

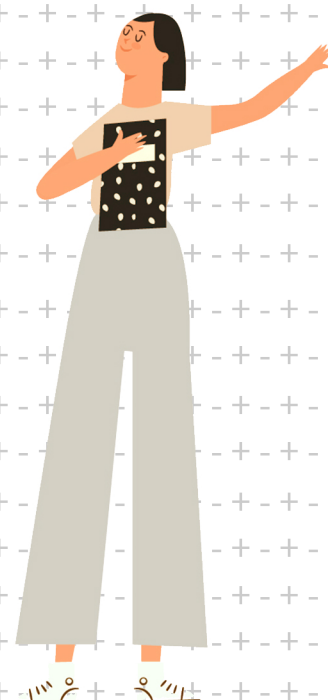
**INSTITUTUL DE CHIMIE  
MACROMOLECULARĂ  
“PETRU PONI”**



**ICMPP  
POARTĂ  
DESCHISĂ  
SPRE VIITOR**

**SESIUNEA DE COMUNICĂRI  
ȘTIINȚIFICE A TINERILOR  
CERCETĂTORI**

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19 noiembrie 2020





**SESIUNEA DE COMUNICĂRI ȘTIINȚIFICE A  
TINERILOR CERCETĂTORI  
POARTĂ DESCHISĂ SPRE VIITOR**

**19 Noiembrie 2020 • Iași • România**

*Dedicată centenarului nașterii  
Acad. Cristofor I. SIMIONESCU*

**Organizator**



**PETRU PONI**

**INSTITUTUL DE CHIMIE MACROMOLECULARĂ „PETRU PONI”**



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## **PROGRAM ȘTIINȚIFIC**





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9.00-9.05	<b>CUVÂNT DE DESCHIDERE</b> <b>EVOCARE Acad. Cristofor I. SIMIONESCU</b> <u>Dr. Valeria Harabagiu</u> , Director ICMPP	
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9.05-10.35	<b>SESIUNEA 1</b> <i>Moderator: Dr. Marcela Mihai</i>	
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9.05-9.20	<b>Ring-Opening Polymerization as a technique for the obtaining of soluble chitosan derivatives</b> <u>Bianca-Iustina Andreica</u> , Daniela Ailincăi, Luminita Marin	8
9.20-9.35	<b>Mass spectrometry monitoring of polymerization reactions in the presence of cyclodextrins</b> <u>Diana Blaj</u> , Valeria Harabagiu, Cristian Peptu	9
9.35-9.50	<b>Stabilization of cerium oxide nanoparticles by natural derived polymeric matrices</b> <u>Madalina E. Culica</u> , Andreea L. Chibac-Scutaru, Violeta Melinte, Sergiu Coseri	10
9.50-10.05	<b>Metal-organic frameworks based on a functionalized terphenyldicarboxylic acid for gas and water sorbtion</b> <u>Ioan-Andrei Dascălu</u> , Sergiu Shova, Rodinel Ardeleanu, Narcisa Marangoci, Mariana Pinteală	11
10.05-10.20	<b>Dual crystalline - amorphous Schiff Base complexes with unusual mesogen phase behavior</b> <u>Mădălin Dămoc</u> , Mihaela Dascălu, Mihai Asăndulesa, Maria Cazacu	12
10.20-10.35	<b>Polyurethane degradable hydrogels</b> <u>Alexandra-Diana Diaconu</u> , Valeria Harabagiu, Cristian Peptu	13

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10.50-12.20	<b>SESIUNEA 2</b> <i>Moderator: Dr. Petrișor Samoilă</i>	
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10.50-11.05	<b>Cellulose nanocrystals sonochemical production using organic acids</b> <u>Bianca-Ioana Dogaru</u> , Carmen-Mihaela Popescu, Maria-Cristina Popescu, Eduardo Robles, Jalel Labidi	14
11.05-11.20	<b>Crystallization and thermo-mechanical behavior of poly(lactic acid): effect of additives</b> <u>Daniela Ionita</u> , Manuela Maria Iftime, Doina Dimonie, Mariana Cristea	15



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11.20-11.35	<b>On the photoisomerization process in 4,4'-dihydroxyazobenzene functionalized with epoxy groups</b> <u>Dragoș Lucian Isac</u> , Nicușor Fifere, Anton Airinei, Elena Rusu, Dan Maftai	16
11.35-11.50	<b>Shear flow, wettability and biocompatibility of some aromatic/partial aliphatic polyimides</b> <u>S.L. Nica</u> , R.M. Albu, L.I. Buruiană, A.I. Barzic	17
11.50-12.05	<b>An original approach to wetproofed heterogeneous Pt(0) catalyst</b> <u>Alexandru-Constantin Stoica</u> , Madalin Damoc, Maria Cazacu	18
12.05-12.20	<b>Investigation of the substituents effect on electro-optical and adhesion characteristics of some conjugated polymers for optoelectronic applications</b> <u>Marius Soroceanu</u> , Andreea Irina Barzic, Liviu Sacarescu, Valeria Harabagiu	19
<hr/>		
13.20-15.05	<b>SESIUNEA 3</b> <i>Moderator: Dr. Florin Bucătariu</i>	
<hr/>		
13.20-13.35	<b>New xanthan-Co ferrite materials for removal of dyes from wastewater</b> <u>Irina Apostol</u> , Narcis Anghel, Iuliana Spiridon	20
3.35-13.50	<b>High-performance polymeric material for removal of cationic dye</b> <u>Laurențiu Baltag</u> , Corneliu Cojocaru, Petrișor Samoila, Valeria Harabagiu	21
13.50-14.05	<b>Sorption properties of wool-based composites for cleaning oil spills from the water surface</b> <u>Bogdan-Constantin Condurache</u> , Corneliu Cojocaru, Petrișor Samoilă, Valeria Harabagiu	22
14.05-14.20	<b>Sorption of heavy metal ions by chitosan hydrogels functionalized with various ligands</b> <u>Claudiu Augustin Ghiorghita</u> , Maria Marinela Lazar, Maria Valentina Dinu	23
14.20-14.35	<b>Design of chitosan/amidoximated starch beads for wastewater purification applications</b> <u>Diana Felicia Loghin</u> , Marcela Mihai	24
14.35-14.50	<b>Alkoxides as titania source: a study on the synthesized TiO<sub>2</sub> properties</b> <u>Mahu Elvira</u> , Ignat Maria, Coromelci Cristina, Liviu Sacarescu, Harabagiu Valeria	25



14.50-15.05	<b>Heavy metal ions water pollution: Tarnița closed mine case</b> <u>Marius-Mihai Zaharia</u> , Florin Bucatariu, Marcela Mihai	26
15.20-17.05	<b>SESIUNEA 4</b> <i>Moderator: Dr. Corneliu Cojocaru</i>	
15.20-15.35	<b>Alginate-based membranes with possible applications in fuel cells</b> <u>Ionela Greco</u> , Petrișor Samoilă, Corneliu Cojocaru, Valeria Harabagiu	27
15.35-15.50	<b>Influence of cross-linker nature on chitosan- sulfated titania ionic conductive membranes</b> <u>Andra-Cristina Humelnicu</u> , Petrișor Samoilă, Corneliu Cojocaru, Valeria Harabagiu	28
15.50-16.05	<b>Iminoboronate-chitosan nanofibers with antimicrobial activity for burn wound healing applications</b> <u>Alexandru Anisie</u> , Irina Rosca, Luminita Marin	29
16.05-16.20	<b>Tumor growth inhibition compounds based on PEGylated phenothiazine</b> <u>Sandu Cibotaru</u> , Andreea-Isabela Sandu, Dalila Belei, Luminita Marin	30
16.20-16.35	<b>Evaluation of silicone-based biomaterials from the bio- and mucoadhesive perspective</b> <u>Bianca-Iulia Ciubotaru</u> , Maria Cazacu	31
16.35-16.50	<b>Chitosan/oxidized pullulan hydrogel beads for controlled drug delivery</b> <u>Ioana A. Duceac</u> , Sergiu Coseri	32
6.50-17.05	<b>Tunable properties of poly(vinyl alcohol) modified with phosphoester groups for biomedical applications</b> <u>Alina-Mirela Ipate</u> , Diana Serbezeanu, Tachita Vlad-Bubulac, Elena Hamciuc, Corneliu Hamciuc	33
17.05-17.10	<b>CUVÂNT DE ÎNCHEIERE</b> <u>Dr. Marcela Mihai</u> , Secretar științific ICMPP	



## **REZUMATE**



## RING-OPENING POLYMERIZATION AS A TECHNIQUE FOR THE OBTAINING OF SOLUBLE CHITOSAN DERIVATIVES

**Bianca-Iustina Andreica,\* Daniela Ailincăi, Luminita Marin**

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

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Lately, a tremendous awareness of the suitability of using natural biopolymers for diversified applications in life is increasing. Particular attention was paid to chitosan (Ch), the completely or partially deacetylated form of chitin, obtained by treatment with strong alkali. Considering its biodegradability, biocompatibility, nontoxicity and antimicrobial activity, chitosan has attracted much research interest and has found potential applications in pharmaceutical, textile, paper and food industries, as well as in agriculture and medicine [1].

Nevertheless, the applicability of chitosan in biomedical field is still limited, due to its main drawback, which is the lack of solubility in physiological pH. In order to improve the solubility of chitosan both at neutral pH and in a basic media, the point of interest of the researchers was its chemical modification, synthesizing novel classes of compounds: carboxymethyl chitosan, quaternary ammonium salts of chitosan or chitosan grafted copolymers [2].

In this line of thought, the objective of this study was the synthesis and characterization of novel chitosan derivatives, by Ring-Opening Polymerization (ROP) technique of a 6-membered cyclic carbonate, using chitosan as an initiator. The reaction was conducted using different molar ratios between chitosan and monomer, in melt bulk or in heterogeneous system in presence of a swelling agent for chitosan [3].

The obtained derivatives were characterized from the structural point of view, using <sup>1</sup>H-NMR and FTIR spectroscopy. The supramolecular changes induced by grafting the side chains on the chitosan backbones, along with the morphology of the films casted from solution were investigated using polarized light microscopy (POM), atomic force microscopy (AFM).

The solubility of the chitosan grafted copolymers was evaluated by varying different parameters, including the solvent, pH and temperature. Some derivatives presented the property of being water soluble, in comparison to the pristine chitosan that presents solubility only in acidic media. An improvement regarding the biocompatibility of the chitosan derivatives was also observed, this being the first step for the upcoming research.

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**Acknowledgment:** This work was supported by the Romanian National Authority for Scientific Research MEN – UEFISCDI project number PN-III-P1-1.2-PCCDI2017-0569 (10PCCDI/2018).



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## MASS SPECTROMETRY MONITORING OF POLYMERIZATION REACTIONS IN THE PRESENCE OF CYCLODEXTRINS

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The work is focused on the applicative potential of matrix assisted laser desorption ionization mass spectrometry concerning the in-depth study of the polymers synthesis. Thus, ring opening polymerization of lactides in the presence of dually active cyclodextrins, acting as catalysts and initiators, represents a rather difficult reaction system from the point of view of classic structural characterization.

The present study aims to develop an analytical technique by mass spectrometry (MALDI MS) for monitoring the synthesis reaction of CDLA, following in detail, at the molecular level, the influence of synthesis parameters on the structure of cyclodextrin based products. First, the characterization techniques start from classical methods such as NMR and GPC and compared with MALDI MS, as the main technique for detecting structural changes resulting from the reactions occurring in this system. Unlike the commonly used characterization techniques, mass spectrometry is distinguished by the precision and clarity of the results obtained. The reaction conditions influence is followed using MALDI MS (temperature, molar ratio between monomer units, total concentration of monomers in the solvent and the type of solvent). For this particular system, the following parameters are quantified using the data obtained by MALDI MS: the evolution of the average molecular masses, dispersion indexes and the degree of side reactions (inter-chain transesterification reactions and backbiting).

**Acknowledgement:** This work was supported by a grant of the Romanian Ministry of Research and Innovation, PCCDI-UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0428/PCCDI/2018, contract no. 40PCCDI, within PNCIDI III.



## STABILIZATION OF CERIUM OXIDE NANOPARTICLES BY NATURAL DERIVED POLYMERIC MATRICES

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The common issue when using nanoparticles in various applications consist in their high tendency to agglomerate, leading finally to lack of the activity. Metal oxides nanoparticles have gain a lot of interest in the last years, as they are powerful catalysts under various environments. Among them, CeO<sub>2</sub> nanoparticles especially, has been extensively used in photocatalysis as well as other catalytic processes. This great interest on the CeO<sub>2</sub> nanoparticles rely on the specific properties exhibited by these nanoparticles, namely large surface area and particular composition of surface defects and oxygen vacancies [1].

In order to achieve an efficient dispersion and stabilization of the CeO<sub>2</sub> nanoparticles, a polymeric matrix is often considered, ensuring also a considerable growth of the catalytic activity, but also an efficient manipulation and recovering of the nanoparticles. Therefore, in our work, we have considered a natural-derived polymer, *i.e.*, cellulose acetate (CA) aiming to serve as a new matrix for the CeO<sub>2</sub> nanoparticles incorporation. CA films containing different amounts of CeO<sub>2</sub> nanoparticles were prepared. Before the films preparation, we functionalized the CeO<sub>2</sub> nanoparticles using a silane derivative aiming to improve the nanoparticles dispersion in the CA films.

A wide range of techniques, including spectral (FTIR, UV-Vis), microscopic (SEM, TEM, EDX) and thermal ones were employed to in deep characterize the resulted materials.

All these analyses proved that the CeO<sub>2</sub> nanoparticles were uniform dispersed into the CA matrix. Moreover, the mechanical properties of the as prepared films were considerably increased, due to the strengthening effect exerted by CeO<sub>2</sub> NPs. Finally, the optical properties of nanocomposite films revealed strong absorption bands in the UV domain (around 312–317 nm) as a consequence of the CeO<sub>2</sub> NPs presence.

### References

[1] Y. Lee, G. He, A.J. Akey, R. Si, M. Flytzani-Stephanopoulos, I.P. Herman, *J. Am. Chem. Soc.* 2011, 133, 12952–12955.

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## METAL-ORGANIC FRAMEWORKS BASED ON A FUNCTIONALIZED TERPHENYLDICARBOXYLIC ACID FOR GAS AND WATER SORPTION

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Metal-organic frameworks MOF are coordination polymers composed of organic linkers connected by metal ions or clusters [1]. The size, shape and nature of the coordinating sites of the organic ligand and, furthermore, the type of coordinating metal constitute the major factors governing the properties of the resulting coordination networks (*i.e.* thermal and hydrolytic stability, porosity, ability to interact with guest molecules, etc.)

Two new coordination polymers have been prepared based on 2',3',5',6'-tetrakis(hydroxymethyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid and Zn(II) and Cu(II) nitrate. Single crystal X-ray diffraction revealed that the zinc-containing MOF is a three-dimensional coordination polymer, that crystallizes in *R-3m* space group of trigonal system, while the copper-based MOF is a two-dimensional coordination polymer, that crystallizes in *C2/m* space group of monoclinic system.

In addition to the structural characterization of the compounds by single crystal and powder X-ray diffraction, the thermal and hydrolytic stability were evaluated. The specific surface area was determined by nitrogen and water adsorption measurements.

### References

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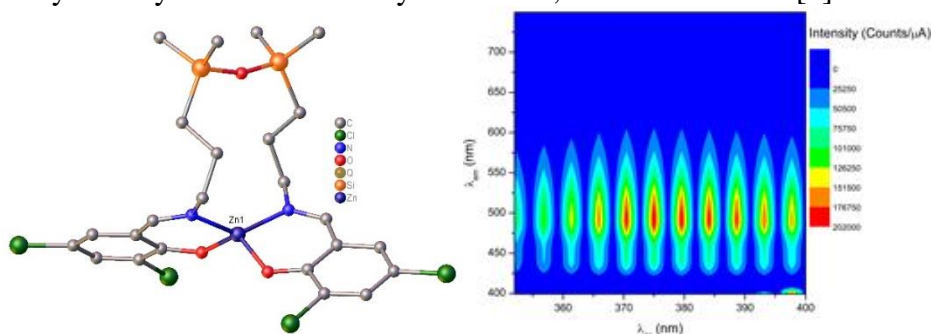
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## DUAL CRYSTALLINE - AMORPHOUS SCHIFF BASE COMPLEXES WITH UNUSUAL MESOGEN PHASE BEHAVIOR

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A new series of Schiff base complexes with siloxane spacer was obtained with different metal ions as  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  and confirmed by X-ray diffraction. Due to the amphiphile nature of the new compounds, they are able to self-assemble, both in solution and in solid state, the latter leading to the supramolecular architectures as liquid crystals induced by precipitation in water or thermal treatment. An unusual feature, both amorphous induced by siloxane moiety and crystalline induced by metal ions, will be discussed [1].



**Figure 1.** General X-ray structure exemplified for Zn complex (left); excitation-emission matrix of Zn complex suspension in DMF-water showing highly fluorescent properties (right).

The new compounds have proven to be very promising in application due to fluorescent, ferroelectric, conductive, amorphous or supramolecular architectural properties. The conformation, geometries or assembly of aggregates are explained by intra or intermolecular interactions fully demonstrated in this paper, with the emphasis on halogen binding or  $\pi$ - $\pi$  stacking. The difference between the amorphous and the crystalline state in the conduction of the different properties was noticed owing to the tetramethyldisiloxane spacer. The surroundings of the chromophore for emission seemed to be a key element in enhancement of fluorescence as the lack or the presence of the water, glass matrix, state of matter, the type of noncovalent interactions, size of the aggregates or more important carefully selection of the angle of the irradiation [3].

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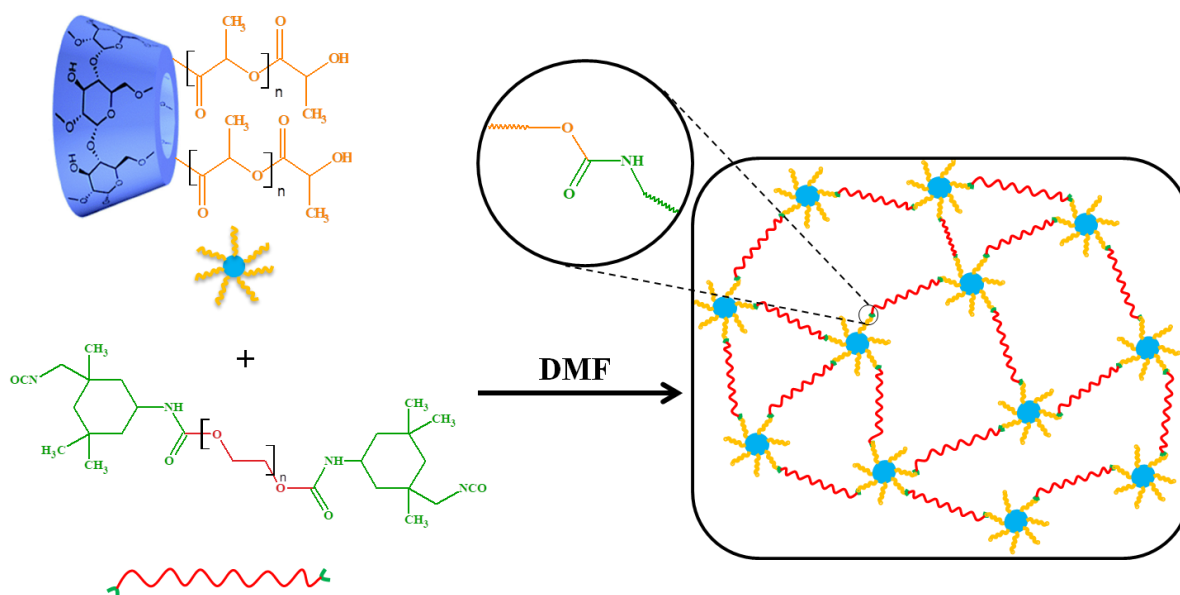
## POLYURETHANE DEGRADABLE HYDROGELS

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Polyurethane degradable hydrogels were prepared by the crosslinking reaction of bis-isocyanate-polyethyleneglycol oligomers (PEG-2NCO) with native  $\beta$ -cyclodextrin ( $\beta$ -CD) or oligolactide modified  $\beta$ -cyclodextrin (CDLA). The reason behind the introduction of the oligolactides in the structure of these hydrogels is to render them a biodegradable character. In a first step, diisocyanate prepolymers based on polyethyleneglycol (PEG) and isophorone diisocyanate (IPDI) were synthesized.



**Figure 1.** Synthesis of hydrogels

The reaction conditions for obtaining PEG-2NCO (catalyst amount, temperature, solvent, reaction time) were optimized using the matrix assisted laser desorption ionization mass spectrometry (MALDI MS). At the same time, CDLA prepolymers were obtained by the ring-opening of D, L-Lactide in the presence of  $\beta$ -CD. In the second step, PEG-2NCO was crosslinked in the presence of neat CD or CDLA (**Figure 1**), using different molar ratios of prepolymers in the reaction feed. The obtained hydrogels were purified and characterized (FTIR, swelling degree, SEM, capacity of drug release, cytotoxicity and water degradation) in order to determine the influence of the initial prepolymers ratios over the hydrogels properties.

**Acknowledgement:** This work was supported by a grant of the Romanian Ministry of Research and Innovation, PCCDI-UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0428/PCCDI/2018, contract no. 40PCCDI, within PNCDI III.



## CELLULOSE NANOCRYSTALS SONOCHEMICAL PRODUCTION USING ORGANIC ACIDS

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In the present work, cellulose nanocrystals (CNC) were produced through sonochemistry with various organic acids due to low-environmental harm of the process. The organic acids used were oxalic, maleic and citric, chosen for their acid dissociation constant and their availability in nature, making them green and cheap acidic media to produce CNCs. In all cases, the acid concentration used was 0.2 moles. By varying the pH, reaction time and temperature and depending on this, the yields ranged between 20 and 40%, similar with the yields obtained on typical CNC production [1]. Physicochemical analyses showed little differences between the different CNCs, thus indicating that the yields are mainly influenced by longer reaction times. The use of organic acids resulted in mild esterification, as observed by FTIR spectroscopy and also presented higher thermal stability than those elaborated with sulfuric acid [2]. Furthermore, the surfaces of obtained CNCs contained carboxylic acid groups which facilitate functionalization and dispersion in aqueous processing.

**Table 1.** Reaction conditions for each experiment

Sample	Acid	Direct sonication time (min)	Indirect sonication time (min)	Reaction temperature (°C)
C1	Citric	10	120	60
C2	Citric	10	150	60
C3	Citric	15	120	60
M1	Maleic	10	120	60
M2	Maleic	10	150	60
M3	Maleic	15	120	60
O1	Oxalic	10	120	60
O2	Oxalic	10	150	60
O3	Oxalic	15	120	60
S1	Sulfuric		90	60

The results show that the most effective reaction to hydrolyze cellulose into nanoparticles was O3, which is related to oxalic acid lower dissociation constant. Also, the reactions with longer periods resulted in a higher DS and carboxyl content, in particular noticeable for oxalic acid and maleic acid.

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## CRYSTALLIZATION AND THERMO-MECHANICAL BEHAVIOR OF POLY(LACTIC ACID): EFFECT OF ADDITIVES

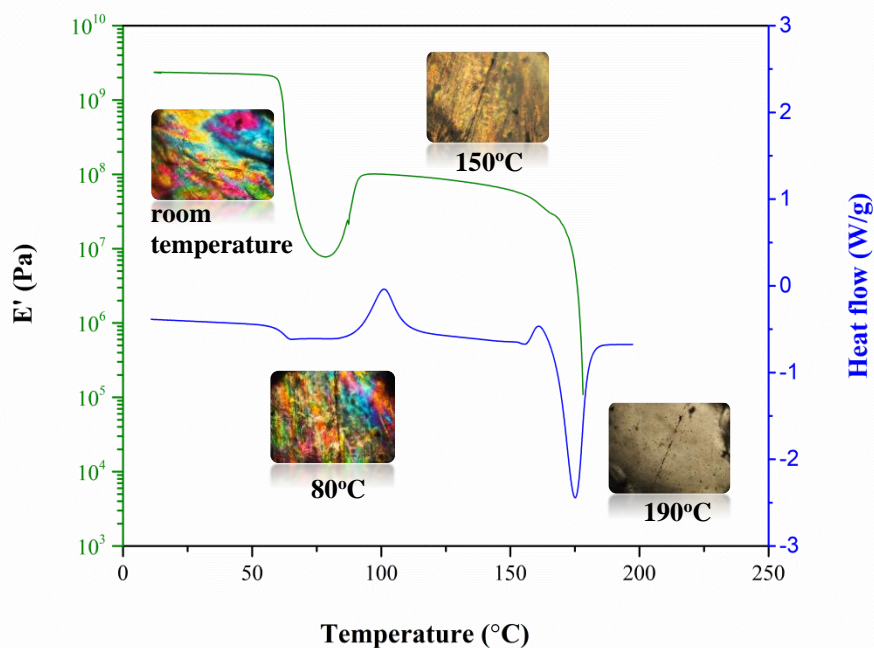
**Daniela Ionita,<sup>1\*</sup> Manuela Maria Iftime,<sup>1</sup> Doina Dimonie,<sup>2</sup> Mariana Cristea<sup>1</sup>**

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In recent years, due to increasing importance of environmental issues, biodegradable polymers, especially poly(lactic acid) (PLA) have attracted attention as a valuable biosource alternative in long term applications. Despite its huge potential some poorer properties of PLA like high brittleness and its low glass transition temperature ( $50^{\circ}\div 60^{\circ}\text{C}$ ) have hindered its use in many applications. One possible strategy in extending the use of PLA is the control of its crystallinity. Understanding the crystallization behavior is particularly essential to control PLA's thermal stability as well as thermo-mechanical properties.



The present study aims to highlight the relation between crystallinity and the thermo-mechanical properties through reinforcement and/or heterogeneous nucleation of PLA-based materials using DMA, DSC and optical microscopy. The addition of nucleating agent improves the crystallization, but hinders the melting. The synergistic effect of the nucleating agent and the reinforcement diminishes the magnitude of the  $E'$  decrease during the glass transition and results in a more complex crystallization and melting process.

**Acknowledgment:** Part of this work was supported by a grant of the Romanian Ministry of Research and Innovation, PCCDI-UEFISCDI, project number PN-III-P1.2-PCCDI-2017-0428/PCCDI/2018, contract no. 40PCCDI, within PNCIDI III.

## ON THE PHOTOISOMERIZATION PROCESS IN 4,4'-DIHYDROXYAZOBENZENE FUNCTIONALIZED WITH EPOXY GROUPS

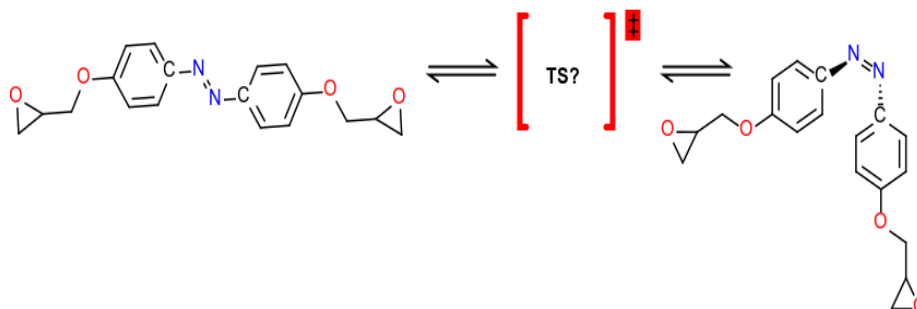
**Dragoș Lucian Isac,<sup>1\*</sup> Nicușor Fifere,<sup>1</sup> Anton Airinei,<sup>1</sup> Elena Rusu,<sup>1</sup> Dan Maftai<sup>2</sup>**

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Azobenzene derivatives (AB), in the last decades have been investigated in many directions, especially in fundamental characterization (e. g. investigation of the charge-transfer excitations in AB maleimide compounds [1]) as well as in various application fields (such as AB dye semiconductor complexes [2]). In the present study, the 4,4-dihydroxyazobenzene functionalized with epoxy groups was investigated by theoretical and experimental point of view. In particular AB exhibits two isomers: (i) trans-azobenzene (more stable by energetically point of view) and (ii) cis-azobenzene (being metastable compound). Trans-azobenzene isomer presents in electronic absorption spectra two transitions ( $\pi \rightarrow \pi^*$  which is an intense transition) and  $n \rightarrow \pi^*$  (weakly or low-lying transition). However, cis-azobenzene presents a lower intensity  $\pi \rightarrow \pi^*$  transition than in trans-isomer, but with higher intense for  $n \rightarrow \pi^*$  character. The interconversion between trans to cis forms and reverse can occur through four mechanisms [3] as follows: rotation, inversion, concerted inversion, and rotation assisted inversion, but a specific isomerization mechanism for AB compounds is still unclear and open for discussion. On the other hand, the epoxide functional group can utilize in the substitution, addition, cycloaddition or polymerization reactions. The main goal of this study was to investigate the mechanism of isomerization that can occur during the interconversion of 4,4-dihydroxyazobenzene derivative in both directions trans  $\leftrightarrow$  cis, using TD-DFT methods (PBE0 and CAM-B3LYP). Computational results indicate that the isomerization can occur by inversion pathway for trans  $\rightarrow$  cis conversion, and inversion assisted by rotation in case of cis  $\rightarrow$  trans isomerization.



**Figure 1.** Interconversion of 4,4-dihydroxyazobenzene derivative.

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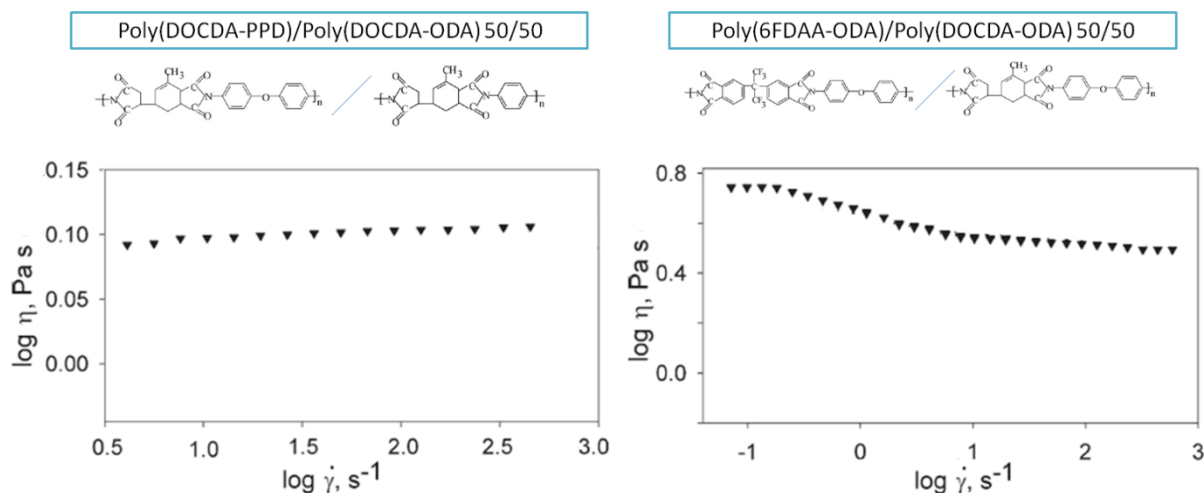
## SHEAR FLOW, WETTABILITY AND BIOCOMPATIBILITY OF SOME AROMATIC/PARTIAL ALIPHATIC POLYIMIDES

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Polyimides (PIs) containing alicyclic sequences are polymers with high chemical stability, good optical clarity and excellent mechanical properties [1]. PI blends, with aromatic/partial aliphatic sequences, were prepared by solution mixing approach [2]. Two PI systems, exhibiting a common monomer, were obtained by two-step polycondensation reaction: (1) the first one relies on the same dianhydride 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic acid anhydride (DOCDA) combined with 4,4'-oxydianiline (ODA) or *p*-phenylene diamine (PPD), and (2) the second one starts from the same ODA diamine in reaction with either DOCDA or 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA). Subsequently, the PIs were analyzed via rheological tests and the achieved data was discussed in correlation with their chemical structure. The registered data indicate a Newtonian behavior for poly(DOCDA-PPD)/poly(DOCDA-ODA) system at all shear rates, whereas for poly(6FDA-ODA)/poly(DOCDA-ODA) system, one can notice two Newtonian regions at different shear rates, separated by a pseudoplastic domain - see Figure 1. The surface hydrophobicity of the PI films influences the compatibility with red blood cells and platelets [3]. In this context, the hydrophilic/hydrophobic balance affects the hemocompatibility properties of the prepared PI samples.



**Figure 1.** Shear flow curves of the studied polyimide blends in solution phase.

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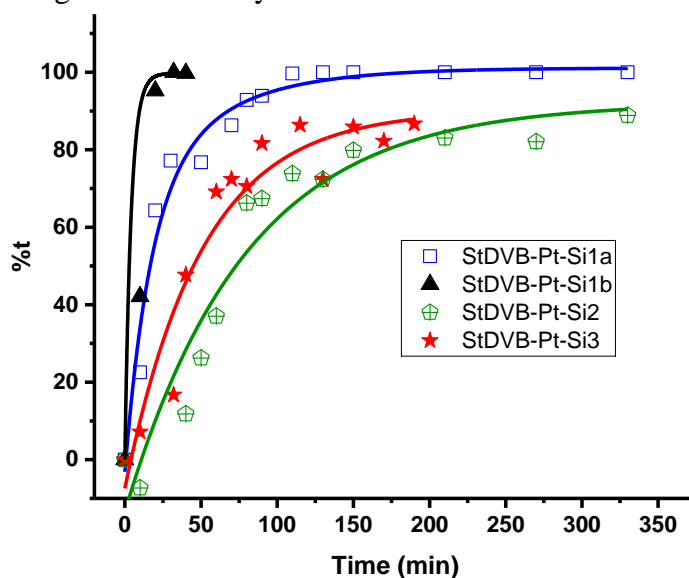
## AN ORIGINAL APPROACH TO WETPROOFED HETEROGENEOUS Pt(0) CATALYST

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New approaches and results obtained in the preparation of hydrophobic heterogeneous platinum catalyst are reported. Heterogenization is performed by depositing the platinum precursor ( $H_2PtCl_6$ ) on macroporous styrenedivinylbenzene beads followed by reduction of Pt(IV) to Pt(0) with an original reducing agent, 1,1,3,3-tetramethyldisiloxane (TMDS). This instantly reduces platinum without the need for special conditions. Simultaneous, the condensative coupling product formed as a result of TMDS dehydrogenation confers increased hydrophobicity to the resulting system. Several mixtures of TMDS with other methylsiloxane precursors have been tried in order to find an optimal formulation, which at the same time as increasing the hydrophobicity, stabilizes the platinum on the support against leaching. Catalytic efficiency is estimated in two reactions, one involving non-polar reagents (hydrosilylation), figure 1, and the other polar ones (ethanol oxidation with molecular oxygen in an alkaline medium). The catalysts have proven to be very effective in the latter case, maintaining their activity almost unchanged in several cycles of use.



**Figure 1.** Illustration of the reaction progress by the conversion degree of Si-H groups (%) in the hydrosilylation reaction in the presence of the four Pt(0) catalytic systems

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## INVESTIGATION OF THE SUBSTITUENTS EFFECT ON ELECTRO-OPTICAL AND ADHESION CHARACTERISTICS OF SOME CONJUGATED POLYMERS FOR OPTOELECTRONIC APPLICATIONS

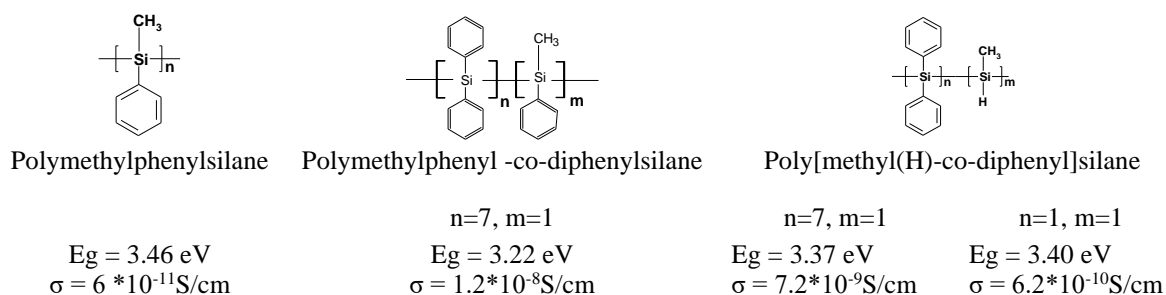
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Polysilanes possess Si-Si backbones characterized by  $\sigma$  conjugation due to significant delocalization of  $\sigma$  electrons along the macromolecular chain. This characteristics lead to interesting optical (quite low band gap energy of 3.22–3.46 eV) and semi-conductive properties that are strongly dependent on the chemical nature of silicon substituents. These polymers have attracted interest for using in different optoelectronic devices, like displays, o-leds etc. It is also known that a better adhesion of the polymer film induces a better electrical contact of the polymer with the electrode/support and implicitly improves the performance of the device [1,2].

This study deals with the electro-optical properties of differently substituted polysilanes (Figure 1) before and after doping with iodine. By using Tauc method and the standard four-point probe method, the optical band gap was proved to decrease from 3.22–3.46 eV for pristine polysilane films to 2.47–2.64 eV, while the electrical conductivities increased by 2-3 orders of magnitude for the doped ones. The best results were obtained on polysilane samples characterized by high content of phenyl groups (Figure 1).



**Figure 1.** The chemical structure of the studied polysilanes

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## NEW XANTHAN-Co FERRITE MATERIALS FOR REMOVAL OF DYES FROM WASTEWATER

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Water pollution with dyes represents a serious environmental problem nowadays as a result of persistence and toxicity of these organic contaminants [1]. Dyes are used in many industries like textile-dyeing, pharmaceutical, cosmetics or papermaking [2]. One of the most efficient technique to remove these compounds from aqueous system is adsorption on different types of materials. In this study we used several materials based on xanthan gum and cobalt ferrite to retain two dyes: Methyl Blue (MB) and Basic Fuchsin (BF). Nanocrystalline spinel ferrite  $\text{CoFe}_2\text{O}_4$  powder (CF) was synthesized by a modified coprecipitation method using iron (III) chloride, cobalt (II) chloride and castor oil solution as dispersant agent. Thin film of Xanthan gum (XG) was prepared as reference material. By dispersion of spinel ferrite powder in a Xanthan gum solution (0.5%), under ultrasonication, a film was prepared (XGCF). The last investigated material is based on Xanthan gum and silica- $\text{CoFe}_2\text{O}_4$  (XGCFT) which act as a hybrid adsorbent.

Scanning electron microscopy (SEM) and Fourier transform infrared spectrometry (FT-IR) were utilized for characterization of the all materials. CF presents ferromagnetic behavior under magnetic field (Vibrating Sample Magnetometer, VSM). The batch adsorption experiments have been performed at three different temperatures (20, 35 and 45 °C). Adsorption capacity (%) was evaluated for each material. For majority of the experiments, the XGCF material presented the highest adsorption capacity (mean value of 87%). The adsorption of MB and BF onto the adsorbents was thermodynamically evaluated. It was found that the dyes adsorption process is endothermic and spontaneous.

Considering the adsorption capacity, as well as the ease of separating the adsorbent from the environment by placing it in a magnetic field, the use of these composite materials in the purification of wastewaters become economically feasible.

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## HIGH-PERFORMANCE POLYMERIC MATERIAL FOR REMOVAL OF CATIONIC DYE

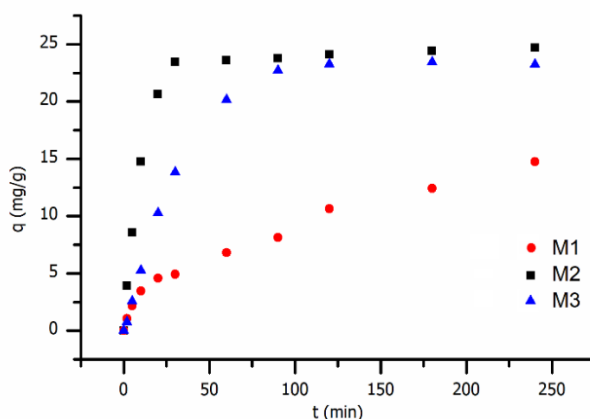
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The increment of water demand owing to population growth and economic development has conducted to the decrease in water quantity and quality [1]. The methods and materials used for water treatment and purification are diverse, depending on the nature and concentration of pollutants. An important class of materials employed for water purification deals with polymers. The polymer-based materials can be used as sorbents, catalysts, membranes (for filtration and diffusion processes), as well as flocculants [2].

This work aims to prepare adsorbents based on poly(ether ether ketone) (PEEK) for water purification. The PEEK has excellent chemical and thermal stabilities and good mechanical properties. To develop a high-performant adsorbent, the polymer (PEEK) was sulfonated. In this respect, we prepared three types of sulfonated poly(ether ether ketone) (SPEEK) with different degree of sulfonation (M1, 94%, M2, 64% and M3, 54%). These samples were applied for the adsorption of cationic dye (Methylene Blue, MB) from aqueous solutions. After a preliminary kinetic study, we selected the best sample of SPEEK (*i.e.* M2) showing the highest adsorption capacity and uptake-rate, see Figure 1. The experimental kinetic-data for M2 were fitted to the pseudo first-order (PFO) and pseudo second-order (PFO) models by linear and non-linear methods. Equilibrium parameters for MB absorption onto SPEEK were estimated from Freundlich and Langmuir isotherm equations.



**Figure 1.** Adsorption kinetics for the uptake of Methylene Blue onto SPEEK

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## SORPTION PROPERTIES OF WOOL-BASED COMPOSITES FOR CLEANING OIL SPILLS FROM THE WATER SURFACE

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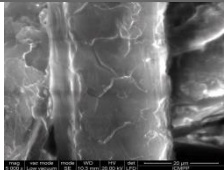
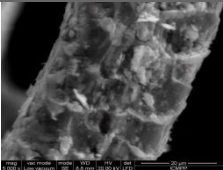
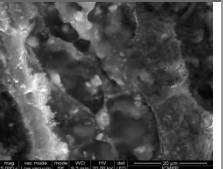
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Sheep wool has a complex structure that determines unique physical and chemical properties [1]. Oil sorption using wool-based sorbents can be an attractive method for water remediation due to their low cost, availability, buoyancy, hydrophobicity, and high sorption capacity [2]. However, wool materials show high propensity to retain large amounts of water.

To obtain wool-based high-added value sorbents for petroleum oils accidentally spilled on water surfaces, this study proposes to provide magnetic and more hydrophobic properties to wool fibers. Thus, wool-magnetite composites were prepared by in situ transformation of FeSO<sub>4</sub> in the presence of H<sub>2</sub>O<sub>2</sub> and NH<sub>3</sub> and further covering the composite surfaces with poly(dimethyl-hydrogenmethyl)siloxanes.

The structure and the properties of the composites were investigated by infrared spectroscopy (FTIR), wide angle X-ray diffraction (XRD), scanning electron microscopy (SEM), water-contact angle (WCA), thermal decomposition (TG), magnetic properties and kinetic sorption measurements. Table 1 presents several data on the preparation and properties of the wool composites.

**Table 1.** Preparation\* and characterization of wool composites

Sample code	Wool	Wool/MNP	Wool/MNP <sub>h</sub>
Morphology (SEM)			
WCA (degrees)	40	45	130
Saturation magnetization (emu/g)	-	4,90	3,98

\* Wool/MNP prepared by heating (wool, 0.457 g; 5 g, FeSO<sub>4</sub>; H<sub>2</sub>O<sub>2</sub> 3%, 10 mL; NH<sub>3</sub>, 6.4 mL; stirring at 90 °C for 1 h); Wool/MNP<sub>h</sub>: hydrophobization composite with poly(dimethyl-hydrogenmethyl) siloxanes 2%

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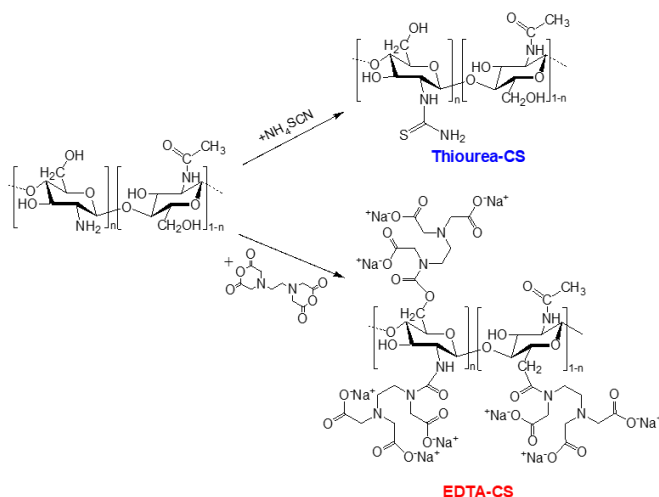
## SORPTION OF HEAVY METAL IONS BY CHITOSAN HYDROGELS FUNCTIONALIZED WITH VARIOUS LIGANDS

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A growing concern nowadays is the constant release of heavy metal ions into the aquatic environment due to anthropogenic activities (agricultural practices, landfills, industrial and urban waste) [1]. Therefore, there is an urging race worldwide aiming at the development of new and efficient materials for water purification. In this respect, sorbents based on bio-available polymers are getting an increased attention as environmentally-friendly and renewable solutions for removal of heavy metal ions from contaminated waters [2]. One such polymer is CHITOSAN (CS), a natural polycation which possesses numerous donor functional groups (amino and hydroxyl). Furthermore, the chelating properties of CS can be subsequently improved by grafting various ligands with an increased content of donor atoms onto its backbone. In this work, the preparation of some new hydrogels based on ligand-functionalized CS is investigated (**Figure 1**) [3,4]. The structural characteristics of two new CS derivatives, i.e. thiourea-CS and ethylenediaminetetraacetic acid (EDTA-CS), were followed by FTIR and <sup>1</sup>H-NMR spectroscopies, while the morphological features of the hydrogels were investigated by SEM analysis.



**Figure 1.** The synthesis of thiourea-CS and EDTA-CS

Finally, the obtained hydrogels were tested in the sorption of several heavy metal ions from simulated contaminated waters.

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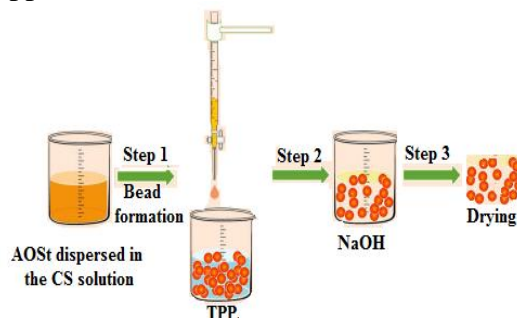
## DESIGN OF CHITOSAN/AMIDOXIMATED STARCH BEADS FOR WASTEWATER PURIFICATION APPLICATIONS

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Polysaccharides are the most abundant renewable resource on earth, with an annual rate exceeding world production of synthetic polymers [1,2], showing specific properties, such as: biocompatibility, biodegradability, polyfunctionality, high chemical reactivity, sorption capacity and chelating of different ionic species. The sorption capacity of polysaccharides is ascribed to the high hydrophilicity, due to the presence of hydroxyl groups from the glycoside units, and to the presence of a large number of functional groups (acetamide, primary amine, and hydroxyl) with high chemical reactivity. Chemical modification of polysaccharides, in particular crosslinking and grafting, can lead to interesting macromolecular suprastructures, such as gels, hydrogels, polymeric resins, beads, membranes, fibers, composites, offering many opportunities for different applications [3,4].



**Figure 1.** Schematic illustration of the preparation of composite beads.

The goal of this research is to development of a new, original method for graft copolymers of different sorts of starch (potato, wheat and rice) and acrylonitrile, in aqueous solution, by free-radical polymerization, using as initiator  $Ce(SO_4)_2$ , then modification of the starch-g-poly(acrylonitrile) nitrile groups to amide and carboxylic groups by hydrolysis with NaOH and by amidoximation with  $NH_2OH$ , respectively. Furthermore, composite beads based on cross-linked chitosan, as matrix, and amidoximated starch, as entrapped chelating resin as beads, were obtained by thorough mixing of previously prepared amidoximated starch in the chitosan solution followed by the bead formation (Figure 1). The obtained beads represent suitable macromolecular cross-linked supports with foreseen applications in wastewater cleaning, by binding metal ions and dyes from wastewater.

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## ALKOXIDES AS TITANIA SOURCE: A STUDY ON THE SYNTHESIZED TiO<sub>2</sub> PROPERTIES

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Synthesis of mesoporous titanium oxide with tailored properties is of great interest because of their potential in environmental applications. It is considered to be one of the most promising semiconductor due to his great optical, electrical, and photo-electronic properties [1]. Present study focuses the use of three different titania precursors (alkoxides) in the sol-gel synthesis process, that would tailor the properties of titania. There powdered TiO<sub>2</sub> samples were prepared by ultrasound assisted sol-gel method using titanium ethoxide, titanium isopropoxide and titanium butoxide as precursors, and pluronic F127 as mesostructuring agent. Afterward, in order to remove the surfactant from the powdered samples and empty mesopores, the samples were calcined in a furnace 723 K, for 4 hours. The obtained samples have been characterized from textural, structural, morphological, and optical point of view, showing adequate physical properties to be used in future applications, like photocatalysis. The photocatalytic activity of TiO<sub>2</sub> synthesized materials was investigated for degradation of Congo Red dye.

**Tabel 1.** Physical properties and photodegradation efficiency of TiO<sub>2</sub> eth, TiO<sub>2</sub> izo and TiO<sub>2</sub> but nanoparticles

Samples	S <sub>BET</sub> , cm <sup>2</sup> /g	Particle size, nm	Band gap energy, eV	Photodegradation %
TiO <sub>2</sub> eth	116	5.59	3.3	96.76
TiO <sub>2</sub> izo	136	5.22	3.3	98.27
TiO <sub>2</sub> but	98	8.99	3.2	95.56

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## HEAVY METAL IONS WATER POLLUTION: TARNIȚA CLOSED MINE CASE

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Different heavy metal ions pollution has become one of the most serious environmental problems nowadays [1]. The mining activity led to the contamination of surface and underground waters, being one of the most important ecological disasters in Romania with a major and continuous impact on the local community [2]. We chose Tarnița closed barite mine (Figure 1), as a case study, because it is very polluted with heavy metal ions [3] and the ecological disaster is very pronounced, being necessary a rapid recovery of the entire zone.



**Figure 1.** Tarnița closed mine polluted area

The goal of this research is to determine feasibility and efficacy of the remediation method based on ion exchange resins with high affinity toward heavy metal ions dissolved in Tarnita surroundings surface waters. Therefore, Tarnita surface water investigation was first planned, sampling for identification of contaminants (heavy metal ions) and determination of their concentrations (by Atomic Absorbance Spectroscopy). Measurements will be addressed to the qualitative/quantitative analysis of metal ions concentrations in surface waters. The environmental problem remediation is intended to be solved by obtaining sorption materials using effective preparation procedures, obtaining a library of ion exchange resins based on acrylic copolymers for the use in subsequent static and dynamic sorption experiments. Adaptive methods to obtain highly versatile materials are intended, by tuning the synergic effects of ion exchanger copolymer constituents on metal ions removal, making thus more versatile sorbents at pollutant variation in terms of chemical nature, concentration and pH.

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## ALGINATE-BASED MEMBRANES WITH POSSIBLE APPLICATIONS IN FUEL CELLS

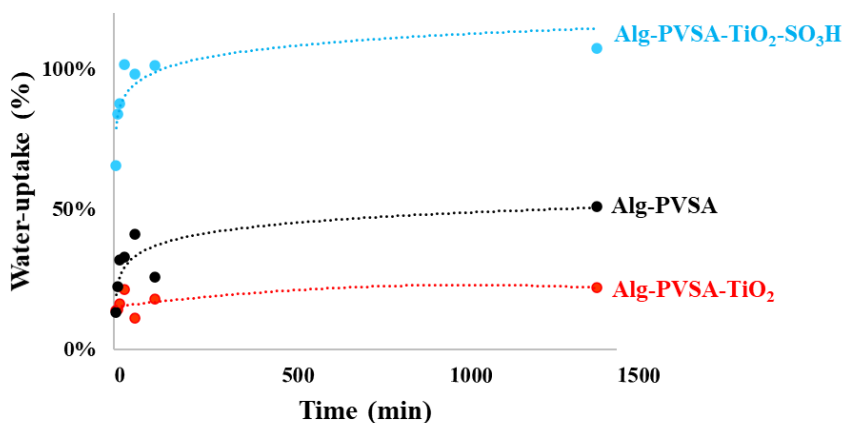
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In recent years, Proton-Exchange Membrane Fuel Cells (PEMFCs) have been under the limelight as promising clean energy conversion devices in transportation, stationary and portable applications [1]. This study focuses on the preparation and physico-chemical characterization of new alginate-poly(vinyl sulfonic acid) (Alg-PVSA) composite membranes with possible application in fuel cells.

In this respect, we prepared Alg-PVSA membranes by mixing these two polymers in aqueous solution, casting and cross-linking with  $\text{CaCl}_2$  solution. Moreover nanoparticles of  $\text{TiO}_2$  and sulfated  $\text{TiO}_2$  were added into membranes in order to improve the properties of studied materials. The developed membranes were tested for their water-uptake capacity and endurance in oxidative environment, using Fenton reagent, and acidic solution with a pH of 3. Water is required as the mobile phase to facilitate proton conductivity, playing a key role in the exploitation of PEMFC. Usually, the proton conductivity is decreasing directly proportionally with the loss of water. The high values of water uptake and the reasonable weight loss in oxidative and acidic medium suggest that these materials can be suitable for fuel cell applications. The characterization of membranes was also carried out by other appropriate techniques, such as: Fourier transform infrared spectroscopy (FT-IR), mechanical measurements and scanning electronic microscopy (SEM).



**Figure 1.** Water-uptake of alginate-poly(vinyl sulfonic acid) membranes

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## INFLUENCE OF CROSS-LINKER NATURE ON CHITOSAN-SULFATED TITANIA IONIC CONDUCTIVE MEMBRANES

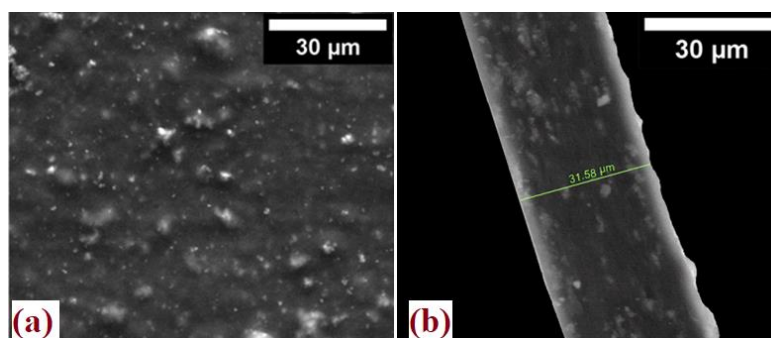
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Depletion of fossil fuel resources, along with environmental issues, are encouraging the research community to find and develop alternative energy sources, such as fuel cells, which convert chemical energy into electricity. The performance of a fuel cell is closely related to the properties of the polymer exchange membrane (PEM), which is responsible for charge transfer between electrodes and fuel leakage prevention [1].

This work proposes the development of chitosan-based composite membranes with suitable properties for use as effective PEM [2]. Sulfated titania was used as inorganic filler in order to improve both mechanical and conductivity properties. Moreover, the chemical stability of the membranes was enhanced by crosslinking with sulfuric acid, pentasodium tripolyphosphate and bis(glycidoxypropyl)-terminated polydimethylsiloxane. The chemical interaction between chitosan and sulfated titanium dioxide, also the crosslinking processes were confirmed by Fourier Transform Infrared spectroscopy. The morphological analysis provided by Scanning Electron Microscopy revealed uniform dispersion of inorganic filler in the membranes (**Figure 1**). Differences in the mechanical and thermal properties of membranes, prior and after cross-linking reactions were investigated. Also, typical tests usually applied to evaluate PEMs, such as water absorption, chemical stability and proton conductivity behaviour were performed and indicated that crosslinked membranes developed in the present study may be successfully recommended for fuel cells applications.



**Figure 1.** Surface (a) and cross-section (b) microstructure of chitosan-sulfated titanium dioxide membrane.

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## IMINOBORONATE-CHITOSAN NANOFIBERS WITH ANTIMICROBIAL ACTIVITY FOR BURN WOUND HEALING APPLICATIONS

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The aim of this study was to prepare chitosan-based nanofibers functionalized with 2-formylboronic acid by the imination reaction in heterogeneous medium.

The proposed fibers were prepared in 3 steps. First, CS/PEO fibers were electrospun from a blend solution of CS/PEO (weight ratio of 2/1) in 80% acetic acid at room temperature. The obtained fibers mat was treated with 5% NaOH to remove the residual acetic acid and then washed with ultra-pure water to obtain pure chitosan nanofibers by removing the PEO. The imination reaction was carried in heterogeneous medium, by reacting the pure chitosan nanofibers with 2-formylphenylboronic acid in different conditions to vary the degree of substitution of the obtained samples.

The as obtained functionalized chitosan nanofibers were morphologically characterized by scanning electron microscopy and polarized optical microscopy. The imination reaction and substitution degree were monitored by FT-IR and <sup>1</sup>H-NMR spectroscopy and the thermogravimetric analysis was used in order to appreciate the influence of the imination degree on the intermolecular forces developed between the functionalized chitosan chains. The water adsorption capacity was investigated by dynamic vapor sorption technique and the antimicrobial activity was screened against relevant bacterial and fungal strains. It was concluded that the as prepared materials keep a high potential for wound healing applications.



**Figure 1.** Iminoboronate chitosan nanofibers after antimicrobial tests

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## TUMOR GROWTH INHIBITION COMPOUNDS BASED ON PEGYLATED PHENOTHIAZINE

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Phenothiazine based compounds are well known for their successful application in biomedicine [1]. In the last two decades, the phenothiazine derivatives proved potential for the cancer treatment [2]. The main issue that reduces the application area of the phenothiazine derivatives is their low solubility in bio-dispersants [3]. To overcome this issue, our studies focused on the synthesis of new PEGylated phenothiazine derivatives with improved water solubility. To do this, a series of three new PEGylated phenothiazine derivatives were prepared by grafting PEG chains to the phenothiazine core. The structure of the targeted molecules was confirmed by FTIR and NMR spectroscopy. The capacity of the synthesized compounds to self-assembly in water was studied by DLS and UV-vis techniques. The particularities of the formed aggregates were investigated by fluorescence spectroscopy, SEM, AFM, POM and UV light microscopy. Their biocompatibility was assessed on normal human dermal fibroblasts and five human cancer cell lines. The synthesized compounds showed the formation of luminescent aggregates and proved excellent biocompatibility on normal cells [4]. A concentration dependent cytotoxicity against four cancer cell lines was noticed for the PEGylated phenothiazine containing an ester unit and against two cancer cell lines for direct PEGylated phenothiazine. In vivo anti-tumor investigations are in progress.

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## EVALUATION OF SILICONE-BASED BIOMATERIALS FROM THE BIO- AND MUCOADHESIVE PERSPECTIVE

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Bioadhesion is an interfacial phenomenon that would not be different from the conventional adhesion process if it did not have the special properties and characteristics which are similar to those of natural tissues. Indeed, this phenomenon encompasses not only the adhesive behavior of synthetic components (for example synthetic polymers) to the biological tissue, but also the adhesive behavior of the biological components to the tissue [1]. There has recently been a significant interest in the use of bioadhesive biomaterials in areas like the artificial soft tissue replacement and controlled release systems for the local release of bioactive agents. Such applications include systems for the delivery of drugs in the oral or nasal cavity, for intestinal administration or even for applications of the urinary bladder [2]. Silicones have unique material properties that make them ideal for certain biomedical applications. Their hydrophobic nature, low surface tension and chemical and thermal stability give favorable bi durability and biocompatibility properties [3].

The property of mucoadhesion is of particular interest due to the numerous applications in the medical field, in obtaining medical devices in the form of patches and controlled drug delivery systems. There are already many mucoadhesive formulations for medical applications such as tablets, films, powders or gels with absorption in the oral, nasal, gastrointestinal or ocular mucosa [4]. Despite the strong research interest in these fields, the specialty literature contains a limited number of contributions that relate to the fundamentals of bioadhesion and of mucoadhesion, especially on silicone biomaterials. For this reason, this study aims to discover the bioadhesive and mucoadhesive interaction between silicone-based biomaterials and simulated biological environment as well as real biological environment represented by the gastrointestinal mucosa.

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## CHITOSAN/OXIDIZED PULLULAN HYDROGEL BEADS FOR CONTROLLED DRUG DELIVERY

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Chitosan is widely used for biomedical applications due to its abundance, structure, attractive biological properties and versatility. The amino groups present in chitosan structure have a crucial role in the antibacterial activity, and also give the opportunity for drug incorporation and facile derivatizations: acylation, quaternization, esterification etc. Other strategies were reported in the literature to overpass chitosan limitations, such as blending, cross-linking or grafting. [1,2]

On the other hand, pullulan, a bacterial polysaccharide with unique properties (high water solubility, inherent non-toxic, non-immunogenic, and biodegradable), gained lately a lot of interest for various biomedical applications, and particularly for drug delivery systems. [3]

By combining the excellent biological properties of the two polysaccharides, we envisaged that new and valuable materials with increased biological performance for drug delivery applications could be obtained. Therefore, our approach for this study was to prepare chitosan beads with modified surface, using oxidized pullulan. Two strategies were employed in this scope:

- synthesis of 6-carboxy-pullulan by TEMPO-oxidation of pullulan, and
- synthesis of 2,3-dialdehyde-pullulan by periodate-oxidation of pullulan.

The oxidized samples were firstly in deep characterized, then used for the hydrogel preparation. The as prepared hydrogels were structurally characterized by means of FTIR and NMR spectroscopy. Their morphology was analyzed by recording SEM images, the sorption behavior assessed by using DVS studies and the thermal properties were also evaluated.

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## TUNABLE PROPERTIES OF POLY(VINYL ALCOHOL) MODIFIED WITH PHOSPHOESTER GROUPS FOR BIOMEDICAL APPLICATIONS

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Phosphorylated poly(vinyl alcohol) has attracted considerable interest because of its nonflammability and ability to form metal complexes, anionic polyelectrolyte hydrogels and to obtain cationic exchanged resins [1, 2]. Recently, phosphorylated poly(vinyl alcohol) has been taken into consideration for biological applications [3]. In the current study, phosphorylated poly(vinyl alcohol) (PVA/PPE) has been prepared by polycondensation technique. The chemical structure of this new formulation was confirmed by FTIR and NMR spectroscopy. The value of solid-liquid interfacial tension obtained for PVA/PPE composition was close to the value which describes a good blood-biomaterial compatibility, as a result of the presence of the hydrophobic CH<sub>3</sub> groups of *p*-methyl-phenyl phosphonic dichloride. The semi-interpenetrated polymer networks (semi-IPNs) based on phosphorylated poly(vinyl alcohol) (PVA/PPE) and chondroitin sulfat, in various mixing ratios, were prepared by chemical crosslinking. The semi-IPNs display microporous structure, with the pore diameters depending on the chondroitin sulfate content (Table 1). The swelling profiles revealed a dependence on chondroitin sulfate content, showing that an increase of the chondroitin sulfate content in hydrogel composition lead to a higher swelling ratio. Swelling and drug delivery studies were conducted in phosphate buffer solution (pH = 7.4) which mimics the pH of the intestinal fluid, at 37 °C. The hydrogels were evaluated for the release of metoprolol tartrate.

**Table 1.** Yield, pore dimensions and kinetic parameters of swelling for PVA/PPE (P3)–CS semi-IPN hydrogels.

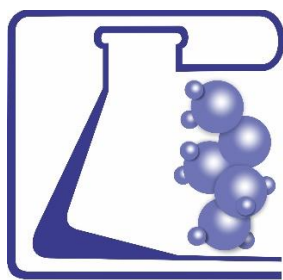
Composition (%)	Yield (%)	Pore dimension (µm)	n <sub>sw</sub>	K <sub>sw</sub> (min <sup>-n</sup> )
100/0 PVA/PPE-CS	89	60.28±0.62	-	-
90/10 PVA/PPE-CS	78	57.3±0.5	0.14	0.64
80/20 PVA/PPE-CS	76	36.6±0.4	0.06	0.92
70/30 PVA/PPE-CS	75	30.7±0.53	0.01	0.94
60/40 PVA/PPE-CS	73	22.34±0.54	0.07	0.98
50/50 PVA/PPE-CS	71	6.15±0.44	0.17	0.98

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