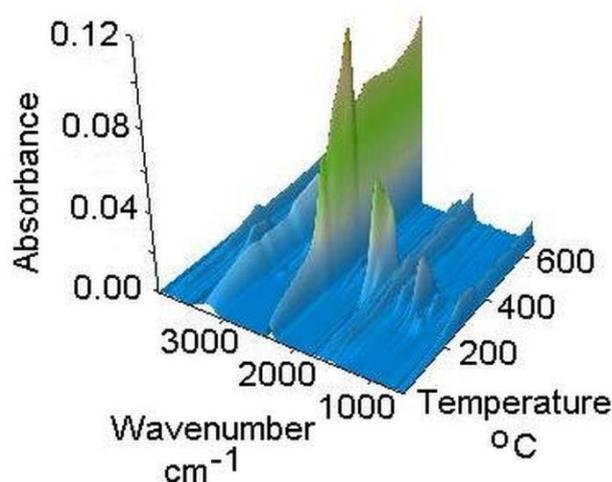
The use of biosorbents from agricultural waste represents an accessible, cheap, widely available and effective alternative in the treatment of polluted waters, being proved that they possess suitable physicochemical properties and also an increased affinity for various compounds, from organic compounds to heavy metal ions [2]. One of the most readily available agricultural wastes is walnut shells (WS), as the walnut plant being the second largest producer of nuts (after almonds), with a growing global demand and consumption due to its wide pharmacological uses and health benefits [3].

In this context, this study aims to promote two eco-friendly methods of WS treatment (by mercerization or by hot water treatment) for improved adsorption efficiency of organic compounds, such as cationic dyes (Crystal Violet and Methylene Blue), with the possibility of WS recovery and reuse as graphically represented in Figure 1.



**Figure 1.** Schematically representation of walnut shell processing for the adsorption of Crystal Violet from aqueous medium.

The raw WS samples were initially investigated by using X-ray diffraction (XRD) analysis, thermogravimetric analysis (TGA) coupled to Fourier transform infrared spectroscopy (Figure 2), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). By comparison with the raw WS material, the morphology of the treated WS granules, also the structural modifications were evidenced by scanning electron microscopy (SEM), polarized light microscopy (POL), energy dispersive X-ray (EDX) analysis and infrared spectroscopy (FTIR), respectively.



**Figure 2.** Three-dimensional FTIR spectra of the gases resulting from the thermal degradation of raw walnut shells.

The kinetics study of the cationic dyes adsorption onto modified WS was investigated to determine the rate of the adsorption process, and the experimental data were processed by pseudo-first order (PFO), pseudo-second order (PSO) and intraparticle diffusion (ID) kinetic models. The adsorption isotherms were investigated at two levels of temperatures (300K and 330K) to determine the relation between the equilibrium dye concentration and the adsorption capacity. Experimental data obtained at equilibrium were fitted using Freundlich and Langmuir mathematical models.

In addition, Dubinin-Radushkevich (D-R) isotherm model was applied to identify the nature of the adsorption process, by determination of the mean free energy of adsorption,  $ES$  (kJ/mol). The thermodynamic parameters (e.g., enthalpy, entropy, and Gibbs free energy) were also calculated in order to provide information on the adsorption process. Furthermore, the reusability of the WS modified materials was investigated, to final proof that these agricultural wastes represent a sustainable solution for water treatment.

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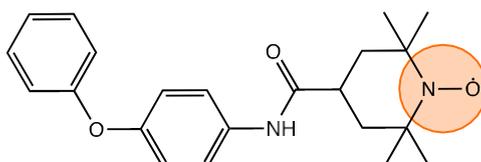
## INTERACTION OF SPIN LABELLED-4-PHENOXYANILINE WITH BSA IN WATER AND TREHALOSE SOLUTION

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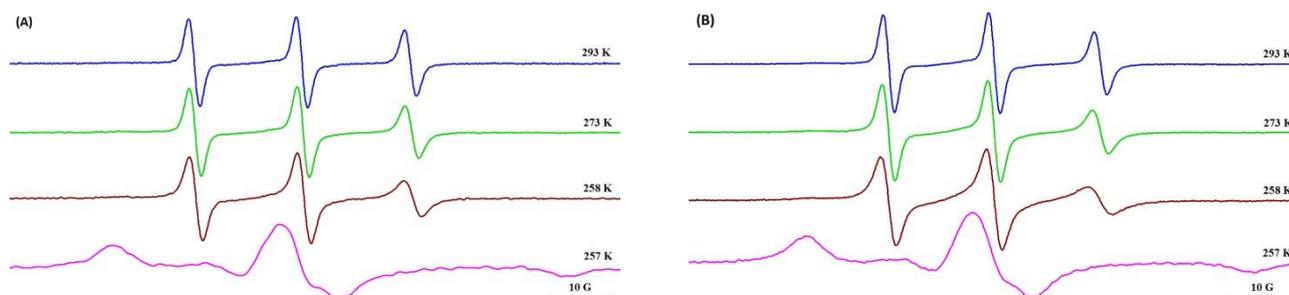
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Neurodegenerative disorders such as Alzheimer's and Parkinson's diseases are linked to neuronal cell death. Recent studies have shown that substituted N-acyl derivatives of 4-phenoxyaniline have a neurotoxic effect [1]. Bovine serum albumin (BSA) is a protein with high stability and sequence similarity to human serum albumin (HSA) used as a model protein for drug delivery [2,3]. Trehalose is a non-reducing disaccharide containing  $\alpha,\alpha$ -1,1-glycosidic bonds which confers resistance in solution, at high temperatures and in acidic environments [4]. These biocompatible systems, which have pharmaceutical and medicinal applications, are investigated in this study using a new probe containing a chromophore and a paramagnetic moiety, 4FA\_4CT (Figure 1). The instrumental methods used are electron paramagnetic resonance (EPR), circular dichroism (CD) spectroscopies and differential scanning microcalorimetry ( $\mu$ DSC).



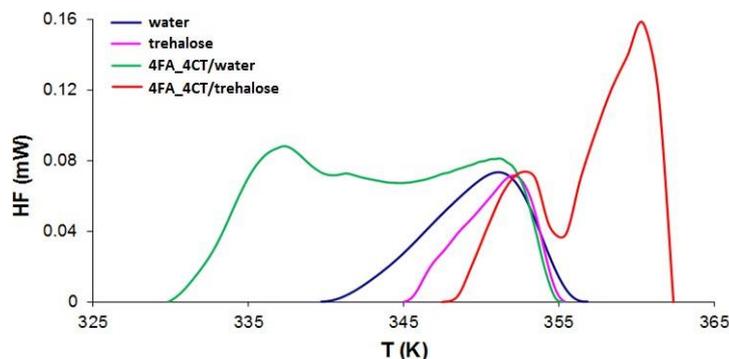
**Figure 1.** The structure of the 4FA\_4CT nitroxid investigated in this study.

Spin probes are useful tools in determining the freezing point of a solution, by means of a drastic change in molecular mobility/spin probe dynamics reflected in the EPR spectrum by a distortion of the spectral lines. It was observed that the change in the spin probe dynamic occurs at a lower temperature in the presence of trehalose (248 K) as compared to water (254 K). The interaction of 4FA\_4CT with BSA in water and in trehalose 20% (Figure 2) was investigated in the temperature range 257-293 K. The motion of the spin probe in BSA is slightly less restricted at 298 K. The effect of trehalose can be observed in the temperature range of the fast motion regime of spin probe.



**Figure 2.** The EPR spectra of the 4FA\_4CT spin probe in BSA/water (A) and in BSA/trehalose 20% (B) obtained upon cooling in the temperature range 293–257 K; [BSA] =  $1.5 \times 10^{-4}$  M.

The changes in the thermodynamic parameters characterizing the denaturation of BSA reveal the effect of trehalose and 4FA\_4CT on the thermal stability of the protein (Table 1). The presence of trehalose induces a slight increase in the denaturation temperature and enthalpy values for both components of the BSA thermogram (Figure 3), evidencing a stabilizing effect of the protein structure.



**Figure 3.** The  $\mu$ DSC scans for BSA thermal denaturation in water or in trehalose 20% solution, in the absence or in the presence of the 4FA\_4CT probe.

**Table 1.** Thermodynamic parameters of BSA thermal denaturation in the investigated systems.

BSA sample	$T_{\text{peak1}}$ (K)	$T_{\text{peak2}}$ (K)	$\Delta H_1$ (kJ mol <sup>-1</sup> )	$\Delta H_2$ (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )
<i>water</i>	347.93	352.02	161.27	144.34	305.61
<i>trehalose</i>	349.48	352.59	164.48	154.41	318.89
<i>4FA_4CT/water</i>	336.91	351.52	745.87	489.84	1235.71
<i>4FA_4CT/trehalose</i>	351.27	359.41	216.08	634.30	850.38

The presence of trehalose does not alter the secondary structure of BSA, as revealed by circular dichroism spectra. The protein recovers in a proportion of 84% in the presence of trehalose than in its absence (Table 2).

**Table 2.** Secondary structure content of BSA samples in the systems under investigation.

BSA sample	$\alpha$ -helix (%)			$\alpha$ -helix loss	$\alpha$ -helix recovered
	298 K	$T_{\text{peak1}}$	298 K (on cooling)		
<i>water</i>	57	33	41	42%	72%
<i>trehalose</i>	55	29	46	47%	84%
<i>4FA_4CT/water</i>	54	30	45	44%	83%
<i>4FA_4CT/trehalose</i>	52	25	45	52%	87%

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## SOLUTION AND SOLID-STATE WHITE LIGHT EMISSION FROM POLYFLUORENE-BASED ORGANIC BLENDS

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Polymer-based white light-emitting devices generated intense attention in both scientific and industrial communities due to a plethora of applications in displays, back-lighting sources for liquid-crystal displays, next-generation solid-state lighting sources, a.o. Modern white LED applications embrace light-emitting polymers due to their many inherent advantages, such as flexibility, light weight, versatile design and scalability in terms of both processing area and cost due to their low toxicity [1].

OLED devices demand less energy for light emission compared to other light sources. Despite the rapid pace in the development of white emitting polymeric LEDs, there are still many unresolved hurdles, the improvement of color purity being one key, materials-related need. When compared to alternative methods such as multi-layer, tandem, striped WPLEDs, the single layer concept is typically considered more commercially viable in terms of cost, processing steps, stability and lifetime, and is based on small-molecule doped polymers and blended polymeric systems. However, such a strategy requires a complex and time-consuming method and is based on a trade-off between a several properties in order to achieve different functionalities in a single material [2].

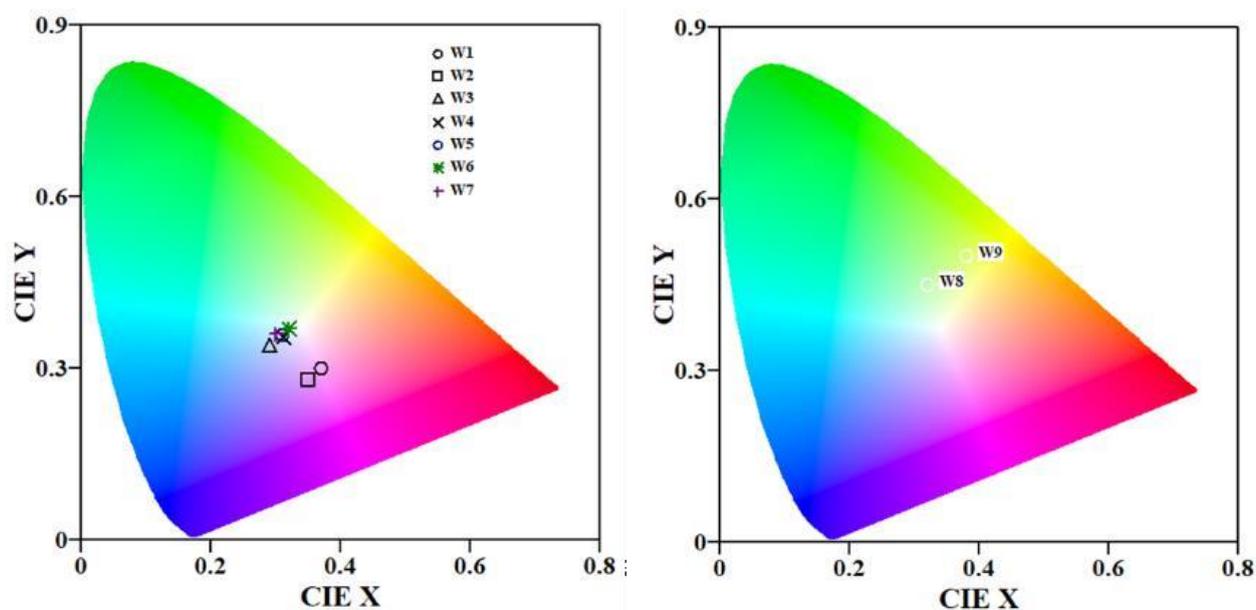
The present work is focused on finding the optimum combination of several (active/emissive and passive/non-conjugated) chemical tools to provide various organic dyes and polymeric materials which are able to emit light of a certain color in order to follow the white light emission blueprint of additive color mixing. In practice, this is done by mixing the three primary colors (red, green, and blue, RGB) or two complementary colors (blue and orange). One efficient experimental approach in this regard is to dissolve small, organic, emissive materials into a blue-emitting polymeric matrix, polyfluorenes being one of the best options for the latter [3].

The final active layer should meet a minimal set of important characteristics such as: high quantum yield of luminescence in the solid state, the ability to obtain films with good thermal and chemical stability, efficient n and/or p carrier mobility and, most of all, color purity. One design pathway to improve the color of the emitted light is based on accessing of donor-acceptor systems that poses intramolecular charge transfer features, because both electron donor and electron acceptor can contribute to charge-transfer absorption and emission enhancement, while hole and electron carriers can be nearly balanced [4].

Therefore, several types of small organic and macromolecular species incorporating various structural elements were prepared, optimized, and combined. The first step was the synthesis of monochrome organic species that are able to emit red, green, blue and orange light based on phenoxazine, triphenylamine, fluorene and combinations thereof. The optical properties of these new compounds were evaluated by UV-VIS and fluorescence spectroscopy to determine the light absorption and emission and the chromaticity diagram. The optimization process was centred on modulating the structural segments for better processing and/or charge transport to lead to native and hybrid,

luminescent polymeric materials with improved processability.

The aim of this work was to obtain white emissive materials by blended systems. This was achieved by solution-processed, hybrid polymeric materials developed by physically mixing monochrome, blue-emitting polymers with complementary organic dyes in a single layer able to emit each individual color. The judicious selection and adjustment of the nature and ratio of blended partners, homogeneity assessment, solvent polarity tuning and thorough physico-chemical evaluation (with an emphasis on the optical behavior and proper control of energy transfer) allowed to obtain color emission in the white domain (W), as defined by the CIE chromaticity coordinates (Figure 1).



**Figure 1.** Chromaticity diagram of polymeric blends in solution (left) and solid state (right).

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## INNOVATIVE POLYMER FIBROUS BIOMATERIALS WITH IMPARTED ANTIFUNGAL ACTIVITY

**Nasko Nachev<sup>1\*</sup>, Mariya Spasova<sup>1</sup>, Nevena Manolova<sup>1</sup>, Iliya Rashkov<sup>1</sup>, Mladen Naydenov<sup>2</sup>**

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Nowadays, plant diseases are a worldwide problem. Fungi cause more plant diseases than any other group of pests. Esca disease is one of the earliest known diseases of grapevines. The disease is spreading rapidly and is a real threat to vineyards in Europe. It is known that the causative agents of the disease are the fungi, mostly of the species *P. chlamydospora* and *P. aleophilum*. In practice, there are no known approaches and means of direct fighting with esca. In the last few decades, polymer materials have been increasingly used in agriculture solving diverse problems [1]. Obtaining nanofibers by electrospinning and applying them for agricultural purposes has many advantages due to the fact that these fibers are relatively easy to obtain, possess pores, have a large specific surface area, and diverse bioagents can be effectively incorporated into them. The incorporation of low molecular weight derivatives of 8-hydroxyquinoline into fibrous polymer materials obtained by electrospinning is of interest because it allows combining the valuable biological properties of 8-hydroxyquinoline derivatives with the advantages of electrospun materials [2, 3].

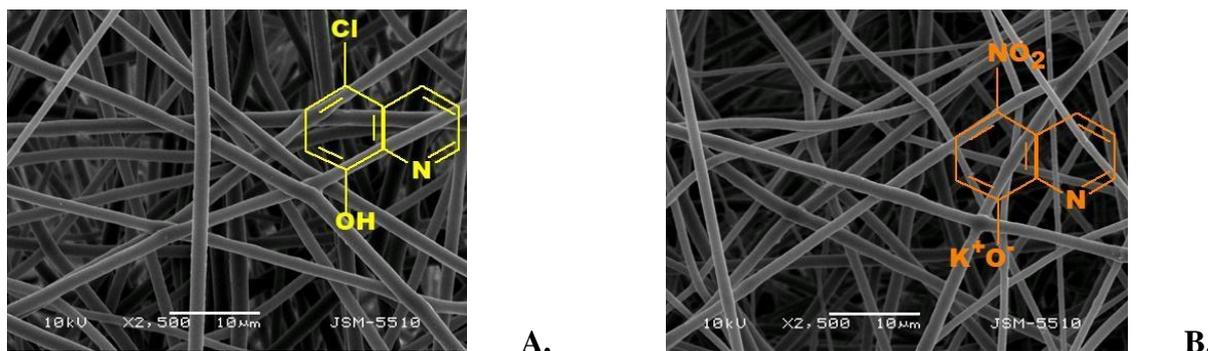
The study presents the preparation and characterization of electrospun composite materials from biocompatible and biodegradable polyester - poly(lactic acid) (PLA) and 8-hydroxyquinoline derivatives with antifungal activities.

*Materials.* Poly(L-lactide) (PLA, Ingeo™ Biopolymer 4032D, NatureWorks LLC - USA;  $M_w = 259,000$  g/mol;  $D = 1.94$ ; as determined by size-exclusion chromatography using polystyrene standards), 5-nitro-8-hydroxyquinoline (Pharmachim, Sofia, Bulgaria) and 5-chloro-8-hydroxyquinoline (5-Cl8Q, Sigma-Aldrich, St. Louis, MO, USA) were used.

*Morphological analysis.* The electrospinning of PLLA resulted reproducibly in fabrication of fibers with average fiber diameters of  $1045 \pm 320$  nm. The addition does of the low molecular derivatives of 8-hydroxyquinoline do not lead to significant change in fiber morphology and fiber diameters and distribution (Figure 1).

*Contact angle measurements.* The values of the water contact angles for all obtained samples were determined. All the obtained and studied electrospun fibers were hydrophobic with water contact angle values ca.  $120^\circ$ .

*XRD analysis.* In the XRD patterns of 5-Cl8Q and K5N8Q (powder) characteristic sharp diffraction peaks of the compounds were observed. These peaks showed that the fungicides (powders) were highly crystalline. In the spectra of PLLA/5-Cl8Q and PLLA/K5N8Q composite fibrous materials amorphous halo was detected. This result indicates that each component in the composite fibrous materials prepared by electrospinning was in amorphous state.

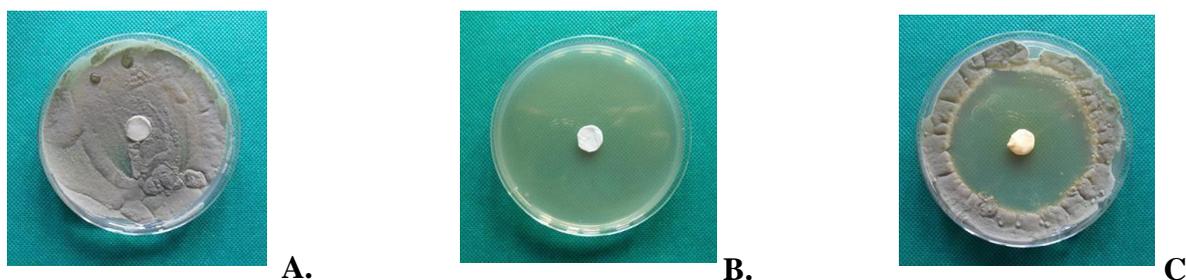


**Figure 1.** Representative SEM images of electrospun fibrous materials of: A. PLLA/5-Cl8Q and B. PLLA/K5N8Q.

*Mechanical properties.* Stress-strain curves of PLLA, PLLA/5-Cl8Q and PLLA/K5N8Q electrospun materials were obtained. The PLLA mat showed the highest values of tensile strength (3.4 MPa). PLLA/5-Cl8Q and PLLA/K5N8Q composite fibrous materials show mechanical properties similar, however, a bit lower than those of PLLA fibrous mats.

*Cumulative drug release analysis.* The release of the 5-Cl8Q and K5N8Q from PLLA fibrous materials was studied. After 50 h, the amounts of the released 5-Cl8Q and K5N8Q were 52.8% and 72.5%, respectively.

*Antifungal activity of the fibrous materials.* The antifungal activity of the electrospun fibrous materials (diameter 17 mm) was determined by carrying out antifungal tests against *P. chlamydospora* and *P. aleophilum*. There were wide inhibition zones around the discs containing 8-hydroxyquinoline derivatives. In contrast, the neat PLLA fibrous materials did not exhibit any antifungal activity (Figure 2).



**Figure 2.** Digital pictures of the zones of inhibition against *P. chlamydospora* after contact of the fibrous materials: A. PLLA, B. PLLA/5-Cl8Q and C. PLLA/K5N8Q with fungi cells.

*Conclusions.* Innovative fibrous materials were created by combining PLLA, chemical fungicides and electrospinning method. The obtained novel materials possess strong antifungal activity and are perspective candidates for protection of vines from penetration and growth of fungal pathogens.

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## STRATEGIES TO IMPROVE THE HYDROPHOBIC PROPERTIES OF XYLAN HEMICELLULOSES FOR FOOD PACKAGING APPLICATIONS

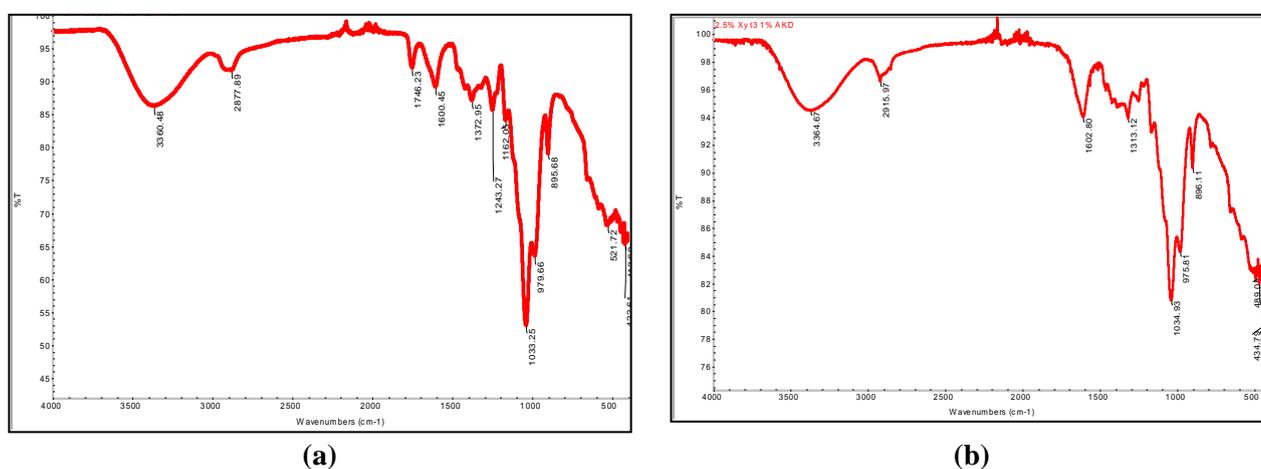
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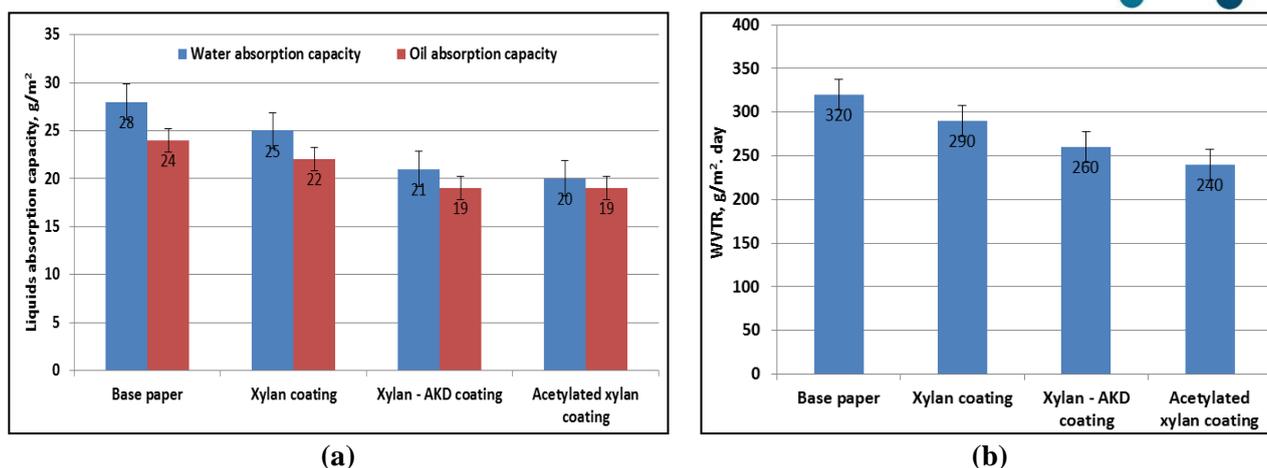
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After cellulose and lignin, hemicelluloses are an important component of plant cell wall that represents about 20%-35%, depending on the biomass source [1]. About 200 billion tons of biomass are produced annually of which 60 billion tons are hemicelluloses [2, 3]. In the last two decades, studies have shown a greater application potential of hemicelluloses, but has not yet been exploited on an industrial and commercial scale [4,5]. Xylan polysaccharides are the main hemicellulose component in hardwood being available in large quantity in secondary cell wall of agro-residues or as secondary product of wood or pulp and paper industry [6]. The industrial application of xylan hemicelluloses (XyHCs) is limited due to their hydrophilic nature. However, the extensive free hydroxyl groups distributed along the backbone of xylan monomer unit make it an ideal candidate for chemical functionalization using a variety of chemical reactions. Recent studies on its modification have shown their potential wider application in films and coatings for foods preservation, as well as to obtain the biomedical products [7]. It has been reported that films based on XyHCs provide good barriers against the oxygen and other gases, grease and aroma that enhance their potential for application on food paper packaging, also. In this context, the esterification of XyHCs is frequently reported to obtain functionalized xylan films with improved water and grease barrier properties and low oxygen permeability [7,8]. In this paper, the chemical modification by esterification of hardwood xylan was performed in order to improve its hydrophobic character. Two different esterification methods were used: (1) the acetylation of xylan using acetic anhydride [9,10] when was obtained acetylated xylan with 0.96 DS, and (2) the reaction of xylan with alkyl ketene dimer (AKD) that reacts with hydroxyl groups of xylan to form  $\beta$ -keto ester compounds [11]. The functionalized xylan was characterized by FT-IR analysis and used in coatings for surface treatment of packaging paper. The hydrophobic features of functionalized XyHCs were evaluated by analysing of the water and oils barrier properties of coated paper samples.



**Figure 1.** FT-IR spectra of (a) acetylated xylan; (b) AKD esterified xylan.



**Figure 2.** The influence of functionalised XyHCs on: (a) water and oil barrier properties of coated papers; (b) water vapours transmission rate (WVTR) of coated papers.

The structural analyses indicated the presence of absorption peaks at 1746 cm<sup>-1</sup> which are associated to C=O vibration stretching from acetyl and -COOH groups (Figure 1(a)) and the vibration stretching characteristic absorption peaks of β-ketone ester bond formed between xylan hemicelluloses and AKD at 1602 cm<sup>-1</sup> and 1733 cm<sup>-1</sup> (Figure 1(b)).

The coated papers with functionalised XyHCs have improved water, oil and water vapours barrier properties compared with those of paper coated with native xylan hemicellulose (Figure 2 a,b).

Based on obtained results, it can be concluded that chemical modification of xylan hemicellulose by esterification reactions could extend the utilisation of this biopolymer, currently available in nature, in food packaging area.

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## SYNTHESIS AND EXPERIMENTAL INVESTIGATIONS OF POLY(UREA-URETHANE) COMPOSITES FOR DEFENSE AND SECURITY APPLICATIONS

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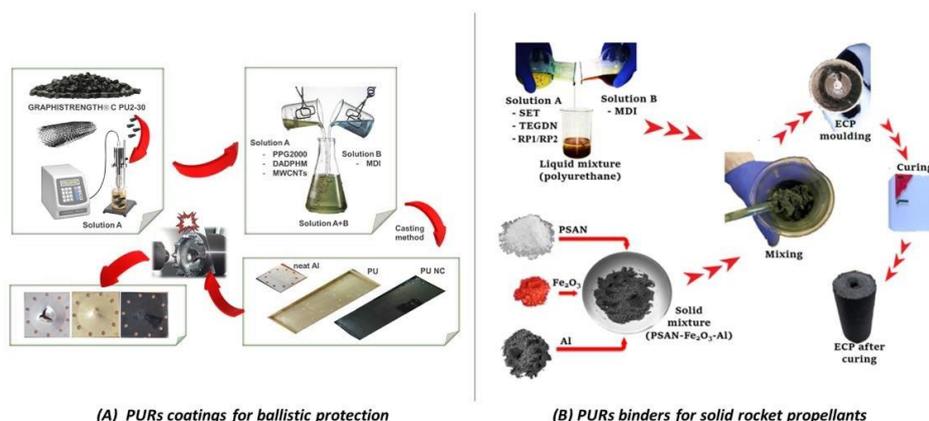
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This study describes the synthesis of versatile poly (urea-urethane) matrices and analogous composites, which are typically suitable for defense and security applications. Composite materials are the most sustainable option for developing performant defense technologies. However, creating new materials that meet the performance and safety requirements of defense and security products continues to pose significant challenges nowadays. Elastomers are known for their outstanding chemical and physical properties, ease of fabrication, and excellent processability. Polyurea, polyurethane, or analogous emerging poly (urea-urethane) materials, (PURs), are among the most notorious elastomers [1,2]. In defense and security applications, polyurea and polyurethane are mainly used as coatings for ballistic systems [3] and as binders for energetic formulations [4], respectively. Other examples of PURs applications include protective garments for CBRN protection, adhesives, foams, constructions, coatings, textiles, medical devices, cars, electronics, etc. [1,2, 5-7].

PURs-based materials gained interest from relevant industries due to their versatility in mechanical, chemical, and biological properties and the ease of tailoring them according to the required patterns [6]. The present work describes the synthesis and characterization of poly (urea-urethane) composites suitable for the defense and security industry. The experimental investigations described below focused on two research directions: PURs coatings for ballistic protection and PURs binders for solid rocket propellants, schematically illustrated in Figure 1 (formulations in Table 1).



**Figure 1.** Schematic illustrations of the fabrication (laboratory scale) of PURs-based composites.

**Materials.** (A) Poly (propylene glycol) bis(2-aminopropyl ether) - Mn $\approx$ 2000 Da (*PPG2000*, Sigma Aldrich), 4,4'-diaminodiphenylmethane (*DADPHM*, Sigma Aldrich), diphenylmethane-4,4'-diisocyanate (*MDI*, Desmodur® 44V20L, Bayer), multiwalled carbon nanotubes (*MWCNTs*, Graphistrength® CPU2-30, Arkema). (B) Sethatane D1160 (*SET*, Allnex®), two polyester–polyols

(*RP1* and *RP2*, from PET degradation [8], *MDI*, triethylene glycol dinitrate (*TEGDN*, ref. [9])).

**Table 1.** Formulations of PURs composites.

(A)	Sample	MWCNTs (wt. %)	(B)	Sample	RP1(wt.%)	RP2 (wt.%)
	<i>PU (blank)</i>	0		<i>PUR (blank)</i>	0	0
<i>PU-NC1</i>	0.05	<i>ECP_1</i>	2.5	0		
<i>PU-NC2</i>	0.1	<i>ECP_2</i>	0	2.5		
<i>PU-NC3</i>	0.2	<i>ECP_3</i>	5	0		
<i>PU-NC4</i>	0.3	<i>ECP_4</i>	0	5		

Novel poly(urea-urethane)-based binders and coatings were synthesized and characterized through numerous analytical techniques (SEM-EDX, microCT, mechanical and thermal investigations, etc.). (A) Due to their high energy absorption capacity and ability to shield the structure on which they are applied, polyurea-based nanocomposite coatings have proven to be suitable for ballistic protection. Dynamic regime tests validated that the nanocomposite-coated metal sheets could maintain their integrity. (B) The synthesized poly(urea-urethane) binders demonstrated they could enhance the thermal performances of the energetic formulations while their high flexibility ensures resilience and superior mechanical resistance.

PURs nanocomposite coatings proved their suitability as complementary materials for ballistic protection, while the PURs binders demonstrated their efficiency in future environmentally responsible composite rocket propellants.

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## REACTIVITY INSIGHTS IN $\beta$ -CYCLODEXTRIN- $\epsilon$ -CAPROLACTONE OLIGOMERIZATION REACTIONS BY MALDI MASS SPECTROMETRY

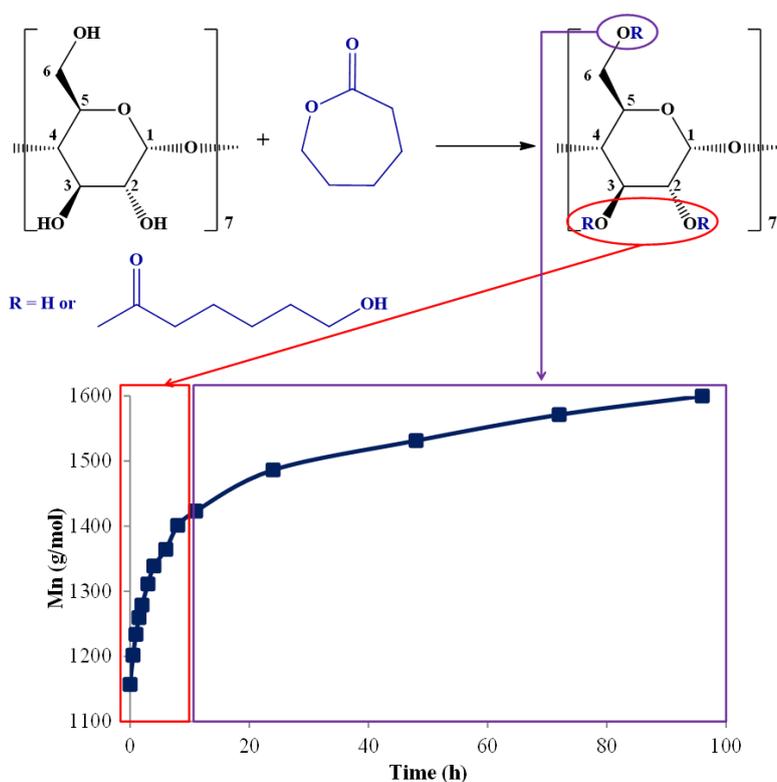
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Cyclodextrin-polyester conjugates are important for biomedical applications as they combine the properties of both cyclodextrins and polyesters, (encapsulation capacity, low toxicity, biocompatibility, and biodegradability) [1]. Native cyclodextrins, especially  $\beta$ -cyclodextrin, have relatively low water solubility, and complex chemical modifications at the hydroxyl groups of cyclodextrin are often employed to improve their solubility. Among such derivatives, cyclodextrin-polyester derivatives can be prepared by facile ring-opening reaction of cyclic esters using the cyclodextrin molecule as an initiator (core first approach), through its many hydroxyl groups. Common ring-opening organocatalysts were previously used to prepare cyclodextrin-oligoester derivatives using the core first procedure, such as 4-dimethylaminopyridine for lactide and (-)-sparteine for  $\beta$ -butyrolactone [2-5]. The organocatalysts have the advantage of being easily removed from the reaction mixture, thus, resulting in low-toxicity products [6].

Herein, the synthesis of  $\beta$ -cyclodextrin- $\epsilon$ -oligocaprolactone derivatives (CDCL) through the ring-opening reaction of  $\epsilon$ -caprolactone, using  $\beta$ -cyclodextrin as initiator and in the presence of different organocatalysts (4-dimethylaminopyridine, (-)-sparteine) and solvents (N, N-dimethylformamide, dimethyl sulfoxide) is evaluated (Figure 1).



**Figure 1.** The  $\beta$ -CD initiated ring-opening reaction of  $\epsilon$ -caprolactone and the evolution of the substitution mode of CDCL derivatives with molecular weight ( $M_n$ ) increase.



More specifically, we focused on the optimization of CDCL derivatives' synthesis using the advanced structural characterization of reaction mixtures by Matrix-Assisted Laser Desorption/Ionization mass spectrometry (MALDI MS). MALDI MS represents a powerful analytical technique for characterizing complex chemical structures and, lately, was employed for monitoring minute changes in molecular weight in ROP of D,L-lactide initiated by  $\beta$ -CD [7]. Therefore, the ring opening kinetics of  $\epsilon$ -caprolactone in the presence of  $\beta$ -cyclodextrin was followed by MALDI MS to determine the influence of different media on the molecular weight evolution. The evolution was also followed by  $^1\text{H}$  NMR spectroscopy to validate the obtained results. Moreover, the mass spectrometry evaluation was further enhanced by MS/MS fragmentation studies to confirm the attachment of oligoesters to cyclodextrin and to gain further insights into the influence of reaction parameters on the structure of modified cyclodextrins.

The highest monomer conversion values, determined by MALDI MS, were obtained using the (-)-sparteine organocatalyst, but close values were also reached using 4-dimethylaminopyridine, after a longer reaction time. Besides assessing the reactivity of different systems, the evaluation of molecular weight by MALDI MS also brought indirect proof of backbiting reactions. Also, MALDIMS kinetics disclosed that the reactions performed in DMF were more reactive than those in DMSO, with or without the addition of organocatalysts, because of amide cleavage processes which led to dimethylamine formation that acted as a supplementary organocatalyst. MALDI MS revealed the chemical modification of CDCL derivatives with formate units, and MS/MS fragmentation studies confirmed their structure. In conclusion, MALDI mass spectrometry allowed a good evaluation of cyclodextrin-initiated ring-opening systems of  $\epsilon$ -caprolactone.

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## MOLECULAR ARCHITECTURE OF BIOPOLYMER COMPLEXES

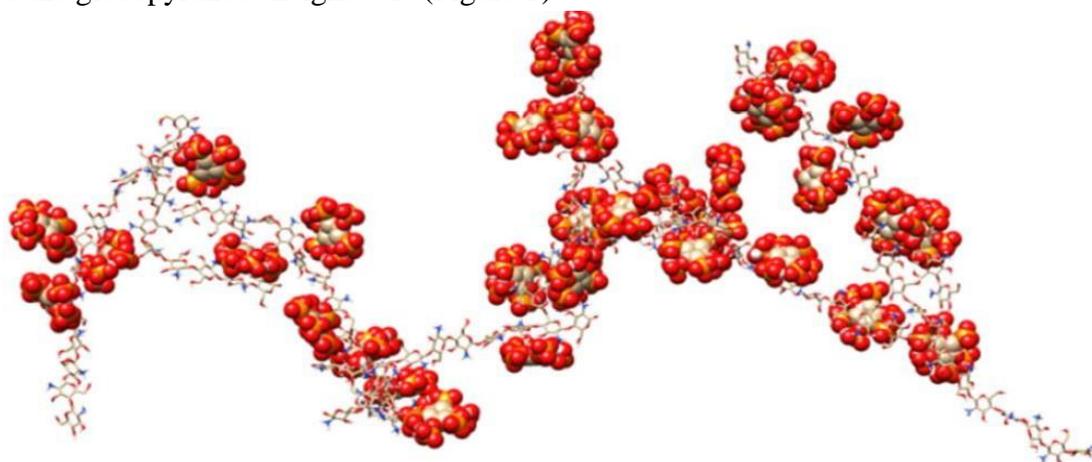
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Developing novel materials based on natural polymers (chitosan, CT) starts with the possibility of functionalized active groups with specific crosslinking agents (polyphosphates, alginate or polyacrylic acid) in order to obtain patterns for further delivery studies of hydrophobic and hydrophilic drugs. CT represents a cationic biopolymer, which can be shaped in many particular ways to finally achieve thin films, nanoparticles or microspheres [1]. Phytic acid (PA) represents a natural plant-based substance with six phosphate groups bind to an inositol ring, which can establish extremely strong electrostatic interactions with protonated amino groups from the glycosidic units of CT.

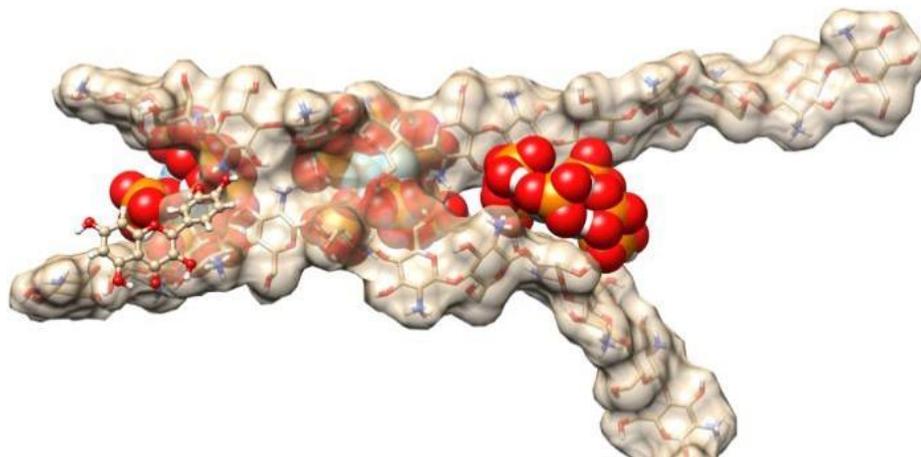
CT-PA nanomaterials were synthesized using the phytate anion (PA) as a physical crosslinker and investigated by dynamic light scattering (DLS) and Fourier transform infrared spectroscopy (FT-IR). Moreover, a computational model for CT-PA with atomistic details was created to explore the physical crosslinking pattern. The molecular architecture of the formed complexes was consistently examined by molecular dynamics (MD) simulations, to understand the impact of PA concentration and the functional groups of the CT on the reticulation process. The physical crosslinking pattern was determined by the number of polymer chains bound by one phytate anion and the phytate orientation relative to the glucopyranose neighbours (Figure 1).



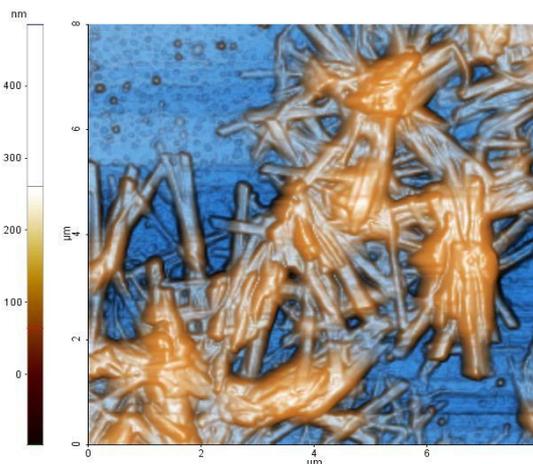
**Figure 1.** The final configuration and structural details for the CHT-083-40 chain. The backbone is represented with sticks and PA molecules with red spheres.

In the presence of polyphosphate compounds, chitosan (CT) can form insoluble hydrogels capable of drug entrapment and safe and efficient release [2]. Quercetin (QE) represents a natural yellow plant-based polyphenolic compound with good free radical scavenging properties. We moved our previous research forward with the entrapment of a hydrophobic drug (QE) in a CT-PA network. Further, loaded complexes were analyzed through experimental and computational methods. QE-CT-PA nanoparticles were synthesized by ionotropic gelation method. The computational design of the complexes, their morphological and fluorescent characteristics, the encapsulation efficiency

(EE%), in vitro release rate, and features of size were deeply investigated (Figure 2 and 3). The obtained complexes were spherical in shape, with a tendency to establish aggregates or nanofibers in function of CT concentration. The charged systems formed a very stable and well-defined network. The computational simulations provide information about molecular interactions between QE, CT and CT-PA.



**Figure 2.** The final configuration of QE, represented with sticks and balls binding to two CT chains crosslinked with PA (red spheres).



**Figure 3.** Atomic force microscopy image of the QE loaded CT-PA.

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## CORE-SHELL MICROPARTICLES FOR ENZYME IMMOBILIZATION

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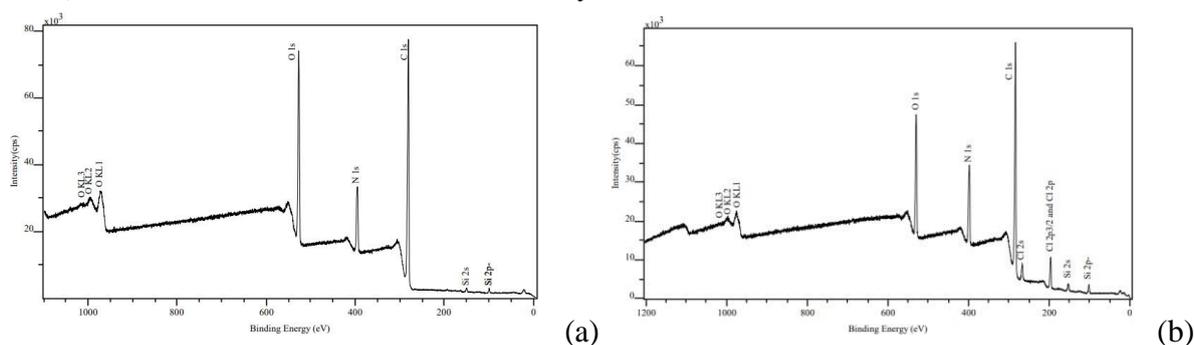
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Enzymes are versatile natural catalysts that can be used in a large number of chemical processes such as the synthesis of valuable chemical compounds, the degradation of emerging pollutants or the fabrication of biosensors. Nevertheless, enzymatic catalysts are characterized by a low stability to extreme conditions of pH, temperature or in the presence of organic solvents and are difficult to recover and reuse, reasons why their employment in industrial processes is limited [1]. In order to overcome these limitations and to increase the possibility of reuse of enzymatic catalysts, methods such as immobilization had imposed. By immobilization, enzymes are chemically or physically linked to various types of support materials, leading to the fabrication of stable composite materials that preserve the catalytic activity and secure the use of these biocatalysts in multiple reaction cycles or in extreme reaction conditions [2,3]. This study proposes the fabrication of stable core-shell polymer/enzyme composite materials that can be further used as catalysts in various processes.

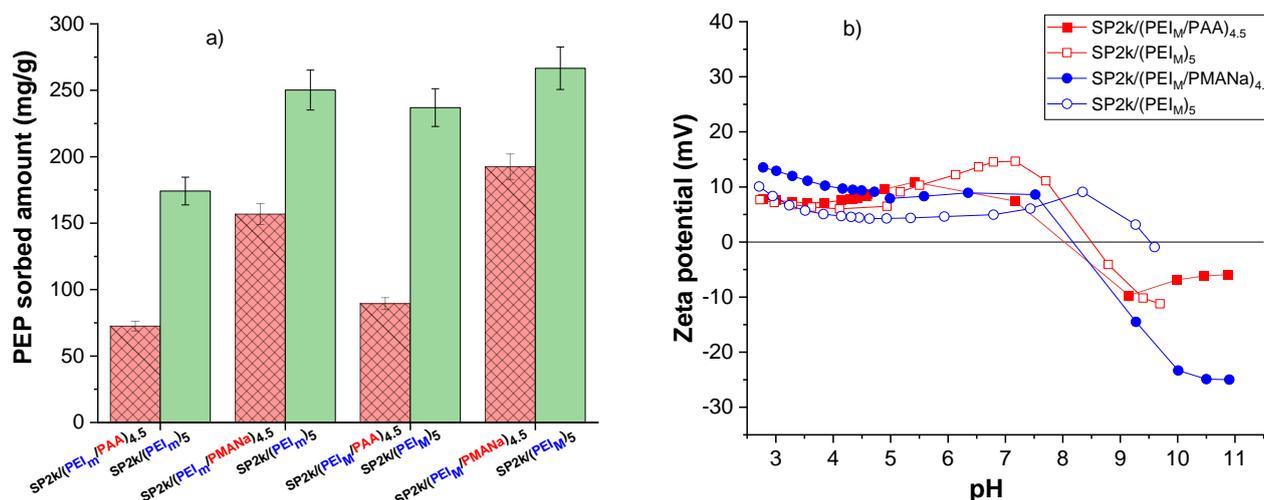
The fabrication of the core-shell composite microparticles was achieved by layer-by-layer deposition of branched poly(ethylene imine) of low ( $PEI_M$ ) and high ( $PEI_M$ ) molar mass, poly(acrylic acid) (PAA) or poly(sodium methacrylate) (PMANa) on silica microparticles (SP2k type, Daiso Co., Japan). The stability of the organic shell was ensured by chemical cross-linking and the polyacid chains were extracted in strong basic media. The composite microparticles were characterized by polyelectrolyte and potentiometric titrations, thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS) and streaming potential measurements and were further used for the immobilization by sorption of pepsin (PEP).

The deposition of the four pairs of polycation/polyanion on the SP2k microparticles led to the fabrication of core-shell composites with different thicknesses of the organic layer. The stability of the organic shell, which can be directly correlated to the pair of the used polyelectrolytes, was studied by XPS and streaming potential measurements. In terms of stability, between the four combinations assessed, the best results were registered for the  $PEI_M$ /PAA pair that lead to the fabrication of composites with a relatively thick organic shell and with highest stability during rinsing and extraction steps, as observed from the XPS spectra registered before and after the extraction of PAA chains (Figure 1) which shows a decrease in the intensity of the O 1s and C 1s after the extraction.



**Figure 1.** XPS spectra of Sp2k/( $PEI_M$ /PAA)<sub>4.5</sub> (a) and Sp2k/( $PEI_M$ )<sub>5</sub> (b).

The successful removal of the polyanion chains was also demonstrated by the [C]/[Si] atomic ratios that decreased from 65.72 to 30.81 after the extraction of the polyanion chains. The obtained composites were further employed as support materials for the immobilization by sorption of PEP, observing that the composite microparticles present a good affinity for the negatively charged enzyme, with the highest amounts of PEP immobilized on the composites obtained with the pair PEIM/PMANa, as presented in Figure 2a.



**Figure 2.** (a) Amount of immobilized PEP in the composite materials, before and after the extraction of polyanion chains, (b) zeta potential variation as a function of the pH for the composite material before and after polyanion extraction.

The amount of enzyme immobilized on the composite material was strongly influenced by the availability of positively charged functional groups that can interact with the negatively charged PEP, the highest amount of enzyme being retained in the extracted composites. The surface charge of the composite microparticles before and after the extraction of the polyanion chains was assessed based on streaming potential measurements (Figure 2b). The registered results confirmed that the composite materials with higher isoelectric points (located in the basic pH) are able to retain higher amounts of PEP, based on the electrostatic interactions between the positive charges of the polycation and the negative ones of the enzyme. The successful immobilization of PEP in core-shell layer-by-layer composite materials was achieved and depends on the number of available positive functional groups on the organic shell, the higher amount of enzyme being immobilized after polyacid chains extraction. The obtained results recommend the enzyme/polymer composites as stable materials that could be used as catalyst in biomedical and environmental applications.

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**Acknowledgements:** The authors would like to acknowledge Leibniz Institute of Polymer Research in Dresden, Germany for the support offered in the development of this study.

## NMR STUDY OF SOME $\beta$ -CYCLODEXTRIN-OLIGOCAPROLACTONE DERIVATIVES

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Cyclodextrins are natural oligosaccharides with applications in various fields due to their ability to form inclusion complexes with a variety of organic and inorganic compounds. Chemical modification of cyclodextrins is often used to improve their properties and broaden their application range [1,2].  $\beta$ -cyclodextrin has seven primary and fourteen secondary hydroxylic groups which can be chemically modified resulting products with interesting architectures and different substitution degrees. Due to the high number of reaction sites, it can be challenging to perform a thorough structural characterization of the products. NMR spectroscopy can be successfully used for structure elucidation of such compounds since it can offer information on both the degree of substitution and the substitution sites [3]. The present paper discusses the use of NMR spectroscopy in monitoring the chemical reactions from which  $\beta$ -cyclodextrin-oligocaprolactone derivatives are obtained and full structural characterization of the final products.

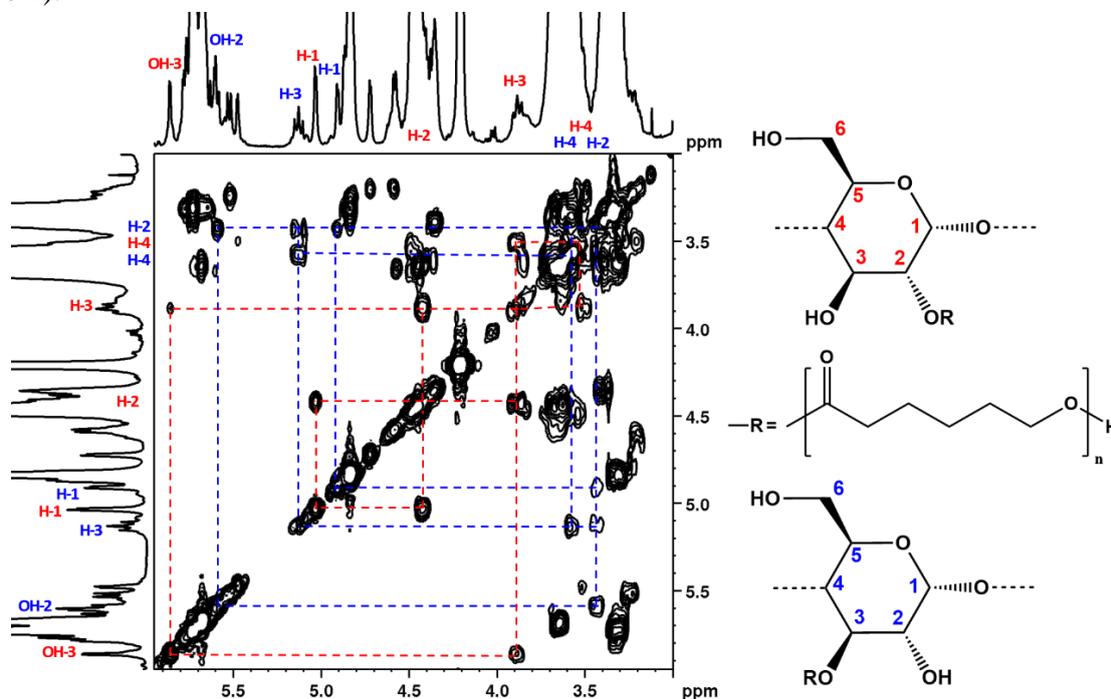
The NMR spectra have been recorded on a Bruker Avance Neo 400 MHz instrument, equipped with a 5 mm multinuclear inverse detection z-gradient probe. The chemical shifts are reported in  $\delta$  units (ppm), and were electronically referenced to the residual peak of the solvent. The experiments were recorded using standard pulse sequence, as delivered by Bruker with TopSpin 2.1 PL6 spectrometer control and processing software.

Four  $\beta$ -cyclodextrin-oligocaprolactone (CDCL) derivatives, obtained via ring-opening of  $\epsilon$ -caprolactone in different reaction conditions (without catalyst and using three different catalysts) were fully characterized using NMR spectroscopy. The  $^1\text{H}$  NMR spectra show the peaks for the substituted and unsubstituted glucopyranose units of  $\beta$ -cyclodextrin, as well as the peaks for the oligocaprolactone chains attached to the macrocycle. Moreover, by comparing the integral values of different protons from oligocaprolactone and from  $\beta$ -cyclodextrin, the chain lengths and substitution degrees were calculated (Table 1).

**Table 1.** Oligocaprolactone chain length and the substitution degree of the four CDCL products, as calculated from  $^1\text{H}$  NMR.

	Oligocaprolactone chain length	Substitution degree
<i>CDCL1 (no catalyst/80°C)</i>	1.08	2.4
<i>CDCL2 (DMAP/120°C) [4]</i>	1.28	2.8
<i>CDCL3 (DBu/room temp.)</i>	1.67	4.1
<i>CDCL4 (TBD/room temp.)</i>	2.70	6.7

The  $^{13}\text{C}$  NMR, combined with  $^{13}\text{C}$ -DEPT135 and 2D NMR spectra indicated that the substitution occurred randomly, at both primary and secondary hydroxylic groups of  $\beta$ -cyclodextrin. By analyzing the NMR spectra of samples taken at different reaction times we observed that the reaction occurs in two stages: first the monomer is rapidly attached to the secondary hydroxylic groups of cyclodextrin and secondly, the monomer conversion is slower with attachment to the primary hydroxylic groups (Figure 1).



**Figure 1.** H, H-COSY spectrum evidencing different substitution at C3 (blue) and C2 (red).

NMR characterization of the final CDCL products revealed a random substitution, at the 2, 3, and 6 positions on the glycoside rings of  $\beta$ -cyclodextrin. NMR characterization allowed a good evaluation of the cyclodextrin reaction systems. Analysis of the spectra recorded at different reaction times showed that in the first stages, rapid attachment of caprolactone occurred at the secondary hydroxylic groups of cyclodextrin followed by a slower attachment at primary hydroxylic groups. Also, by choosing appropriate catalysts and reaction conditions the chain length of oligocaprolactone and the cyclodextrin substitution degree can be adjusted. Monitoring these reactions by NMR spectroscopy can lead to obtaining products with customized structures.

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## INSIGHT INTO THE COMPLEX RELATIONSHIP AMONG FILAMENTOUS FUNGI AND CEMENT MORTAR

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Concrete infrastructure is vulnerable to deterioration by physicochemical and biological processes. To improve its structure and durability, self-healing of concrete has been achieved through autogenous healing, encapsulation of polymeric material, and biomineralization of CaCO<sub>3</sub>, with primary focus on bacteria [1]. The main limitations of the latter are reduced long-term cellular viability, reduced compressive strength in concrete and inability to precipitate enough calcium carbonate to repair wide cracks [2]. For this reason, in recent years, there has been widespread interest in fungi, which are presumably able to precipitate increased amounts of CaCO<sub>3</sub> due to their high biomass yield and extensive mycelium networks [3].

On the other hand, the mechanism of microbial deterioration of cement-based materials has been taken into consideration, particularly in regards to fungi. The degradative ability of fungi is taking effect both mechanically, through hyphal penetration, and chemically, through the production of various inorganic and organic acids [4, 5].

The aim of the present study was to analyse the interaction between filamentous fungi and cement mortar for applications in the biogenic healing of concrete as well as in counteracting the biodegradative effects of common pathogenic fungi.

Multiple fungal strains were isolated from concrete samples obtained as part of the PED 392/2020 project and were further identified by MALDI-TOF mass spectrometry. Qualitative and quantitative screening was performed for biomineralization assay, based on ureolytic activity and carbonate precipitation, and biodegradation assay, based on the production of acid metabolites and calcite solubilization. The ureolytic activity was determined using modified Christensen's agar medium and evaluated based on color intensity and rate of change in the medium's color, correlated with the enzymatic reaction [6], and further quantified based on Nessler method. Liquid media were used for assessing the potential to precipitate CaCO<sub>3</sub> using urea-CaCl<sub>2</sub> medium [7], and the potential to lower the pH of the medium using broth minimal medium. Calcite solubilization was determined using CaCO<sub>3</sub> solid medium [8]. The formation of carbonate crystals was observed by light microscopy.

The isolated fungi were identified as belonging to the following genera: *Penicillium* sp, *Chrysosporium* sp, *Aspergillus* sp, *Alternaria* sp, *Arthrinium* sp, *Coniosporium* sp and *Stachybotrys* sp. Performing qualitative analysis, strong urease activity was identified for *Coniosporium* sp, *Chrysosporium* sp. and *Penicillium* sp, whereas *Alternaria* sp. and *Stachybotrys* sp. displayed a moderate activity. In the case of *Aspergillus* sp., the medium's color turned lighter compared to the

control sample, indicating a potential to produce acid metabolites. Following quantitative analysis, high amounts of  $\text{NH}_3$  associated with urease activity were identified for *Stachybotrys* sp, *Alternaria* sp, *Chrysosporium* sp, *Coniosporium* sp and *Penicillium* sp. Also, for all urease-positive fungi, the microscopical observations confirmed the presence of numerous carbonate crystals.

Further tests were carried out on *Stachybotrys* sp, *Aspergillus* sp and *Penicillium* sp, common contaminants of buildings that contribute to what is known as the –sick building syndrome. Preliminary results show their biodegradative potential in regards to calcite, through the production of organic acids. *Penicillium* sp and *Aspergillus* sp exhibited acid production by significantly lowering the pH of the medium, from 7 initially, to 3 and 2 respectively, whereas *Stachybotrys* sp lowered the pH to 6.

Through our study, we have successfully identified the potential of fungi isolated from concrete as biomineralization agents for  $\text{CaCO}_3$  precipitation, due to their strong and moderate urease activity and ability to precipitate carbonate crystals. We have also confirmed the biodegradative ability of common pathogenic strains. Future studies will be focused on examining the effect of fungal cells on the mechanical properties of cement mortar, and on developing antimicrobial mechanisms against the identified pathogenic strains.

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## STIMULI-SENSITIVE MICROSPHERES FOR DRUG DELIVERY TO THE TUMORS

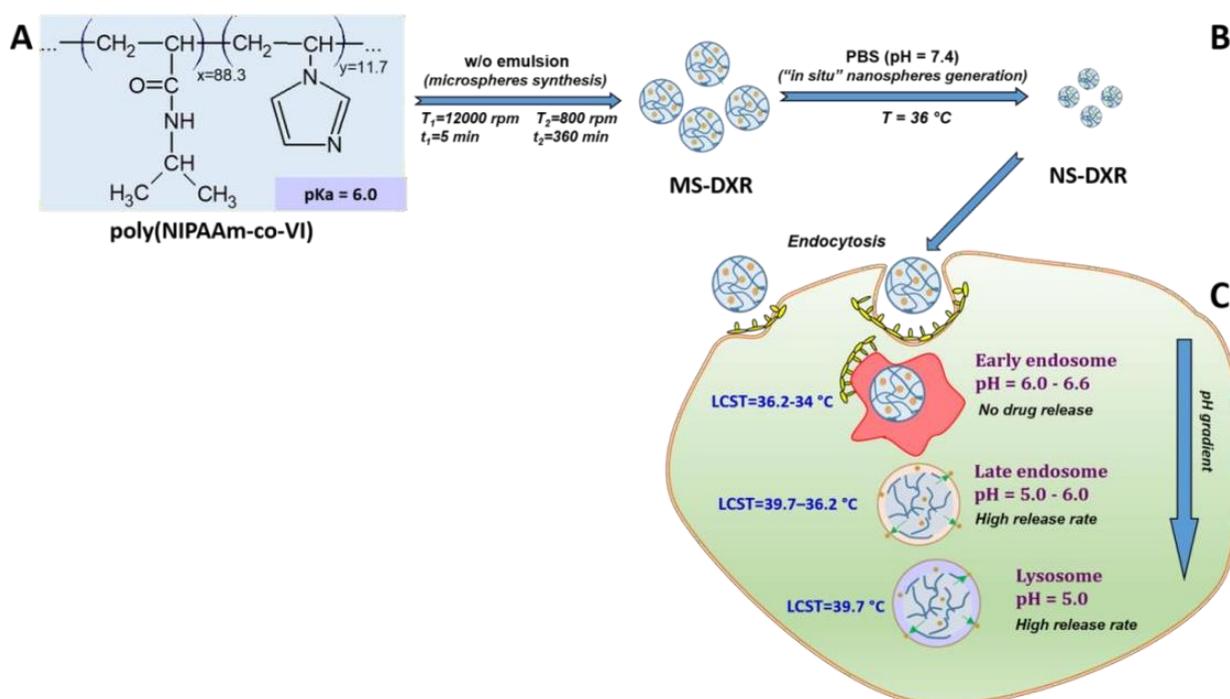
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Cancer has been and still is one of the most serious diseases for which an acceptable remedy has not yet been found. The systematic administration of drugs on the common routes does not have the necessary efficiency and results in strong side effects. As a result, the transport and release of antitumoral drugs to the desired site of action has become an increasingly used option [1]. To this purpose, we designed and developed microparticulate systems able to transport the drug intact to the desired location and release it in a controlled manner.

Firstly, poly(N-isopropylacrylamide-co-vinylimidazole) copolymer was prepared by free radical copolymerization of N-isopropylacrylamide (NIPAAm) and 1-Vinylimidazole (VI) in 1,4-dioxane, using AIBN as initiator. Poly(NIPAAm) was chosen for this study because in aqueous solution possesses a sharp phase transition (lower critical solution temperature, LCST) at a value of about 32°C [2]. On the other hand, 1-Vinylimidazole is an excellent candidate for obtaining pH-sensitive polymers because it has weak basic amino groups with a pKa of around 6.0, a value found in the cell compartments after particle internalization [3]. To maximize site-specific delivery of drugs, the development of a polymer with multi-stimuli-sensitive characteristics is imperatively required. Therefore, the copolymerization of VI with a temperature-sensitive monomer, such as N-isopropylacrylamide (NIPAAm), gives rise to copolymers possessing double sensitivity and the physico-chemical characteristics are modulated both by pH and temperature [4].



**Figure 1.** Schematic representation of the potential behaviour of DXR-loaded microspheres after intravenous administration interaction with a tumour cell.

Secondly, the obtained copolymer poly(NIPAAm-co-VI) was transformed in microspheres by solvent evaporation method. The encapsulation of doxorubicin (DXR) into nanoparticles took place during microsphere synthesis and leads to the reduction of its side effects (e.g., cardiotoxicity, nephrotoxicity, myelosuppression) Also, DXR loaded nanoparticles accumulate into tumor tissue (Figure 1) due to the enhanced retention and permeability (EPR) effect and a lesser amount is found in healthy tissues [5].

After administration, the microspheres disintegrate in monodisperse nanospheres under conditions similar to that found in the bloodstream (pH = 7.4, temperature of 36°C) releasing a small amount of payload. However, in environments that simulate the endosomal and lysosomal conditions, nanospheres solubilize, releasing the entire amount of drug.

The nanospheres are internalized greater by HepG2 cells than A549 cells, moreover, administered *in vivo*, nanospheres localized in the liver and kidneys of mice, and the loading of doxorubicin into nanospheres resulted in the reduced renal clearance of drug.

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## IMPACT OF CYCLODEXTRIN DERIVATIVES' STRUCTURE ON THE POLYURETHANE CROSSLINKING REACTION AND NETWORK PROPERTIES

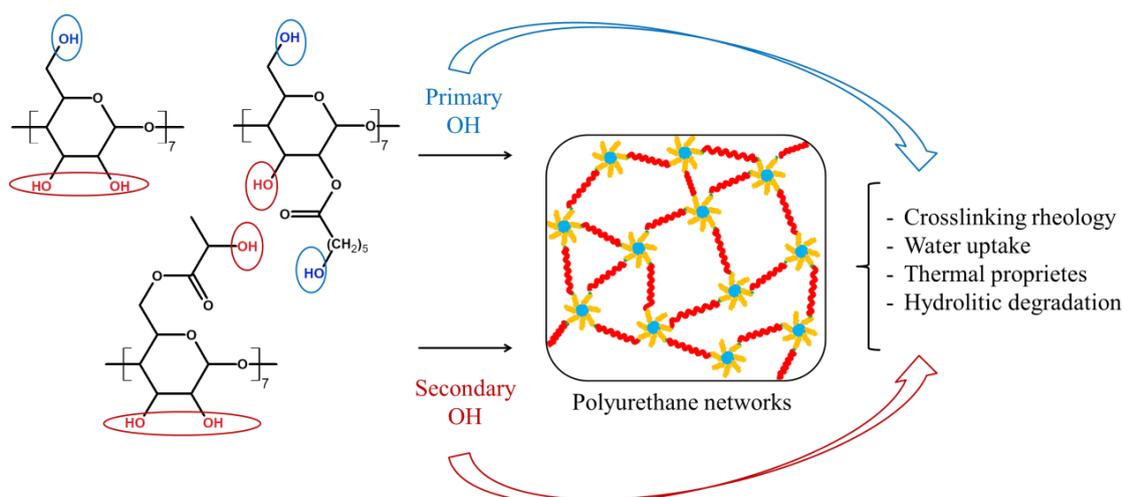
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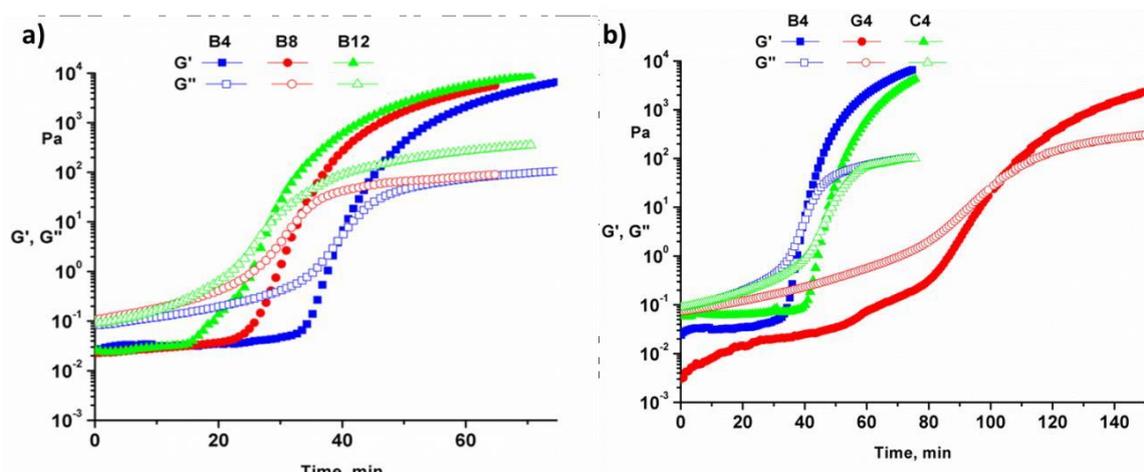
Cyclodextrin based polymer networks are a subject of intense research efforts due to their outstanding properties, and more specifically, to their ability to form host–guest inclusion complexes with various molecules of interest [1-3]. Our objective is to determine the appropriate conditions for the synthesis of cyclodextrin-based polyurethane hydrogels with controlled structure and tunable biodegradable behavior (Figure 1). Classically, the polyurethane networks may be prepared through the crosslinking reactions of diisocyanates with polyalcohol species, such as cyclodextrins (CDs) [4]. The key to the design of complex polyurethane systems is to understand the influence of OH type in multicomponent polyaddition reactions [5].



**Figure 1.** Polyurethane networks based on cyclodextrins.

Given the specific structure of cyclodextrins, with the anisotropy of the hydroxyl groups' chemistry and their polar spatial distribution, one may expect certain influences over the course of the polyaddition reactions. Native  $\beta$ -CDs participate in polyaddition reactions with two types of OH groups, 7 primary (OH-P) and 14 secondary OH groups (OH-S), the reactivity of each type of OH being different [6]. Herein, the OH-type influence on the outcome of the polyaddition reaction is studied by taking into consideration three different hydroxyl sources, namely native CD and two custom prepared cyclodextrin-oligoester (cyclodextrin-oligolactide (CDLA) – having a lower number of OH-P groups [7], and cyclodextrin- $\epsilon$ -caprolactone (CDCL) – having a higher number of OH-P groups than native CD [8]). The hydroxyl component was reacted in different molar ratios with isophorone diisocyanate polyethylene glycol-based prepolymers (PEG-(NCO)<sub>2</sub>) to obtain different hydrogels preparation.

To clearly comprehend the hydroxyl type effects, the gelation process was investigated to observe the differences of the OH type and of the molar ratios between hydroxyl compounds and diisocyanates on the crosslinking reaction. Thus, the presence of more OH groups in the crosslinking feed leads to an increase in the gelation time as demonstrated by the in situ rheological measurements (Figure 2a). A similar gelation time increase was observed when primary OH groups were replaced with secondary ones (Figure 2b).



**Figure 2.** Comparative time sweep rheological test of (a) hydrogels based on native CD using different molar ratios (1:4, 1:8, 1:12), and (b) hydrogels based on native CD (B4), CDLA (G4), CDCL (C4) using a molar ratio of 1:4.

Overall, we noticed that the crosslinking is significantly affected by the nature of OH groups, not only through direct observations, which were based on the investigation of the crosslinking process, but also indirectly, by analyzing the effects on the materials properties.

The purified hydrogels were evaluated by using Fourier-transform infrared spectroscopy (FTIR) to observe the disappearance of isocyanate groups and the formation of the urethane bonds. In addition, the water uptake, thermal behavior, and hydrolytic degradation properties were investigated to determine the influence of the cyclodextrin type in the final structure. Moreover, the degradation processes of CDLA based hydrogels, evaluated gravimetrically and by scanning electron microscopy (SEM), revealed a similar behavior as for polylactide-based materials, proving the potential of the prepared polymer networks for tissue engineering applications.

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## NATURAL POLYMERS-BASED MATERIALS AS ADSORBENTS FOR ANIONIC DYES

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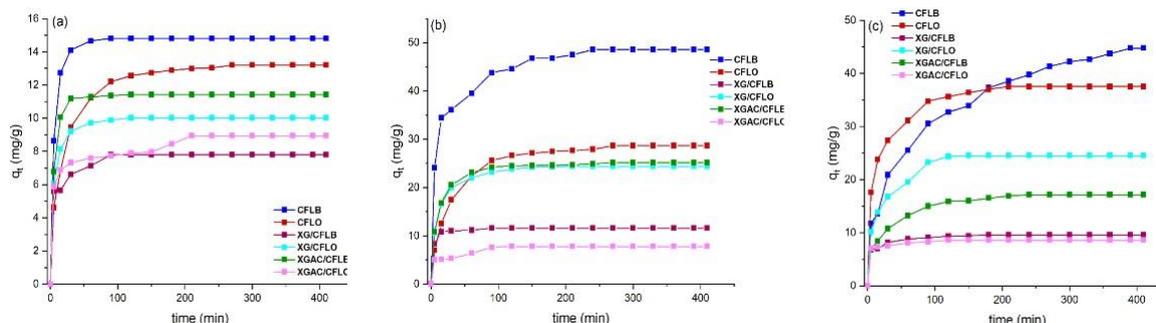
Water pollution represents one of the most severe environmental problems and can lead to various imbalances for all ecosystems [1]. Methyl blue (MB) is an anionic dye that is often used in medical investigations for fungal microscopic visualization [2]. The presence of this type of dye has negative effects on aquatic life due to its ability to block incoming light and thus photosynthesis processes [3]. This is why, diverse systems which can retain dyes from different types of wastewaters have been developed. This study presents the adsorptive properties of materials based on xanthan/esterified xanthan and ferrite-lignin hybrids, able to retain MB from polluted water.

Xanthan gum (XG) was esterified with acrylic acid, resulting xanthan acrylate (XGAC). Ferrite-lignin hybrids (CFLB and CFLO) were obtained by the sol-gel auto-combustion method using organosolv lignin (LO) and Lignoboost® (LB) as chelating-fuel agents. Further, hybrids were embedded into XG/XGAC matrix, resulting new materials denoted XG/CFLB, XGAC/CFLB, XG/CFLO and XGAC/CFLO. Density, porosity and swelling ratio, as well as point of zero charge (PZC) of the adsorbents were determined. Equilibrium, kinetic, and thermodynamic studies have been performed in order to investigate the adsorption behavior of MB from aqueous media at different concentration (15, 50 and 70 mg/L). SEM images of adsorbents, before and after dye adsorption experiments were recorded and analyzed.

Density and porosity of the materials was influenced by the nature of the polymeric matrix and also by the porosity of embedded hybrid. The swelling ratio of the adsorbents was studied at different pH values (5, 7, 8.5, and 10). All materials exhibited rapid swelling behavior (equilibrium was reached in 80 min), the process being pH sensitive. PZC is fundamental to estimate the surface charge of a solid material. According to the obtained data, CFLO and XG/CFLB presented  $\text{pH} < \text{pH}_{\text{PZC}}$  (the material' surface showed an excess of positive charges), being suitable for MB retention.

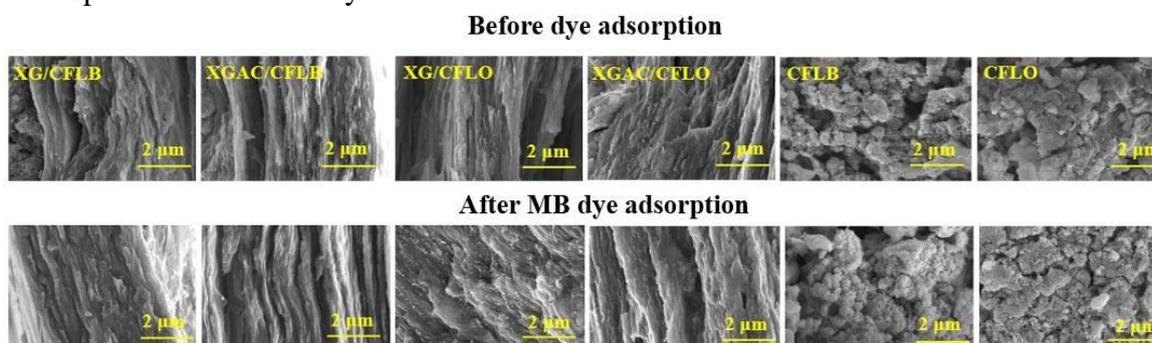
The investigation of adsorption kinetics is helpful to predict the adsorption rate and its mechanism. The correlation coefficients,  $R^2$ , of the pseudo-second-order kinetic (PSO) model were found to range from 0.993 to 1.000, which demonstrates the chemical nature of the adsorption process. Thus, interactions involving electron exchanges could be formed between the lateral bonds of the dye molecules ( $-\text{SO}_3^-$ ) and the adsorptive materials. CFLB, CFLO and XG/CFLO have the highest retention capacity for MB (44.73, 37.54 and 24.54 mg/g, respectively) (Figure 1).

The adsorption equilibrium of MB dye onto adsorbents CFLB, CFLO, XG/CFLB, XG/CFLO and XGAC/CFLB is best described by the Langmuir model. According to this, the dye molecules were deposited as a single layer onto materials. The values of the  $R_L$  (equilibrium parameter) calculated for the developed materials proved their capacity to adsorb MB. The adsorption equilibrium of MB onto XGAC/CFLO is best described by the Jovanović model, which represents the extended form of the Langmuir model, confirming the single layer adsorption.



**Figure 1.** Effect of the contact time on MB adsorption capacity at different concentration. (a) 10 mg/L, (b) 50 mg/L and (c) 70 mg/L.

After the adsorption process, CFLB and CFLO hybrids were uniformly covered with a layer of MB molecules, as evidenced by SEM images (Figure 2). MB adsorption onto XG/CFLB, XGAC/CFLB and XG/CFLO took place as a monolayer. These observations are confirmed by the results obtained from adsorption isotherms study.



**Figure 2.** SEM images ( $\times 10,000$  magnification) of adsorbents, before and after dye adsorption experiments.

The effect of temperature on the adsorption capacity of the prepared materials was investigated at 20, 35 and 45°C, using a dye solution of 15 mg/L concentration. It was evidenced that the MB retention is an endothermic ( $\Delta H^\circ > 0$ ) process. Positive values of free Gibbs energy ( $\Delta G^\circ > 0$ ) revealed that the adsorption process is not spontaneous. The reaction entropy presents positive values ( $\Delta S^\circ > 0$ ), suggesting randomness at the solid/liquid interface.

XG and XGAC were used as polymeric matrices. CFLB and CFLO hybrids were added into the matrix, forming new adsorptive materials. Batch adsorption experiments showed that CFLB, CFLO and XG/CFLO retain the highest amounts of MB dye. The chemical nature of the adsorption process was demonstrated through kinetic studies. The experimental data were better fitted to the Langmuir and Jovanović isotherm models. The thermodynamic study evidenced the endothermic nature of the adsorption process.

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## LOW TEMPERATURE SYNTHESIS OF DOPED AND UNDOPED MANGANESE FERRITE NANOPARTICLES USING THE SOL-GEL AUTO-COMBUSTION ROUTE

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An important class of magnetic metal oxides is spinel ferrites, with the general formula  $MFe_2O_4$ , where M is a divalent cation such as Mn, Co, Zn etc. The properties of these compounds are strongly influenced by the distribution of cations between tetrahedral and octahedral sites. Over the years, these materials have been under the lime light for their unique physico-chemical properties such as excellent magnetic properties, high chemical stability and specific surface area, tunable size and shape, and the relative ease of modification. They are also known for their applications in various fields such as: cancer diagnosis, drug delivery and wastewater treatment via advanced oxidation processes (AOPs) [1].

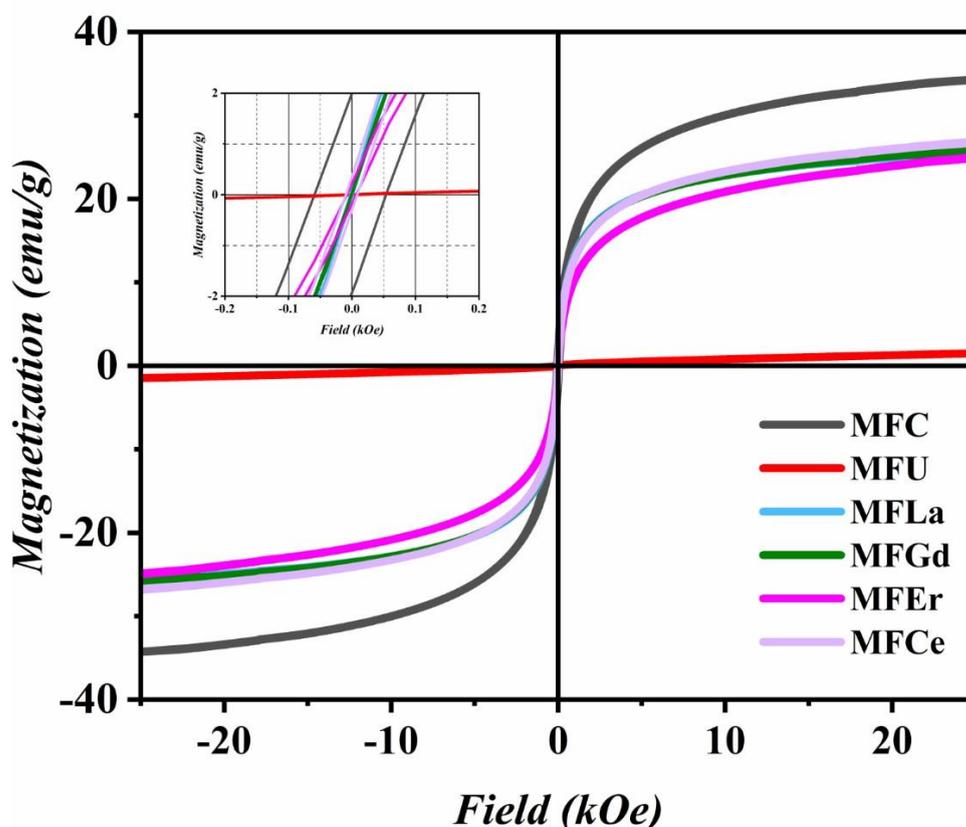
The characteristics of these nanoscale materials can be fine-tuned by a variety of techniques, including altering composition, sintering temperature and/or time, synthesis method, doping, etc. [2]. Numerous classic (typical ceramic processing procedures) and non-traditional (sol-gel, microemulsion, sonochemical, electrochemical, etc.) preparation strategies were employed for the synthesis of spinel ferrites. Many of these strategies are often difficult to implement due to the differences between ionic radii [3]. Among the common synthesis methods of ferrites, the sol-gel auto-combustion technique is usually utilized for this type of cation embedding into the ferrite structure. This synthesis route is simple, versatile and fast. The fuel agent plays a key role in this process, bounding stable complexes with the metal cations, preventing the selective precipitation of the metal ions during water evaporation and providing enough heat for spinel ferrite formation [2].

Recent studies proved that the insertion of very small amounts of rare earth (RE) cations into the ferrite structure strongly influences the ferrites characteristics and performances, by affecting crystallite and grain sizes and/or generating crystal defects in the spinel lattice [4]. To facilitate the insertion of rare earth ions into the spinel matrix, the materials are frequently subjected to a series of thermal treatments at high temperatures ( $\geq 700^\circ\text{C}$ ). A particular case is the manganese ferrite which is unstable at elevated temperatures, because  $Mn^{2+}$  ions tend to oxidize to  $Mn^{3+}$ . Therefore, doping  $MnFe_2O_4$  with lanthanides cations by increasing temperature is detrimental for the phase purity [5].

In this respect, the present study aims to obtain manganese ferrite doped with RE by sol-gel auto-combustion method at relatively low temperatures. The selection of the judicious fuel agent for such purpose is essential. Thus, citric acid and urea were used as chelating/combustion agents to prepare both undoped and rare-earth doped manganese ferrite.

Magnetic hysteresis loops of undoped  $MnFe_2O_4$  using different combustion agents (MFC, MFU) and doped materials, with the general chemical formulas  $MnFe_{1.98}La_{0.02}O_4$  (MFLa),  $Mn_{1.98}Gd_{0.02}O_4$  (MFGd),  $MnFe_{1.98}Er_{0.02}O_4$  (MFEr) and  $MnFe_{1.98}Ce_{0.02}O_4$  (MFCe) measured by vibrating sample magnetometer (VSM) at room temperature are presented in Figure 1.

The manganese ferrite samples display ferrimagnetic type behavior bearing for the samples synthesized using citric acid. By contrast, the  $\text{MnFe}_2\text{O}_4$  sample (MFU) obtained using urea exhibited paramagnetic behavior.



**Figure 1.** Room temperature hysteresis loop for the undoped and doped samples.

The phase purity of spinel ferrite was studied by means of Fourier transform infrared spectroscopy (FT-IR) and X-Ray diffraction (XRD). The morphology of the materials was investigated by transmission electron microscopy (TEM).

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## PHOTOPOLYMERIZATION PROFILE OF MODIFIED CELLULOSE

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According to human needs, photochemical reactions have contributed to the synthesis of materials since antiquity. For instance, the Ancient Egyptians processed papyrus and employed sunlight to preserve the mummies throughout the mummification process. Scientists are concentrating on performing photoreactions now, using the same principles that were merely enhanced through time. Despite the fact that there are many different types of photochemical reactions, each of which offers good and substantial areas for research and applications, the photopolymerization reaction stands out as a crucial area for investigation due to its unique qualities, including its environment-friendliness, accessibility of inexpensive sources, widespread use, and effectiveness [1,2].

The photopolymerization process principle refers to the irradiation of an appropriate material with a visible, ultraviolet, or infrared light source. An appropriate material is one that has photopolymerizable/light-sensitive double bonds in its structure. Of course, using a photoinitiator that can absorb photons in the appropriate spectral domain and produce free radicals when exposed to light is also necessary for photopolymerization. Consequently, the method is based on the free radical polymerization mechanism. Three-dimensional networks made of polymers are often formed as a result of light-induced polymerization [1,2].

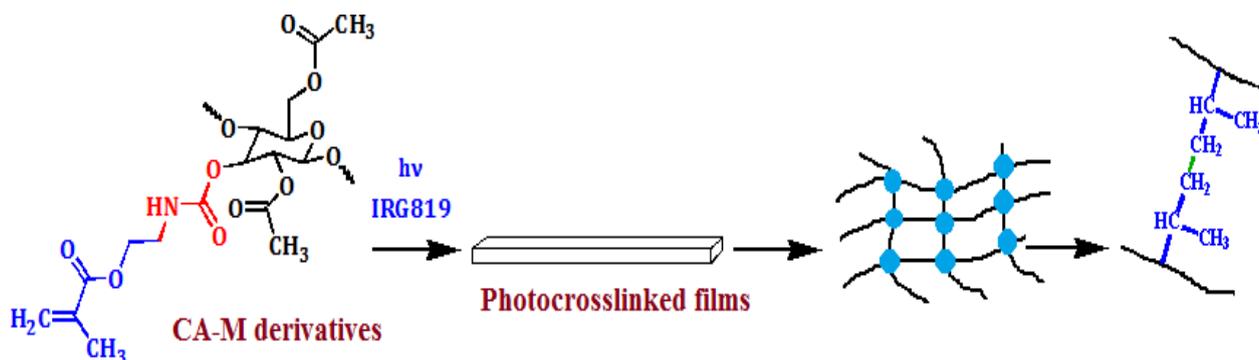
Cellulose is one of the most important biopolymers due to its properties, such as: biocompatibility, renewability, crystallinity, to name only a few. Because of these characteristics, cellulose has recently found new applications that were unheard of just a few years ago [1,2]. Cellulose acetate is one cellulosic derivative that is highly used as it has an increased solubility in organic solvents than cellulose itself. To introduce cellulose acetate in the photochemical field, first it was necessary to modify the available hydroxyl groups in anhydroglucose units by attaching photopolymerizable sequences such as methacrylate groups [3].

FTIR spectroscopy was used to monitor the substitution reactions between the cellulosic derivative and the 2-isocyanatoethyl methacrylate monomer, which resulted in the modification of cellulose acetate with methacrylate units via urethane linkages. Thermogravimetric analysis, water contact angle measurements, and spectroscopic methods such as FTIR, NMR, and XRD spectroscopy were used to analyze and confirm the chemical structures and properties of the resultant compounds. <sup>1</sup>H-NMR spectra allow us to calculate the functionalization degree of each compound (Table 1). In addition, we also investigated the effect that functionalization degree has on samples properties [3].

Further on, each sample was dissolved in tetrahydrofuran, followed by the addition of Irgacure 819 photoinitiator, until a homogenous mixture was obtained. Thereafter, the mixtures were casted as coatings and irradiated with a visible light lamp which led to the formation of three-dimensional networks (Figure 1). The photopolymerization profile, which includes the monitoring of the double bond evolution and conversion during the photopolymerization process, was investigated by using FTIR spectroscopy [3].

**Table 1.** Synthesized cellulose acetate derivatives and their corresponding functionalization degree.

Sample name	Functionalization degree (FD%)
CA-M5	5
CA-M10	10
CA-M25	25
CA-M50	50
CA-M100	100



**Figure 1.** Schematic illustration of tree-dimensional crosslinked networks formation by visible light irradiation of modified cellulose acetate samples.

The conversion degrees were calculated from FTIR absorbance spectra, monitoring the decreasing of the methacrylate characteristic band at  $815\text{ cm}^{-1}$ . Given the fact that the conversion degrees were moderate, up to 55%, we assume to contribute in the method optimization. Therefore, the current task is to find compounds with greater photoreactivity which could be used in combination with cellulose acetate derivatives in order to improve the photopolymerization process by increasing the conversion degree. Modified castor oil with urethane-methacrylate units and urethane methacrylate derived from polypropylene glycol were chosen as second compounds of the mixtures in order to obtain light-induced crosslinked networks with enhanced crosslinking degree [3].

Taking into the consideration everything discussed in previous sections, we can safely say that the photopolymerization research field requires extensive studies and rigorous characterization of the photopolymerizable materials and their corresponding applications [3].

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## STUDY OF SUNFLOWER AND CORN STALK PITH AS RAW MATERIALS IN PREPARATION OF CARBONACEOUS ADSORBENTS

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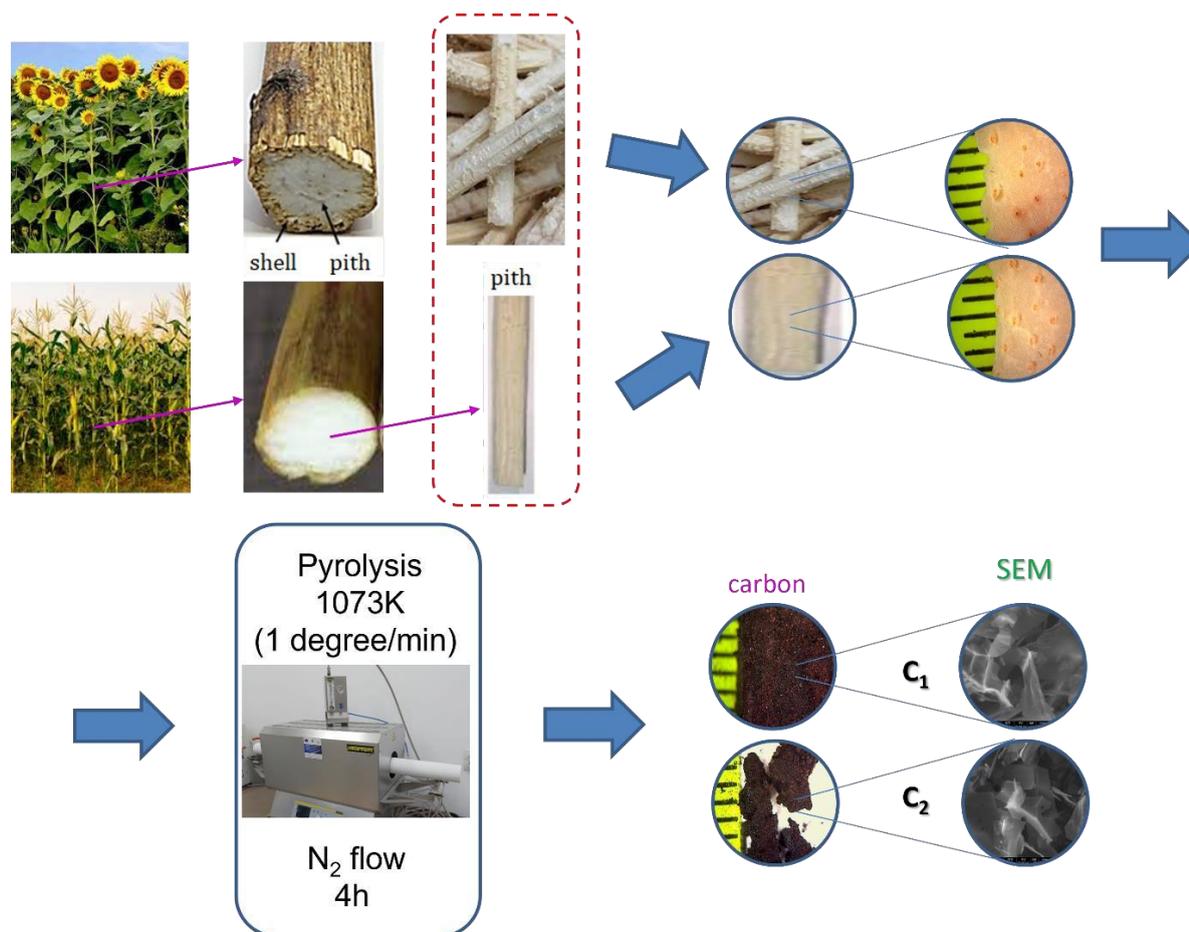
The contemporary period is characterized by an impetuous evolution in various fields such as economic, industrial, and social. This development presents, in addition to success, repercussions in the form of excessive pollution in various forms and levels, climate changes, depletion of energy sources, the emergence of new pathogens, etc. [1,2].

The use of natural or industrial waste is currently seen as a possible resource used for the generation of nanomaterials with important properties needed for further applications. In addition to the high carbon content of natural waste, they show another valuable feature such as amino, sulfuric, carboxyl and hydroxyl groups that, depending on the type of synthesis, can remain on the surface of the carbonaceous material. The presence of these groups favors some phenomena such as increased wettability, passivation, and functionalization on the surface of carbon materials [3]. Durability and the need to obtain new carbon materials with multiple applications are the main goals of the investigation of various plant wastes and biomass in recent years [4].

Plant waste represents a cheap, abundant, and sustainable source compared to traditional chemical synthesis methods [1]. Solid waste is an emerging universal problem mainly due to its harmful environmental aspects and health hazardous consequences. As usually solid waste is classified into carbonic and a carbonic waste [5], and due to the fact that most of the solid waste materials consist of carbonic skeleton as the structural framework, enables nano-science to address this issue. Thus, of high interest is the preparation of carbonaceous materials derived from such carbonic waste.

The goal of our study was to synthesize porous carbon materials starting from foam-like waste carbon-rich materials, preserving the porous structure and transferring it to the carbonic material. Therefore, to achieve this goal two sources of lignocellulosic waste biomass were considered as sunflower stalk pith and corn stalk pith. The dried carbonic sources were subjected to the pyrolysis treatment, in a high-temperature tube furnace for several hours (Figure 1). The advantage of involving such pyrolytic process for waste foam-like organic materials consists in production of valuable porous carbon materials in large quantities.

The properties of the resulted carbonaceous materials were investigated by nitrogen-sorption measurements, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, thermogravimetric analysis and FTIR spectroscopy. Besides these mentioned analyses, the wetting properties of carbonaceous materials have been also investigated. The contact angle (CA) of a water droplet with the carbon surface has been measured.



**Figure 1.** Schematic illustration for the synthesis of porous carbon materials derived from lignocellulosic waste biomass: sunflower stalk pith C<sub>1</sub> and corn stalk pith C<sub>2</sub>.

The retained porous nature of the prepared carbon materials is relevant for adsorption/desorption applications. As well, the hydrophobic features could be considered an important characteristic that can have a determining role in oil sorption process and oil-to-water selectivity.

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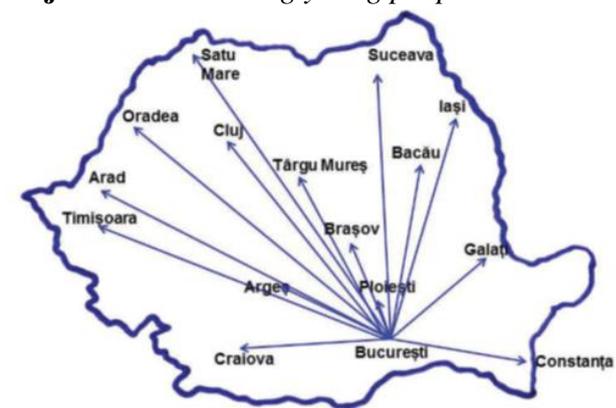


## ROMANIAN CHEMICAL SOCIETY SOCIETATEA DE CHIMIE DIN ROMANIA, SChR

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- ✓ *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 Politehnica 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*



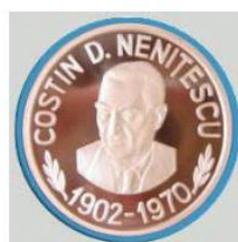
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Many important figures of the chemical world are honorary members of SChR and visited Romania on various occasions. SChR signed bilateral agreement papers with several societies within Europe.

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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/

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## CELLULOSE CHEMISTRY AND TECHNOLOGY

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

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 Corlăţeanu 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 Iaşi, under Prof. Cristofor Simionescu's coordination. The event became a tradition, and 13 editions were further organised under Prof. Cristofor Simionescu's leadership. The 14<sup>th</sup> edition paid homage to Prof. Simionescu's lifelong scientific activity, celebrating his 90<sup>th</sup> 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 2<sup>nd</sup> 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 Iaşi 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 Iaşi 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. Kalninch (USSR), H. Sihtola (Finland), T. E. Timell (USA), V. Diaconescu (Romania). The meeting was held on the occasion of the 3<sup>rd</sup> International Symposium of Cellulose Chemistry and Technology, organised on 18-22 September, 1968, in Iaşi. 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 4<sup>th</sup> 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 56 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 1.52 in 2021), is published in both online ([www.cellulosechemtechnol.ro](http://www.cellulosechemtechnol.ro)) and print forms, and successfully continues its activity, hosting papers from all over the world.

## BIONANOTECH CENTRE YOUR SUPPORT FOR HORIZON EUROPE PROJECTS

*Dr. Teodora Rusu, Sinziana Vlad*

*BioNanoTech Project Support Centre, Petru Poni Institute of Macromolecular Chemistry*

For several years, the European Union has recognized the need for a coordinated and inclusive approach, starting the preparation of policies and actions at the European level that respond to societal problems with implications in the economy. One of the directions of action in this sense is research-innovation. In 2020, the European Parliament and the Council of the EU mandated the European Commission to directly introduce a new way of working in policy areas, areas of expertise and science, engagement with companies, local communities and the research-innovation community. This new way of working took shape in the establishment of priority areas of action at the European level and the creation of work programs dedicated to these areas.

### *European landscape*

Horizon Europe<sup>1</sup> is the EU's key funding programme for research and innovation with a budget of €95.5 billion. The programme aims to facilitate collaboration between all European countries and not only and to strengthen the impact of research and innovation. It addresses the main EU policies while tackling global challenges. It supports the creation and better dispersion of excellent knowledge and technologies. The programme is structured in three pillars:

- **PILLAR 1: The Excellent Science Pillar** aims to increase the EU's global scientific competitiveness. It supports frontier research projects driven by top researchers through the European Research Council, funds fellowships for experienced researchers, doctoral training networks and exchanges through Marie Skłodowska-Curie Actions, and invests in world-class research infrastructures.
- **PILLAR 2: The Global Challenges and European Industrial Competitiveness Pillar** supports research relating to societal challenges and reinforces technological and industrial capacities through clusters. It sets ambitious goals for EU missions. It also includes the Joint Research Centre which supports EU and national policymakers with independent scientific evidence and technical support.
- **PILLAR 3 The Innovative Europe Pillar** aims to make Europe a frontrunner in market-creating innovation via the European Innovation Council. It also helps to develop the overall EU innovation landscape through the European Institute of Innovation and Technology which fosters integration of the knowledge triangle of education, research and innovation.

Other than these three pillars, several horizontal programs have been considered: **Widening Participation and Strengthening the European Research Area (ERA)** by increasing support to the EU Member States in their efforts to make the most of their national research and innovation potential, fostering closer collaborations and spreading excellence.

A novel approach introduced by the Horizon Europe project are the **Missions**. This new approach proposes and implements specific objectives, relating to areas of expertise, such as **cancer prevention, climate**

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<sup>1</sup> [https://research-and-innovation.ec.europa.eu/funding/funding-opportunities/funding-programmes-and-open-calls/horizon-europe\\_en](https://research-and-innovation.ec.europa.eu/funding/funding-opportunities/funding-programmes-and-open-calls/horizon-europe_en)



*change, and food resources*. These proposals encourage engagement from citizens to ensure alignment with EU priorities. The overall impact aims to bridge the gap between citizens and the innovations that affect their daily lives.

These missions directly address several European unprecedented global challenges: extreme weather conditions, natural disasters caused by climate change, the biodiversity crisis (and changes in ecosystem services), the COVID-19 pandemic, health, financial and economic crises, population displacements caused by various wars, with socio-economic problems of great proportions. These challenges did not appear recently or suddenly. The last few years, however, have brought the accumulation and overlapping of both crises and their effects, highlighting the need for solidarity, cooperation at the individual, national and European level.

### ***Romania landscape in Horizon Europe /Horizon 2020 programme***

Romania, the seventh country in the EU, according to the size of its population, managed to attract only 302 million euros from Horizon 2020 programme, representing 0.44% of the total budget available through this programme at the level of the entire Union, according to official data aggregated by the European Commission (Horizon 2020 Dashboard)<sup>2</sup>. This places Romania 20th out of 28 member states (including the UK) and 23rd or lower among member and associated states, according to an analysis published by the Nature journal<sup>3</sup>. In this article the position of Romania was analyzed together with formerly communist eastern Europe and the conclusion was that “there persists a distinct east–west divide in the European research landscape. Scientists and research institutions in Poland, Slovakia, Bulgaria and Romania were among the least successful participants in Horizon 2020, securing a combined total of just over €1 billion”.

According to the latest data available on the Horizon 2020 Dashboard, Romania's situation suggests that the money made available by the European Union for research, from 2014 until now, has mostly passed by potential beneficiaries in Romania. So:

- The net EU contribution to Romanian research, through Horizon 2020, amounted to 249.7 million euros => This means a success rate of only 12.10%
- There is a gap between Bucharest-Ilfov, Cluj and the rest of the country
- There were 10640 (1.06% out of total H2020) submitted projects
- Success proposals 1618 (0.98% out of total H2020) grants were signed

Based on this data, both at a European and national level several actions have been considered to increase participation in Horizon Europe program - the new European Research and Innovation Program.

### ***European initiatives – speeding up the widening actions***

Widening Participation and Spreading Excellence actions under Horizon Europe, contribute to building research and innovation capacity for countries with low participation in the European Research Program. The actions considered for these countries are meant to strengthen their potential for successful participation in transnational research and innovation processes, promote networking and access to excellence. Participants in these actions will be able to upgrade their research and innovation systems, making them stronger and allowing the EU as a whole to advance together, in line with the policy objectives of the

<sup>2</sup> <https://webgate.ec.europa.eu/dashboard/sense/app/a976d168-2023-41d8-acec-e77640154726/sheet/0c8af38b-b73c-4da2-ba41-73ea34ab7ac4/state/0>

<sup>3</sup> <https://www.nature.com/articles/d41586-020-03598-2>

European Research Area. These actions continue the H2020 actions like: Twinning, Teaming, ERA Chair, COST with improved procedures tailored according to the experience gained in H2020.

In order to stimulate the participation of widening countries in Horizon Europe in particular in the Pillar 2 Actions, the European Commission has created the Hop On Facility call. This call will be funded through the Work Programme widening participation, strengthening the European Research Area, and contributes to the inclusiveness ambition of the future European Research Area. This call will provide the possibility for legal entities from low R&I performing countries (=widening countries) to join already selected collaborative projects, subject to the agreement of the respective consortium and provided that legal entities from such countries are not participating in it yet.

### ***Romanian initiatives to increase participation in Horizon Europe Program - BioNanoTech Support***

The BioNanoTech Centre was established in 2020 together with other 11 similar centers, financed by the Romanian Operational Program for Competitivity (2014-2020); Axis 1. Research, technological development and innovation (CDI) in support of economic competitiveness and business development; Action 1.1.3: Creating synergies with the RDI actions of the ORIZONT 2020 framework program of the European Union and other international RDI program. These centers were designed to support the Romanian researcher to participate in Horizon 2020/horizon Europe Programs.

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

One of the BioNanoTech targets is to provide consultancy and support in making proposals within the European Framework Program, in order to increase participation and to promote the European Cooperation in Horizon 2020/Europe projects for Romanian key actors in the field of material science: *Eco-nanotechnologies and advanced materials* (including nanomaterials, nanomedicine etc.).

This is one of the main issues tackled by the Romanian Smart Specialization Strategy in the next programming period and it is addressed both at regional and national level. Outreach and stakeholder engagement will be primarily targeted, during the implementation of the BioNanoTech project, in which all interested parties will be able to provide their input and feedback in a seamless and efficient way.

The experience gained since 2020, as well as the continuous documentation, made the BioNanoTech Centre a reliable partner for consultancy for many research teams. The BioNanoTech Centre succeeded to offer advice on proposals for more than 16 projects so far.

To make a difference in the addressing European Projects and to speed up and increase the excellence of N-E Romanian Region research institutions, the centre started some training sessions for writing projects. A group of PhD students from School of Advanced Studies of the Romanian Academy (SCOSAAR) learned to write a project proposal, in an interactive and innovative training.

The BioNanoTech team has organized several training sessions for other beneficiaries not only from the NE Romanian Region but from all over Romania. Moreover, the BioNanoTech has organized two training session for the Moldavian Academy of Science.

Dissemination and promotion of open calls have also been made with the support of the Romanian Office

for Science and Technology in Brussels and different representatives of the European Commission (up to now 8 such info days have been organized).

The support that the BioNanoMat team can offer does not stop once the proposal is submitted. We are also here to help beneficiaries in the problems encountered during the contracting or development of the project, offering administrative support for the management of financed projects.

Even if the role of the BioNanoTech is to offer support for Horizon Europe project, our involvement goes beyond this, thus we also offer consultancy related to other national and international project such as: Romanian National Research and Innovation Program, Romanian Structural Funds, Romanian National Recovery and Resilience Plan, Norway and SEE Grants, etc.

Our team was asked to contribute at the elaboration of the Gender Equality Plan (GEP) in Petru Poni Institute of Macromolecular Chemistry (PPIMC), a mandatory requirement for contracting projects in Horizon Europe program. The GEP for 2022-2025 was developed in order to ensure and promote equality and diversity to offer knowledge and the acquisition of skills to all personnel. The objectives of the GEP are implemented through specific actions that aim at safeguarding an equal and inclusive organizational culture and promoting gender-equality at all levels. As such, the GE strategy and the GEP will pro-actively enable gender equality, awareness raising, skills and competences; gender balance in decision-making structures and processes, including recruitment; gender equality in research; and integrating the gender dimension in the entire research process. Also, the BioNanoTech is involved in the elaboration of the PPIMC Human Resources Strategy for Researchers (HRS4R). The 'HR Strategy for Researchers' supports research institutions and funding organizations in the implementation of the Charter & Code in their policies and practices<sup>4</sup>. PPIMC is implementing the principles of the HRS4R in order to obtain the European Commission recognition with the 'HR Excellence in Research Award' that rewards the institutions which make progress in aligning their human resources policies to the 40 principles of the Charter & Code, based on a customized action plan/HR strategy.

The BioNanoTech Team is confident that the participation of Romania in Horizon Europe projects will increase with the support of these centers and that the new programming period will foresee similar measures to continue this experience.

## 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.*



<sup>4</sup><https://euraxess.ec.europa.eu/jobs/hrs4r>



## INFRA SUPRACHEM LAB - CENTER FOR ADVANCED RESEARCH IN SUPRAMOLECULAR CHEMISTRY

Marcela MIHAI, Narcisa-Laura MARANGOCI

*Petru Poni Institute of Macromolecular Chemistry*

### 1. General information

- ✓ *Beneficiary:* Petru Poni Institute of Macromolecular Chemistry Iasi (Institutul de Chimie Macromoleculara Petru Poni, ICMPP)
- ✓ 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 formed through a Horizon 2020 ERA CHAIR project (Horizon 2020 WIDESPREAD 2-2014: ERA Chairs Project no 667387). The SupraChem Lab project started in 2015 and with the support of EC investment of 2.5 MEuro, the foundation of a young team of researchers was laid, focused on the principles of supramolecular chemistry knowledge. 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. The group human resource represents a secure core for the training of new generations of specialists, able to continue and develop new fields with great applicative impact.

Over the last ten years, ICMPP's research directions have clearly evolved into interdisciplinary fields and have been adapted to global research trends, while also presenting their own original directions, based on knowledge and experience gained over time. The implementation of the Infra SupraChem Lab project would contribute to the improvement of the existing research within ICMPP and SupraChem Lab team and 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 represents a real support for the development of application fields. The Infra SupraChem Lab infrastructure is a step forward to create the premises for application of the results of fundamental research obtained by the newly created group.

Infra SupraChem Lab will be set up in spaces owned by the ICMPP - 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*
- A2. *Laboratory for the study of special properties and possible applications*
- A3. *Physical and chemical characterization laboratory*

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 (e.g. X-ray diffractometer for wide angles, Photo-DSC, Automatic confocal imaging system for scanning, characterization and data analysis in cell biology, Semi-automatic inverted fluorescence microscope, Diffractometer with dual X-ray source for single crystals, Motorized stereomicroscope with fluorescence with the possibility of in-depth analysis, and many others).

**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, the project being addressed also to other interest groups as follows:

- ✓ graduates of the universities of Iasi and not only who could join the SupraChem Lab 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
- ✓ researchers from ICMPP or other collaborating research institutions, who will be able to perform tests or determinations on the equipment within the center
- ✓ different SMEs that will be able to benefit from technology transfer facilities of the patented results that will be obtained within the center.

## RONEXPRIM YOUR RELIABLE PARTNER FOR INTEGRATED SOLUTIONS IN R&D FOR 30 YEARS



Quality, efficiency and innovation through specialized educational programs and specialized training are some of the core values of Ronexprim. The technological complexity of the products and the high quality of the services offered for the Romanian market are based on a long-term experience of a professional team and a very strong relationship with its world-class business partners. That leads to an excellent customer experience consolidating brands loyalty, pioneering this innovative field of technology since 1991.

### **Business milestone, the foundation of a healthy “family of professionals”**

Ronexprim, which celebrates this year 30 years of uninterrupted activity, was founded in October 1991 by Mircea Stoian. The company started its milestone as the Agency and Service for Philips Industrial Departments in Romania.

Nowadays, the company represents leading international manufacturers, with particularly high standards, including Thermo Fisher Scientific, Malvern Instruments, Edinburgh Instruments, Kruss, AMETEK Spectro Scientific, Milestone, Fluke Corporation and many more. Ronexprim has earned an exceptional reputation for its expertise in the latest generation of equipment and has a strong, extremely well-trained team.

Ronexprim is offering an extensive portfolio of products which are integrating world's latest technologies, for example: electronic microscopes, spectrometers and diffractometers, specific equipment for physio-chemical analysis of various materials including sample preparation systems and certified reference materials, and is also offering calibrators, monitoring and automation processes systems and equipment, consultancy and assistance for various projects related to weighing and dosing, and many more.

### **Outstanding results confirm exceptional team-work efforts.**

The company received an impressive number of national and international awards that confirm the professionalism of Ronexprim team: **46 diplomas** at national & international fairs and **26 awards** of excellence from the market leading international manufacturers which Ronexprim represents.

Since 1991 a wide range of professional services were developed and carefully adapted for the Romanian market. Starting from the specialized consultancy and technical assistance for equipment, configuration, integration, and installation, covering warranty and post-warranty maintenance to customer employee's professional trainings, providing the latest software and hardware upgrades, Ronexprim is well recognized as one of the most efficient companies in their segment of activity on the Eastern European market.

### **Implementing and sustaining qualitative projects in Romania**

Ronexprim will always go the extra mile to make sure its clients are satisfied and updated with the latest technology news or international standards changes. Additionally, since 1992, Ronexprim is continuously sustaining the Romanian research community investing in educational programs of new techniques and applications, new standards, and accredited methods. The company has an impressive expertise and also an important contribution in implementing some major projects financed through various programs approved by European Union.



Ronexprim long term vision is to develop its current strategy to accommodating it to the demands of the Romanian research community well depicted by the National Research, Development and Innovation Strategy 2014 – 2020, as well by the European Union Framework Program HORIZONT 2020.

In its 30 years of business activity, Ronexprim has installed equipment in more than 20,000 industrial, research and university laboratories.

### **Ronexprim – Performances and Challenges**

According to the industrial market needs, standards evolution and research results, the market leading international manufacturers which Ronexprim represent had an accelerate development & evolution in the last 30 years represented by: continuous growth of product range, technological changes, NEW techniques, methods and applications, new standards.

The evolution represents a continuous challenge for Ronexprim team (sales and service) to rise and maintain the standards of professionalism required by both our external partners and national partners represented by our customers.

### **Accelerate know how transfer based on online communication techniques**

To assure the transfer of know-how from the producers using cutting edge technologies to the Romanian customers and especially to the R&D and academic institutes, in 30 years Ronexprim organized and participated to more than 500 seminars, 23 postgraduate courses, workshops, national / international conferences & congresses and trade fairs.

The seminars and workshops were organized for certain fields of applications, i.e., materials science, biology, medicine, electronics, metallurgy, forensics, polymers, open to the entire scientific community for information on state-of-art and worldwide perspective for wide range of products in various fields of research.

Today Ronexprim is a catalyst in the cohesion of national community of electron microscopy from Romania. Ronexprim has organized in 2016 & 2019 with the support of TFS and in partnership with SMER two editions of “Mircea Stoian” Competition of Scientific Papers competition open to all specialists using microscopes **regardless of the manufacturer**.

The COVID 2019 crisis determined an accelerated process of virtualization and integrated digitalization. The producers using cutting edge technologies start to use intensive the new online communication techniques. There are major changes in information (content & transfer), complex possibilities for remote consultancy as support in finding solutions for identifying the best application related projects and for remote customized customer training.

As authorized distributor of these producers, Ronexprim is assuring the accelerate transfer of the know-how according with the newest techniques of online communication and is maintaining its competitive advantages: cutting-edge offered equipment, its capacity to handle the largest and most complex projects, its highly trained personnel, and its outstanding customer service.

Quality, reliability, and professionalism are three of Ronexprim strengths. We are not just a supplier, for 30 years, we are a partner for every customer, we are devoted to its demands, we are supporting him to stay one step ahead, to find new ways to boost some of the most challenging questions that can change the world or to increase the productivity.

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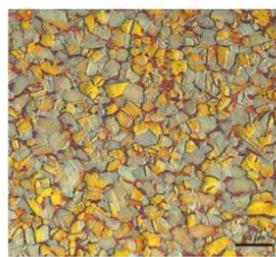
Choose the best microscope for your application: ZEISS systems provide you with information in the micro to nano ranges.



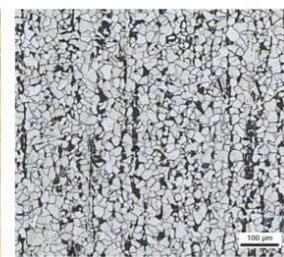
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### ZEISS Axio Observer

Your inverted microscope system for metallography



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



Steel, tempered structure  
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 Courtesy of the Materials Research Institute at Aalen University

#### Configured to your requirements

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 Axio Observer 7 materials (motorized)

**Contrasting techniques**  
 Reflected light: brightfield, darkfield, DIC, C-DIC, polarization, fluorescence  
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Axio Observer, the inverse material microscope from ZEISS, provides almost unlimited sample space. That means you will save all that time and needless effort on extensive sample preparation – a big advantage.

You will get a flexible platform, perfectly adapted to the requirements of your work in metallography. Use all the contrast methods to produce brilliant images of your structures.

Axio Observer is future-proof: simply adapt the microscope to meet your changing requirements.

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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  $\mu\text{L}$  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.

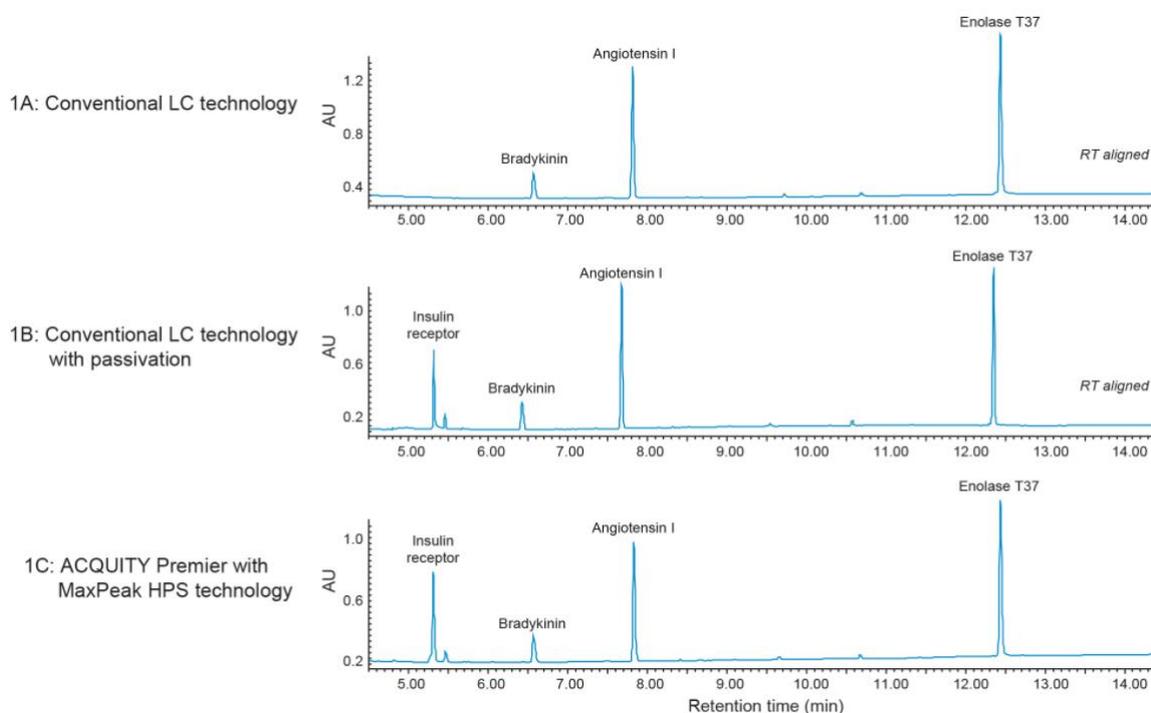
This well-conditioned LC system was a dedicated system for RPLC analysis of proteins and peptides and had performed numerous routine assays meeting various system suitability requirements for retention time

repeatability, peak tailing, and analyte recovery.

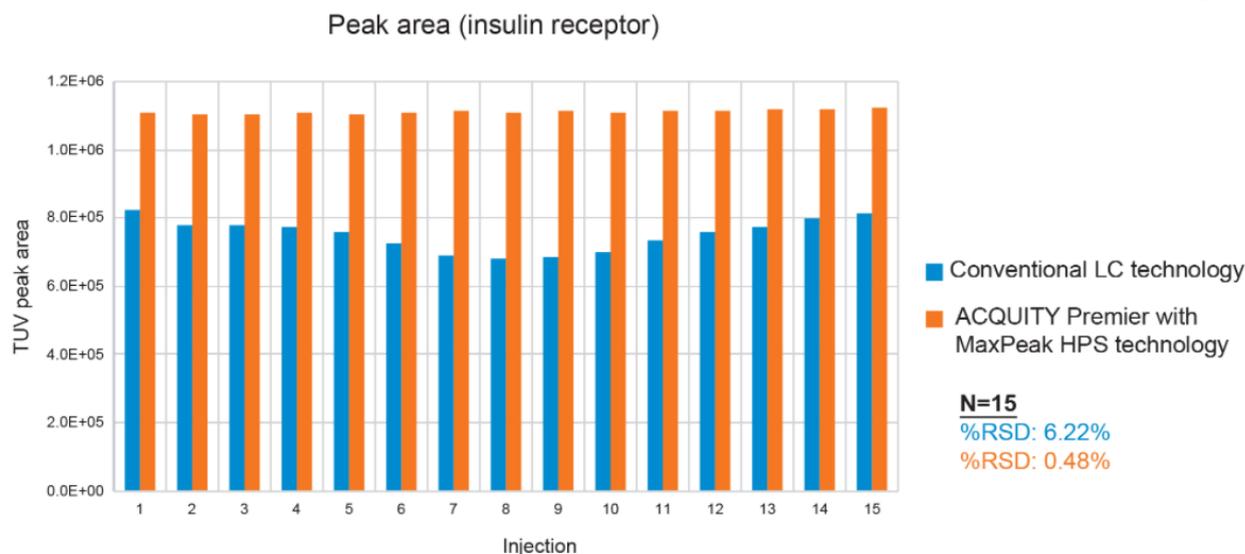
### 3. Results and discussion

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.

**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 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.



**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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