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BOOK OF ABSTRACTS

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ORAL PRESENTATIONS

Preparation of water-soluble carboxylated cellulose derivatives as efficient hydrogel promoters

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The aim of this study was to streamline the process of obtaining new types of hydrogels. We envisaged that, through an ingenious experimental strategy, we can obtain new cellulose derivatives, soluble in water, and moreover, due to their high functionality these derivatives fulfill the requirements of a classical crosslinking agent.

To conduct this study, we used multiple types of cellulosic samples, including cotton linters, microcrystalline, never-dried sulfite pulp, and viscose, with different degrees of polymerization, which were tested as potential sources to prepare cellulose-based derivatives, able to be used in homogeneous systems. Following this treatment, each cellulose sample was processed in such a way as to maximize the water-soluble content of the fractions. Therefore, for each cellulose type (except viscose), we could isolate three oxidized samples. All of these samples were thoroughly characterized using spectral analyses (FT-IR, ^{1}H-NMR, ^{13}C-NMR), content of negatively charged groups, and degree of polymerization. Extending the reaction time to 24 h, larger amounts of carboxyl groups are successfully introduced into the anhydroglucose unit, rendering the products as water soluble cellulose based derivatives[1].

After that new types of hydrogels based on polysaccharides chemically functionalized by oxidation reactions and polyvinyl alcohol, under mild, environmentally friendly reaction conditions, in the absence of any crosslinking agents or organic solvents were prepared and characterized. The hydrogels were prepared by the freeze/thaw technique, using the aqueous solutions of oxidized cellulose were mixed with PVA solutions in different ratios[2]. The spectral methods, FTIR, ^{1}H, ^{13}C-NMR, as well as rheology measurements were used to assess the degree of interaction between the two components.

A next step of our research was directed towards creating magnetic hydrogels, based on PVA and functionalized cellulose, with special properties with potential applications in biotechnology/biomedicine. The magnetic hydrogels were thoroughly investigated by FTIR spectroscopy, SEM microscopy, XRD, VSM, and thermal analysis.

Several improvements of our proposed strategy could be summarized as follow: the synthesized hydrogels using functionalized polysaccharides, allowed us to avoid complex and harmful solvent systems, the only solvent used being water. Moreover, the synthesis method did not require the presence of any additional reagents, such as crosslinking agents, because oxidized polysaccharides due to their high functionality, can successfully fulfil this role.

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Advancements on the selective oxidation of cellulose, via non-persistent phthalimide N-oxyl radical

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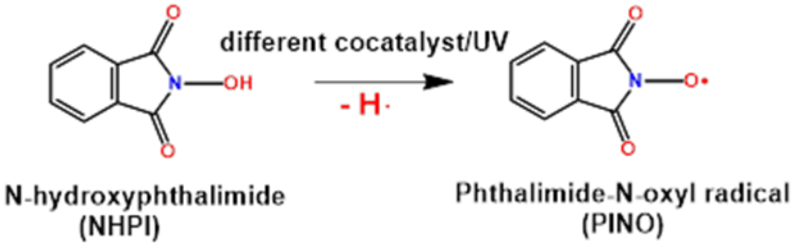
The most abundant natural polymer on Earth, i.e. cellulose, has been already implemented as a key source for a wide variety of products.1 Obviously, from extraction to the end-product, cellulose suffers a long chain of processes including delignification, extraction, purification, often derivatization (functionalization). The most common processes involving chemical modification of cellulose includes oxidation reaction.2-5 The preparation of oxidized cellulose is a challenging task due to the presence of several reactive groups in the original starting material. Introduction of the carboxyl groups is of major interest because of several useful medical properties, such as: adhesion-prevention, antitumor, wound-healing, immunostimulant.

N-hydroxyphthalimide (NHPI) as one of the best and modern catalysts, having great performances in oxidation reaction, when through a homolytic scission of the >N-O-H bond, the active species, phthalimide-N-oxyl radical (PINO) is formed, has been extensively used for the selective oxidation of cellulose, Scheme 1.6-7 This catalyst appears to be highly selective, only the primary hydroxyl groups being oxidized, whereas secondary hydroxyl groups remained unaffected.

In this presentation, we propose a few innovative protocols for the cellulose oxidation using NHPI in different systems.



Scheme 1.

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Single polyelectrolyte multilayers deposited on silica microparticles with enhanced loading/release properties for different pollutants

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Inorganic/organic composites with cross-linked polyelectrolyte multilayer thin films on the surface are very useful materials in solid phase extraction, chromatography, controlled drug delivery, water treatment etc1. This type of composite with specific functional groups, which dictates the properties at nanometric scale, could be obtained using layer-by-layer (LbL) deposition technique. In this study, silica microparticles modified with LbL thin polyelectrolyte films was used for loading/release of dyes [bromocresol green (BCG), Congo red (CR)] and copper ions (Cu2+) from simulated polluted waters. The films, consisting of poly(ethyleneimine) (PEI) (or PEI-Cu2+) and poly(acrylic acid) (PAA) were LbL deposited onto silica particles followed by selective PEI cross-linking and subsequently removal of PAA (or Cu2+ and PAA) from multilayers resulting silica//(PEI)n composite particles. The amount of dyes and copper ions sorbed onto composite microparticles depend on the number of PEI layers, while the kinetic of sorption depended more on the flexibility and accessibility of functional groups inside the (PEI)n film. The maximum recorded value, after 10 cycles of loading/release of dyes and copper ions onto silica//(PEI)n, was ~120 mg BCG/g composite2; ~40 mg CR/g composite2 and ~12 mg Cu2+/g composite3. Silica composite microparticles based on single cross-linked PEI chains on the surface could be very promising solid supports for using in multiple loading/release of different pollutants with applications in water purification or in chromatography.

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Synthesis and Characterization of Biopolymeric Membrane Containing Silver Nanoparticles for Wastewaters Treatment

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- **Introduction**

Biodegradable polymeric membranes are extensively used in various membrane processes with different driving forces (i.e. electrodialysis, nanofiltration, ultrafiltration, reverse osmosis) for removing metals ions and organic compounds from wastewaters. Materials based on eco-friendly polymers such as chitin, chitosan, cellulose and their derivatives has been widely used in many applications, due to their excellent performance characteristics, such as biocompatibility, biodegradability, bioactivity, good toughness and relatively low cost. In recent years numerous nanoparticles (i.e. silver nanoparticles, gold, titanium dioxide) were immobilized onto polymeric substrates, because these have been exhibiting a strong antibacterial activity[1-4]. In this work, a multifunctional polymeric membrane containing cellulose, chitosan and silver nanoparticles has been successfully prepared. The physico-chemical, structural and mechanical properties of prepared polymeric membrane were characterized by Fourier Transform Infrared spectroscopy (FTIR), Thermal Gravimetric Analysis (TGA) and optical microscopy.

- **Experimental methods**

A biodegradable polymeric membrane containing cellulose/chitosan-silver nanoparticles was prepared by phase inversion method. A mixture of cellulose and chitosan-silver nanoparticles was completely dissolved in acetic acid solution and stirred until a homogeneous solution was obtained. The polymeric solution was then left overnight at room temperature. After that, the prepared solution was drawn using a special knife on a glass plate and immersed in the coagulation bath containing distilled water.

- **Results and discussion**

FTIR spectra showed the reduction of the absorbance intensity of hydrogen bonds around 3420 cm^{-1}. The TGA result revealed that the prepared polymeric membrane has a good thermal stability, starting to decompose after 320°C. The optical image indicated that the chitosan-silver nanoparticles incorporated into polymeric matrix reduce the dimensions of pores in the membrane matrix.

- **Conclusions**

The polymeric membrane containing cellulose/chitosan-silver nanoparticles, prepared by phase inversion method, present a good thermal stability. The polymer–chitosan-silver nanoparticles interactions can reduce the dimensions of pores in the membrane matrix. The prepared polymeric membrane might have potential applications in fuel cells, membrane processes (e.g. electrodialysis, microfiltration, ultrafiltration, nanofiltration, reverse osmosis), in biomedical, in biochemical and in environmental fields.

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Biohybrid Materials Obtained From Plant Extracts Supported On Modified Mesoporous Silica

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Mesoporous silica nanoparticles (MSNs) coated with natural polymers are known for their enormous benefits in medical and pharmaceutical fields [1, 2]. The soluble plant polysaccharides such as pectins and mucilages are some of the best candidate on basis of their capacity to constitute their self as a matrix for the biologic active compounds being an excellent support due to their own biological effects such as protective, regenerative or healing properties. The present work reports a successful and efficient method to obtain novel biohybrid supports by coating of mesoporous silica nanoparticles with two types of plant polysaccharides (pectins and mucilages with bioadhesive properties) extracted from Althaea officinalis folium in normal and acid pH conditions. The main compounds identified in the obtained extracts were polysaccharides and polyphenols. MSNs support was synthesized in typical conditions of SBA-15 modified by using of butanol as co-surfactant and co-solvent.

The (HP)TLC studies confirmed the immobilization of active constituents. The analysis of phenol composition reveals a selective polysaccharides fraction immobilized on MSNs and evidences higher concentration of phenols in Althaea extract obtained in natural conditions while acid pH of the extraction conditions favoured immobilization of polyphenols on the surface of silica support. The immobilization efficiency of the main active compounds of extract phytocomplexes was evidenced by elemental mapping images, at the microstructural level (SEM) and by confocal laser scanning microscopy (CLSM). The last images evidenced dispersion of *Althaea officinalis* folium extract and the morphological vertical gradient of the organic compounds on silica surface. Their three-dimensional localization evidenced the nonuniformity from the point of view of the interaction bonds of the fraction compounds with the surface of support particles. SEM and TEM images showed the preservation of the mesoporous silica morphology and of the ordered hexagonal structure of SBA-15 support. The nitrogen adsorption/desorption measurements revealed a significant decreasing of the surface area, pore volume and a change in the form of adsorption-desorption isotherms. These suggest the access to some polysaccharide components into the pores. They close the micropores and some of them are molecularly deposited over the mesopores. The variety of compounds of these extracts also does not exclude the existence of polysaccharide components with larger molecules outside the pores. The higher loading leads to the polysaccharide interaction with the formation of the adsorbed layers outside of the MSNs pores.

The cytotoxicity of MSNs loaded with *Altaeae folium* extracts with different concentration, was determined by evaluating the percentage cellular viability in two cell lines: the cell line of mouse fibroblast (NCTC clone 929) and human epidermoid carcinoma of larynges cells line (Hep-2). The results were compared with that of the supported *Betonica officinalis* enriched extract in polyphenols and flavonoids. The cytotoxicity of SBA-15 silica loaded with *Altaeae folium* extract with the highest concentration (NNI) was determined by evaluating the percentage cellular viability. The results were compared with that of *Betonica officinalis* enriched extract in polyphenols and flavonoids known as natural antioxidant. The low cytotoxicity and good biocompatibility of biohybrid support was obtained as compared with that of supported *Betonica* extract. Thus, both the effect of extracts immobilization on mesoporous silica nanoparticles and the effect of the organic matrix, composition and concentration of polyphenols on cytostatic activity were highlighted.

These results sustain the possibility to develop new biohybrid delivery vehicles for active compounds that can be compatible with the human body and not to cause side effects. These properties made them highly promising in pharmaceutical field.

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Synthesis and characterization of new triphenylamine-based polyimides for electrochromic applications

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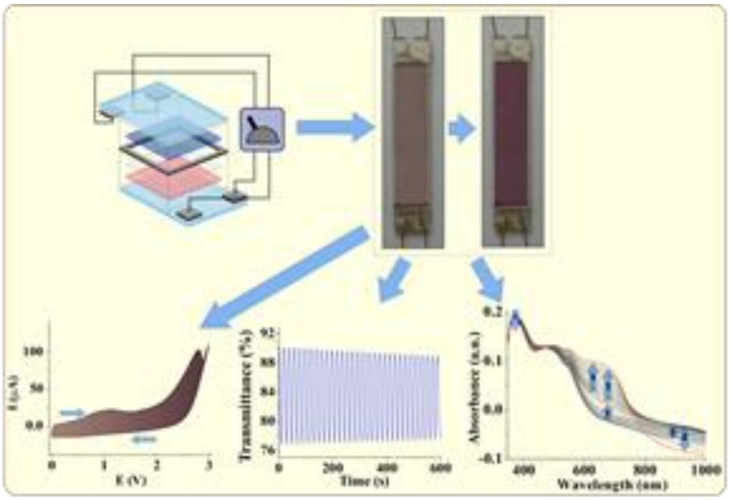
Among the polymers widely studied for applications in advanced techniques, aromatic polyimides have received considerable attention due to their outstanding thermal stability associated with good electrical and mechanical properties.1 Polyimides rank among the most heat-resistant polymers and are widely used in high temperature plastics, adhesives, dielectrics, photoresists, nonlinear optical materials and membrane materials for separation, among others. Additionally, polyimides are used in a diverse range of applications, including the fields of aerospace, defense, and opto-electronics; they are also used in liquid crystal alignments, composites, electroluminescent devices, electrochromic materials, polymer electrolyte fuel cells, polymer memories, fiber optics, etc.2 The electrochromic behavior of polymers is based on the redox behavior of the polymers and the electrochromic effect occurs when their color can be alternated by applying a potential. This interesting property has led to many technological applications, such as smart windows, automatic antiglazing mirrors, largescale electrochromic screens and chameleon materials.3 Owing to their attractive electroactive and photoactive properties, various TPA derivatives and polymers are developed for optoelectronic applications, such as electrophotography, electroluminescent diodes, field-effect transistors, solar cells, memory devices and electrochromic devices. TPA can be easily oxidized to form stable radical cations as long as the para-position of the phenyl rings is protected and the oxidation process is always associated with a strong color change.4 Taking all this into account, four electrochromic polyimides containing different electrochromophores and exhibiting longterm stability have been developed for electrochromic application. Here we report the design, synthesis and investigation of this novel electrochromic polyimides with high molecular weights based on triphenylamine derivatives that were synthesized from two novel diamines and two chromophores-based dianhydride by polycondensation reactions in solution. The influence of the structural motif on the thermal, photophysical, electrochemical properties and their electrochromic behaviours has been thoroughly explored and compared to each other.



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Cellulose - derived matrices for functionalized CeO_2 nanoparticles immobilization, and their photocatalytic behavior

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Today, the society is dominated by new concepts, related to sustainability, ecology, green methods, all deriving from the incessant concern about polluting industrial processes, finite oil resources, which have a negative impact on quality of life. In strong relationship with these global issues, photocatalysis plays a pivotal role, meeting the requirements of sustainable chemistry and green organic synthesis, with applications in a large variety of processes, from organic pollutants mineralization to fine organic reactions, its great benefit consisting in the direct conversion of light energy into chemical energy, ensuring thus a green, sustainable and economic approach to limit the environmental pollution.

The common issue when using nanoparticles in various applications consist in their high tendency to agglomerate, leading finally to lack of the activity. Metal oxide nanoparticles have gain a lot of interest in the last years, as they are powerful catalysts under various environments. Among them, CeO_2 nanoparticles especially, have been extensively used in photocatalysis as well as other catalytic processes. This great interest on CeO_2 nanoparticles rely on the specific properties exhibited by these nanoparticles, namely large surface area and particular composition of surface defects and oxygen vacancies [1,2].

In order to achieve an efficient dispersion and stabilization of CeO_2 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 would like to report the fabrication of a tunable and flexible reproducible cellulose-based platform for immobilization of surface functionalized CeO_2 nanoparticles. To achieve that, cellulose acetate as a versatile and soluble reagent in common organic solvents was used, followed by its deacetylation under alkaline medium, to regenerate the cellulose structure, subsequently oxidized using the TEMPO mediated protocol. The resulted nanocomposites were successfully tested as photocatalysts for the photodegradation under UV irradiation of the hazardous pollutants methyl orange, Congo red and 4–nitrophenol. It was revealed that the amount of attached CeO_2 nanoparticles and the matrix type strongly influence the rate and the mechanism of photodegradation or the reaction pathway, the versatility of the proposed platforms being a promising alternative for other existing catalytic systems.

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Oxidized pullulan for fine-tuning a chitosan-based drug delivery system

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- **Introduction**

Fine-tuning materials for controlled drug delivery can be an efficient approach to address the issues related to conventional drug administration: high dosages, repeated administration, low efficacy, severe side effects, toxicity etc. Therefore, the aim is achieving a drug delivery system that does not only load and release a specific therapeutic compound, but also exhibits properties such as biocompatibility or antibiotic activity, rendering in a challenging research subject. [1]

- **Material design and preparation**

Chitosan porous beads have been chosen for surface modification with oxidized pullulan derivatives due to the fact that they are easily obtained versatile materials. Two coating strategies have been explored – physical *vs.* chemical surface modification-, and, consequently, two selective oxidation reactions of pullulan were employed. The TEMPO-mediated oxidation leads to the introduction of carboxyl groups at the primary hydroxyl moieties of pullulan. By comparison, the periodate oxidation yields in the transformation of secondary hydroxyl groups into aldehyde moieties. Thus, chitosan beads can be coated through the amino groups either by electrostatic interactions with 6-carboxy pullulan or by imide bonds with 2,3-dialehyde pullulan, respectively.

- **Drug loading and release studies**

The drug delivery performance of the prepared materials were studied using 3 model drugs. The results indicated that the loading efficiency and the release behavior are strongly dependent on the final composition of the polysaccharide beads.

- **Model fitting**

The release mechanism was further analyzed by fitting different equations using the Matlab software. Seven empirical mathematical models that are frequently reported in the literature concerning the characterization of drug delivery systems were chosen and fitted to the experimental data: zero order, first order, Higuchi, the power law (Korsmeyer-Peppas & Ritger-Peppas model), Peppas-Sahlin, Weibull, Gompertz. [2-7] The drug release kinetics are best described by the first order equation and by Weibull model, which is correlated with a typical behavior of release of a soluble drug from a porous matrix. Particularly, chitosan-based beads and those coated with TEMPO-oxidized pullulan exhibited an anomalous behavior, while the periodate-oxidized pullulan induced a release behavior primarily based on diffusion.

- **Conclusion**

The reported findings suggest that the fine-tuning of chitosan beads with oxidized pullulan derivatives was successfully achieved, and they can be a promising toolkit for controlled drug delivery.

- **Perspectives**

Further efforts are needed to integrate active principles into the structure of hydrogels, in an attempt to ensure optimal temperature and pH conditions for its controlled release.

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Degradable hydrogels for drug delivery applications based on poly(2-isopropenyl-2-oxazoline)

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- **Introduction**

Hydrogels are three-dimensional hydrophilic cross-linked polymer networks that have the ability to retain high amounts of water.[1] Hydrogels are versatile materials with a wide range of applicability in agriculture, hygiene products and biomedicine.[2] In the swollen state their texture is wet and soft, thus resembling the living tissue and can provide temporal control over the release of various therapeutic agents, including small-molecule drugs, proteins and cells. However, all polymers have their advantages and disadvantages, so that the selection of a certain polymeric material is always a compromise regarding synthetic accessibility, controllable degradability and capability to protect labile drugs from degradation, and biocompatibility. Poly(2-isopropenyl-2-oxazoline) (PiPOx) is a polymer that has recently emerged as a suitable platform for the development of synthetic hydrogel materials due to its interesting properties such as water-solubility, biocompatibility, non-toxic and non-immunogenic response, and versatile post-polymerization modification reaction with di(carboxylic) acids.[3-6]

The present study highlights the use of PiPOx, as biocompatible functional polymer to develop synthetic degradable hydrogel materials for drug delivery applications.

- **Experimental methods**

Hydrogels were obtained by cross-linking PiPOx with water-soluble dicarboxylic acids such as succinic, malic, tartaric, glutamic, aspartic and cysteine. The reaction was performed at 60 °C for 24 hours, using water as the solvent. The incorporation of drugs within the hydrogels was carried out in situ. The drug release experiments were performed in PBS (pH 7.4) at 37°C. The water absorption was monitored gravimetrically, while the drug release was followed using UV-VIS spectroscopy.

- **Results and discussion**

The FT-IR data shows the successful modification reaction and revealed that all dry polymer networks have the same characteristic signals regardless of the cross-linker structure. The ESD increased with the hydrophilicity of the cross-linker. Hydrogels degradation was monitored in PBS, at pH1 and pH8 and was strongly dependent on the nature of the cross-linker. Hydrogels cross-linked with tartaric and malic acid were more susceptible to hydrolysis even in PBS as compared to succinic acid, due to the activating neighboring effect of the hydroxyl group on the ester bond. Finally, the drug delivery potential was also assessed using propranolol as model drug. The drug release rate could be simply controlled through variation of the cross-linker chemical nature.

- **Conclusion**

PiPOx-based hydrogels with tunable water uptake were obtained using a green chemistry approach. The hydrogels displayed pH degradability when tested in simulated physiological fluids, while the drug release at pH 7.4 was affected mainly by drug–hydrogel network interactions.

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Enzyme activity of β-galactosidase immobilized in polyelectrolyte multilayers deposited on corona charged composite substrates

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In the present paper chitosan and xanthan polyelectrolyte multilayers (PEMs) deposited on composite polylactic acid (PDLA) / poly(ε-caprolactone) (PEC) substrates were investigated. The substrates were prepared by casting a mixture of two chloroform solutions of 1% w/v PDLA and 1% w/v PEC at the desired ratios (0/100, 25/75, 50/50, 75/25 and 100/0). The crystal structure of the substrate was investigated by differential scanning calorimetry (DSC). Based on the melting behavior it was suggested, that PLA and PEC are not miscible at molecular level and no co-crystallization is realized. The substrates obtained were charged in a corona discharge by means of a corona triode system for 1 minute under room conditions. The corona triode system consists of a corona electrode (needle), a grounded plate electrode, and a metal grid placed between them. Positive or negative 5 kV voltages were applied to the corona electrode and 1 kV voltage of the same polarity - to the grid. The normalized surface potential dependences on the storage times of positively and negatively charged substrates were investigated. The results obtained show that the values of the normalized surface potential of negatively charged substrates decay faster than those of the positively charged ones. It was also established that the surface potential decay depends on the substrates type. Layer-by-layer (LbL) technique was used for multilayer deposition on the substrates. PEMs with 8 layers were obtained. The enzyme β-galactosidase was immobilized in the obtained polyelectrolyte multilayers. The enzyme activity of the immobilized enzyme β-galactosidase was studied. The experimental results obtained show that the enzyme immobilization in positively charged films show higher activity compared to the negatively charged ones, independently of substrates type.

New sorbents based on poly(amidoxime)/chitosan beads

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The beads ionic composites are a special class of porous composite materials, with different applications in various domains. Depending on their sizes the ionic composites can be macro- or nano-composites. They could be obtained from different organic or inorganic components. Ecological concerns resulted in an increased interest in the use of renewable products.

Beads derived from polysaccharides attracted a strong interest in the last decades as a more cost-effective alternative to the existing sorbents, like activated carbon and synthetic ion exchangers[1-3]. Heavy metals and dyes coming from industrial processes as paper processing, paints and pigments, textiles, food and cosmetics industry, fabrication of electronics, mines activities, ceramic production, are recognized as very dangerous pollutants. Conventional methods such as biological treatment, coagulation/flocculation, chemical precipitation, solvent extraction, membrane filtration, and oxidation, employed for the dye removal from industrial wastewaters, are not always effective. Adsorption is considered an effective and economical method to remove dyes and metals ions even at high concentrations, having some advantages such as flexibility in the selection of the adequate sorbent and operation, and the production of effluents suitable to be reused[4,5].

In recent years, particular attention has been addressed to the synthesis of grafted copolymers based on starch, this being one of the most convenient ways to modify the properties of starch. Particularly, grafting of acrylonitrile on starch gives the possibility to perform further chemical reactions and to synthesize new highly added value materials for various applications, such as: soil conditioners, additives for paper and textiles, adhesives, enhanced oil recovery, sanitary products, drug delivery devices, wastewaters remediation, etc.[6,7].

Herein, some beads sorbents based on polysaccharides grafted with poly(amidoxime) and chitosan were prepared and characterized. The obtained sorbents were used for adsorption of metal ions (Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+}) and anionic dyes (Congo Red and Direct Blue 15) as a function of sorbent composition, synthesis strategy, pH, sorbent dose, contact time, initial concentration of metal ions or dyes, and temperature, respectively. The beads have reusability in sorption/desorption cycles with no significant decrease in sorption capacity.

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Preparation of Hybrid Nanobiocomposites via Synthesis of Biologically Active Silver or Gold Nanoparticles Supported on Cellulose Fibres and Hydrogels

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Polymer nanocomposites which consist of metal nanophase dispersed throughout a polymer scaffold are one of the major application areas for nanoscale technology. Last decades, the use of natural polymers to prepare natural-based composites including hybrid composites with metal nanoparticles (NPs) has been used to develop of environmentally-friendly materials for various applications. One of the most elaborated direction is to join biobased, biodegradable and low-cost material with the antimicrobial properties. In this study the results on the chemical aspects of a modification of cellulose by chemical reduction of the silver and gold ions are considered.

To produce cellulose-metal composites, powder celluloses (PC) obtained from hardwood pulp and flax fiber wastes and super-swollen hydrogels (HG) were used as matrices. The HG were prepared via spontaneous self-assembly and aggregation of cellulose chains from N,N-dimethylacetamide/LiCl solutions[1]. They contained no more than 3 wt.% of cellulose and retained a large amount of water (up to 2500 wt%), had high porosity and specific surface areas, that necessary to fix the reduced metal NPs in the cellulose matrix. The pores perform a barrier function, preventing the agglomeration of NPs.

Synthesis of silver and gold nanoparticles was carried out directly in the matrices of the powder cellulose and in the hydrogels using method of reducing Ag^+ ions from $AgNO_3$ solution and $[AuCl_4]^-$

ions from $HAuCl_4$ solution with a sodium citrate as a reducer, according to Turkevich method[2] (Fig. 1).

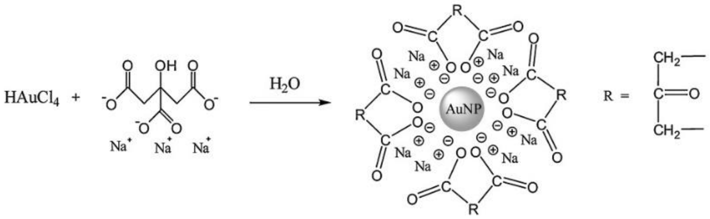

Figure 1. Synthesis of gold nanoparticles by Turkevich method

The presence of end reducing groups in the cellulose chains allowed the reduction without a reducing agent. The content of the reduced metal, in this case, was low; however, in the presence of the sodium citrate, the reduction proceeded at a high rate and resulted in a larger content of reduced metal in the samples. The cellulose fibres and the HGs played the roles of the neutral matrices as the stabilizers of the reduced metal particles. The reduction proceeded to zero-valent NPs of metals directly in the matrix.

The obtained compounds were hybrid composites of cellulose fibers/hydrogel and metals. This was confirmed by the methods of FTIR and X-ray spectroscopy, WAXS, and SEM. The composites HG-Ag and HG-Au contained the low content of Ag(0) (< 1 wt.%), the metal content in the PC was much higher (to 4.4 wt.%). The embedded silver or gold particles were nanoparticles with the size ranged from 5 to 40 nm. The composites containing Ag and Au (from 0.2 to 4.4 wt.%) exhibited the antibacterial properties against gram-positive (*Staphylococcus aureus*) and gram-negative (*Escherichia coli*) bacteria.

Thus, the hybrid composites with silver or gold nanoparticles were synthesized by the "green" method in a matrix of the renewable polymer, at low temperature and atmospheric pressure, and in the presence of environmentally friendly reagents.

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Improved Nutraceutical Based Systems as Benzydamine Hydrochloride Carriers

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Casein, a milk protein that self-assembles and form micelles in aqueous media, can interact with a wide range of drugs (hydrophilic and hydrophobic). This property makes it extremely favorable for drug delivery applications. In the present study nano- and micro-sized casein hydrogels made by ionotropic gelation with sodium trypolyphosphate acting as crosslinker and their properties as drug delivery system are investigated. The active compound which is loaded is Benzydamine hydrochloride.The gel particles are formed at different casein concentrations, different casein/crosslinker ratios, and in the presence of ethanol as cosolvent. The interactions between the casein and the drug are investigated by FT-IR spectroscopy. The particle size was determined by Dynamic light scattering method and varied between some hundred nanometers and several microns. The yield and the loading efficiency of the particles depended strongly on polymer concentration and polymer/crosslinker ratio. The thermal stability and the phases of the obtained structures and the bare materials were investigated with differential scanning calorimetry technique. The release kinetics of Benzydamine Hydrochloride in saline buffer was evaluated and modelled mathematically.

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Study of the Interaction of Fluorescent Polymeric Sensors Containing Fluorescein Derivatives with Some Quenchers and Sensing Characteristics Enhancement by Au NPs

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Progress and development at the nano-scale in chemical sensing fields was focused on controlling of the parameters related to the sensing properties, on improving the detection limits, sensitivity and specificity of both polymeric materials containing fluorescent units (dansyl, fluoresceine, pyrene or stilbene) in the structure and of the hybrid nanocomposites based on metallic nanoparticles, combining the advantages of organic polymers with those of the inorganic phase. On this line, fluorescence-based assays and detection techniques were used as biologically sensitive tests. Gold and silver nanoparticles are among the most studied nanostructured materials [1] used for biomolecule identification and for metal ion detection in environmental screening due to the highly stable optical and chemical properties of gold and the sharp surface plasmon resonance signal of silver. In addition, noble metal NPs showed good compatibility in a wide range of applications such as catalysis, optical imaging, solar cells, electronics, catalysis, sensors [2] and particularly in therapy and bioimaging. Their synthesis implies the possibility of using multiple approaches, followed by chemical modification or encapsulation in order to improved their colloidal stability, biocompatibility, or selectivity directed to specific sites [3].

The present paper reports an attractive way to improve sensor sensitivity by the *in situ* photogeneration of gold nanoparticles (Au NPs) in photopolymer matrices. The solution of previously synthesized fluorescein-based copolymer, poly[N-acryloyl-(*D/L*),(-/+)-phenylalanine-*co*-(*D/L*),(+/-)-N-methacryloyloxyethyl-N'-2-fluoresceinylthiourethane-butyl(urea)] (A-*D/L*-Phe-*co*-*D/L*-MABU-F), was subjected to UV irradiation for 10 min in the presence of Irgacure 819 and $AuBr_3$ precursor. The polymeric materials obtained were tested for the detection and monitoring of a category of compounds with a toxic effect on humans, namely various metal salts such as Co^{2+}, Cu^{2+}, Cd^{2+}, $(UO_2)^{2+}$, Pb^{2+}, Zn^{2+}, Hg^{2+}. The *in situ* growth of Au nanostructures into polymer matrices under the action of light was confirmed by UV spectroscopy and TEM analysis. The TEM images allowed the visualization of the gold NPs (sizes of 1–7 nm in A-*D*-Phe-*co*-*D*-MABU-F and of 2–13 nm in A-*L*-Phe-*co*-*L*-MABU-F) which are mainly spherical in shape. The quenching experiments demonstrated that both copolymeric materials showed a higher sensitivity for uranyl and copper ions compared to the other metal ions.

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Determining the Surface Energy of Nanoparticles from their Interfacial Immersion Depth in Pickering Emulsions

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The nanoparticle' surface functional groups may determine their reactivity but also their collective behavior, such as ability to aggregate, disperse, attach on surfaces, flow, etc. The wettability and surface energy of nanoparticles can serve as one of the essential parameters to describe the surface state of the nanoparticles and predict their collective behavior. For example, nanoparticles with a relatively high dispersive to polar component may have the tendency to aggregate in air and in water but could be excellent for pelleting. This may enable a holistic classification of nano-powders into various categories. Contact angles and surface energies are easy to measure on macroscopic surfaces with the standard methods, but these methods cannot be used for nanoparticles and thus new methods must be developed. The nanoparticle immersion depth determines the type of Pickering emulsion, either oil-in-water or water-in-oil.[1,2] Therefore, the Pickering emulsion phase is already a good gauge for particle polarity. In this work we demonstrate that by trapping nanoparticles at oil-water interfaces in Pickering emulsions and by determining their interfacial immersion depth it is possible to determine their surface energy. Pickering emulsions of water immiscible monomers were generated with a series of surface functionalized silica nanoparticles, which differ in their surface polarity. Next, the Pickering emulsion was polymerized to trap the silica nanoparticles at the interface. The surface energy of nanoparticles was determined from the values of the contact angles at polymer/water interface using different models. This method may become a standard method for determining the surface energy and its components for nanoparticles.

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Aliphatic polyester/thermoplastic polyurethane (TPU) blends

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- **Introduction**

The growing concern of pollution due to landfills and incineration of fossil-based synthetic polymers led to focusing on biodegradable polymers, especially in case of short shelf-life packaging. Aliphatic polyesters i.e. polyglycolic acid, polylactide, polycaprolactone, polyhydroxyalkanoates, their copolymers and blends appear as promising substitutes of fossil-based synthetic polymers due to their valuable characteristics[1]. Microbial polyesters are a fascinating class of biosynthesized polymers, with good mechanical and barrier properties. Their representative materials are polyhydroxybutyrate (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) which are commercially available. They exhibit a high strength and crystallinity degree (around 50%) but also brittleness and have a high price. These drawbacks are usually solved by plasticizing, copolymerizing or blending with elastomeric materials[2]. Polyurethanes are a versatile class of polymers with a broad range of chemical compositions, properties and architectures, from elastic to rigid materials. Their biodegradability may be also tuned by modifying monomer structure and composition[3]. PHB or PHBV properties may be enhanced by blending with suitable polyurethanes. In this work, the influence of a polyurethane with biodegradable sequence (TPU) on the properties of PHBV was studied. The PHBV/TPU blends were obtained by melt mixing and were characterized by thermal and mechanical tests.

- **Experiental methods**

PHBV/TPU blends were prepared in a Brabender LabStation (Duisburg, Germany) equipped with a 30 cm^3 cell at a temperature of 170 °C for 10 min at a rotor speed of 50 rpm. The films for mechanical characterization were prepared by compression molding.

- **Results and discussion**

The characterization of the PHBV/TPU blends by thermo-gravimetric analysis showed no significant influence of TPU on the thermal stability of PHBV. However, the influence on the mechanical properties was important. TPU increased the PHBV flexibility, observed by a decrease of the modulus of elasticity and the increase of the mechanical losses in the dynamic mechanical analysis of the blends. Similarly, the shift of the glass transition temperature to higher values with the introduction of TPU in PHBV may indicate increased compatibility.

- **Conclusions**

PHBV/TPU blends may be a valuable alternative to common synthetic polymers in packaging applications due to the improvement of thermal and mechanical properties as well as the lowering the price of polyhydroxyalkanoate biopolymers.

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Chitosan and Chitin from Unexplored Resources – Unconventional Sources for the Design of Multifunctional Materials

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- **Introduction**

Recent advances in the chemistry of chitosan derivatives have opened up a wide range of medical and pharmaceutical applications, out of which more and more are related to tissue engineering or drug delivery system. These applications are always backed up by the concepts of biodegradability and the impact on the environment. Compositionally, chitosan includes as functional groups C^3 - OH, C^6 - OH, C^2 - NH$_2$, amino acetyl and glycosidic bonds [1]. Out of these, the amino acetyl bond is as stable one due to the fact that the glycosidic bond is not easy to fracture, while C^3 - OH belongs to a secondary hydroxyl, it cannot rotate freely, and it has an important steric hindrance and therefore it does not react easily. Thus, the chemical reactivity of chitosan is the consequence of C^6-OH and C^2 - NH$_2$bonds.The distribution of functional groups together with the supramolecular architecture, closely related to the size of the macromolecules, makes the chitosan structure unique and thus favours the construction of materials with multiple applications [2; 3].

- **Experimental Methods**

The methods used in this study includeanalytictechniques such as FTIR, UV-Vis, fluorescence spectroscopy, potentiometric titration, offering information about the composition and techniques such as SEM, XRD which allow a morphological perspective, highlighting the texture of the structure; along with viscometry, that determines the dimensional size of the compounds and rheometry, which describes the flow behaviour.

- **Results and Discussion**

This study proposes to analyse different chemical modification techniques that alter the structure of chitin-chitosan, in corelation with the specific traits which arise from the origin of the raw material. The main sources used in this paper are samples from *Rapana venosa egg* capsules and crayfish, both previously unexplored ecosystems. The choice of methods is based on the previous conclusion from the literature.

i) **C**lick **C**hemistry **R**eactions offers the possibility to obtain the chitosan materials with tuneable thermosensitive characteristics, photochromic behaviours, pH-sensitivity macromolecular networks, and highly soluble chemo-selective properties. ***ii)*** **G**raft **C**opolymerization is another technique, recognized as a powerful chemical tool in the manufacture ofinnovative materials, favouring the synthesis of hybrid materials with specific properties and useful in applications like food processing, biotechnology, water treatment, biomedicine, etc.***iii)*** Investigating the ways in which these techniques can be adapted to the proposed chitosan types is aimed towards obtaining zwitterion complexes, very useful in the biological processes of repairing / replacing of damaged sequences in the living organism and a useful material platform for the manufacture of electronic devices for: detecting food quality, improving records of physiological parameters, biomedical implants, and biomaterial electronic circuits, that monitor the brain and heart functions of the patient.

- **Conclusion**

The in-detail characterization of the compositional and structural sequences of the hybrid material chitin-chitosan, in correlation with the particularities of the origin ecosystems represent a promising pathway of selecting the best chemical modification method and application selection for a desired sample.

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Natural polymers of Artemisia absinthium a potentially antibacterial medicinal plant in the fight against renal bacterial infections

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- **Introduction**

The importance of correct management of bacterial infections is crucial for modern medicine, both in surgery, in transplantation, in cancer management and in various infections by opportunistic agents. If not only recently, antibiotics were the biggest "revolution" in pharmaceutical history being considered the only "weapons" against bacterial infections, with the advent of penicillin in 1941 and oxymino-cephalosporins (carbapenems and fluoroquinolones) in the 1980s, bacteria developed new resistance mechanisms. Currently, this evolution of antibiotics has slowed down, with several causes: first, technical difficulties in discovering new antibiotics which penetrate the cell wall of Gram negative bacteria; second, the barriers to regulating new and increasingly complex antibiotics. Due to the development of new mechanisms of membrane resistance, by the efflux of antibiotics, as well as by the remarkable tendency to modify the expression of their resistance genes, by the production of extended spectrum β-lactamase enzymes (ESBL), carbapenemases, amino acid blockers, Gram pathogens represent a world-wide concern. The objective of the article is to find and demonstrate the effectiveness of certain natural polymers used in the composition of *Artemisia absinthium* whose antibacterial action exceeds the barriers of synthetic antibiotics.

- **Method and Materials**

MDR bacterial strains isolated from patients with renal infections have been identified at the Urology Clinic “Prof. Dr. Th. Burghele” Bucharest. The antibiotic sensitivity spectrum was determined by the disc diffusion method. To identify the genes for resistance to betalactamic antibiotics, the multiplex PCR screening method was used. *A. absinthium* is a medicinal plant recognized since Antiquity for its parasitic properties. Knowing these properties and its description from popular tradition, we selected it for the study of antibacterial activity on MDR Gram negative strains. To test the antibacterial action of potentially antibacterial compounds from the hydro-ethanol extract of *A. absinthium*, we used the adapted disc diffusion method and the serial microdilution method in 96-well PCR Plate. The active compounds were identified by the thin layer chromatography (HPLC) method.

- **Results**

All the pathogenic strains selected in this study had the phenotype of resistance to amoxicillin / clavulanic acid, ceftazidim and cefepim, characteristic of the production of beta-lactamases and / or cephalosporinases with broad spectrum. Molecular analysis of the genetic profile of resistance to beta-lactam antibiotics by the conventional PCR reaction method revealed the presence of genes for TEM-lactamases of TEM type and high frequency CTX-M as well as carbapenemases of OXA-48 and IMP type. The main compounds identified in the *A. absinthium* extract were: gallic acid, chlorogenic acid, quercitin and kaempferol. Qualitative tests by the disc-diffusimetric method indicated a high antimicrobial activity of the extract, quantified by the appearance of a growth inhibition zone around the stain of mother solution deposited on the seeded culture medium. The MIC of the extract from *A. absinthium* on MDR strains had values between 500 and 31.25 µl / ml.

- **Conclusions**

It can be appreciated that current research shows new perspectives in the use of *A. absinthium* extract, rich in phenolic compounds, for the annihilation of bacterial pathogenic strains with high resistance to antibiotics. These data can be useful for developing new antibacterial formulas and for establishing the protocol for their clinical use.

Keywords: *Artemisia absinthium*, natural polymers, natural compounds, Gram negative MDR bacteria, antibiotics.

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Core-Shell Polystyrene/Polyaniline Nanoparticles with Variable Conductivity and Surface Properties

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One the most investigated semiconducting polymers owing to its unique features such as its versatile redox properties, environmental stability and reversible acid/base doping/dedoping chemistry is polyaniline (PANi)[1]. However, like others conducting polymers, PANi have low solubility in organic solvents and low processibility and these are major drawbacks for practical use and many efforts have tried to surpass these difficulties. Polystyrene nanoparticles have been used frequently as a core material because they are relatively inexpensive and can be very easily prepared[2]. In this study describes preparation of polystyrene nanoparticles coated with polyaniline and copolymers based on polyaniline by in situ polymerization method using different aniline and sulfonated aniline contents. The synthesis method that we used is simple in comparation with other techniques and has a great potential for many applications such sensors, optical device, sorption of metallic ions, etc. We demonstrate that the surface polarity, dispersibility in water, and the conductivity of the obtained core-shell semiconducting nanoparticles can be tuned by varying several synthesis parameters, such as the fraction of aniline and aniline-based monomers.

In the order to better understand the self-organized structure of the synthetized nanoparticles we have complemented these studies with electron microscopy investigations. The thus prepared materials were characterized by various methods including FT-IR spectroscopy, UV-Vis spectroscopy, Zeta-potential and conductivity measurements.

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Conjugated azomethines with donor-acceptor topology and some hybrid materials based on them

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For the expanding field of organic electronics[1,2], π-conjugated molecules containing azomethine bonds can be regarded as viable alternatives to vinylene organic compounds, due to both their simple synthesis and attractive semiconducting and opto-electronic properties[3,4]. Such features can be finely tuned by the judicious structural modification of aryl-azomethine derivatives so as to minimize the twisting around the azomethine bonds which lead to a decreased conjugation length. The incorporation of heterocyclic electron-withdrawing imide rigid core together with an electron donor unit into azomethine molecules is expected to provide donor–acceptor (D–A) systems with improved electrons transport, meanwhile tunable opto-electronic properties.

Here we report on the synthesis and characterization of two D-A azomethines and some hybrid materials obtained with them. Once the structure of the compounds was confirmed by ^{1}H-NMR and FTIR spectroscopies, a thorough investigation of their optical, thermal and electrochemical properties has been accomplished by UV-vis and fluorescence spectroscopies, thermogravimetric analysis and cyclic voltammetry. Thin films were prepared from oligomer solutions in different solvents and investigated by the SEM technique.

The detailed analysis of the photo-physical behavior proved the existence of the intramolecular charge-transfer complex from the donor to the acceptor units. The strength of this transition was strongly dependent on the solvent used, indicating the presence of a solvatochromic process. The azomethine films presented various morphologies, depending on the solvent used for deposition, but also on the deposition method. This definitely affected the position of the UV-Vis absorption maxima of the oligomers. The thermal stability data indicated the absence of any glass transition, but a very good thermal stability. Moreover, all azomethines can be electrochemically oxidized and reduced to corresponding radical cations and anions, demonstrating their *p*- and *n*-type doping capability and ambipolar charge transport characteristics. The electrochemical data have been used to calculate the energy bandgap of the oligomers that was further compared with those calculated on the basis of UV-Vis absorption by Tauc method. To elucidate the predominant electronic character of the synthesized D-A azomethines, bulk heterojunction has been realized both in solution and in solid state with well-established donor and acceptor molecules, and the resulted hybrid materials evaluated in the view of potential applications.

The results of this study may contribute to a deeper understanding of the properties of D-A azomethine oligomers that can be exploited in the future for optoelectronic applications.

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UV-Shielding Ability of Aliphatic Polyurethane – Silane-Functionalized TiO_2 Nanoparticle Elastomeric Coatings

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Thermoplastic polyurethanes (TPUs) are an important category of polymeric materials synthesized by step-growth polymerization of polyols as soft segments and aromatic/aliphatic diisocyanates along with chain-extenders as hard segments[1]. In general, TPUs are elastomers with linear molecular structure that exhibit excellent mechanical properties, high abrasion resistance, low-temperature flexibility, biocompatibility and a large processing window, reason for which thermoplastic polyurethanes are widely used in various applications that include insulating materials, biomedical devices, degradable implants, electronic appliances, sports equipment, etc.[2,3].

More recent, an innovative approach in polyurethane field was the insertion of ionic sequences into these polymers which led to the obtaining of polyurethane ionomers. Although the amount of ionic groups in polyurethane backbone is small (less than 15 mol%), the presence of the ionic sequences determines modifications in the phase structure of polyurethanes, with impact on their physical and rheological characteristics and implicitly on their application potential[4].

Hybrid materials are other interesting materials providing superior mechanical, thermal, optical or electrical properties. The enhancement of the composite properties is conditioned by the homogeneous and complete distribution of the inorganic phase in the organic matrix. Up to now, various inorganic nanoparticles (metals, metal oxides, clays, carbon nanotubes) were successfully embedded in polyurethane matrices. Titanium oxide (TiO_2) nanoparticles have been frequently incorporated into polymer matrices used for applications in coatings, optical devices, photocatalysis, wastewater treatment or UV-shielding due to their excellent chemical stability, optical properties, UV absorption, low cost and environmentally friendly nature[5].

In view of all these facts, this study reports the synthesis of new polyurethane elastomers with variable soft segment composition along with the preparation of TiO_2/polyurethane nanocomposites, by the quaternization of tertiary amine groups from polyurethane with silane-modified TiO_2 nanoparticles. Thus, by the covalent immobilization of the functionalized nanoparticles in the polymer matrix a controlled dispersion of TiO_2 NPs could be achieved, while the presence of ionic sequences could enhance the interfacial interactions inside the composites, with effect on the physicochemical and mechanical properties of the resulting coatings. Also, different quaternization degrees were considered, in order to investigate the influence of TiO_2 loadings on the properties of the formed polymer nanocomposites. Moreover, the absorbance/transmittance measurements of PU/silane-TiO_2 thin films in the wavelength range of 200-700 nm have shown that these partially block UV-A radiation and all UV-B radiation from sunlight and could possibly be used as UV protective elastomeric coatings.

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Wastewater decontamination of heavy metal ions using ion exchange resins based on acrylic copolymers

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Cross-linked functionalized acrylic copolymers, resulting as spherical beads, are insoluble products, due to the three-dimensional network formed by covalent bonds[1]. The acrylic ion exchangers can be obtained by: (i) copolymerization of a vinylic monomer, which contains the acidic or basic group, and a divinylic monomer; (ii) chemical modification of some three-dimensional networks, called precursors, by appropriate polymer analogous reactions, to introduce ionizable groups[2]. The ion exchange resins have a very strong affinity for different ions, including the heavy metals. Therefore, they are suitable in purification of surface water. The principal characteristics of chelating cross-linked acrylic polymers are flexibility in optimization of pore size, type of donor atoms from functional groups, and obtaining methods[3]. Among these functional chelating groups, the amino/imino ($-NH_2$/-NH-), carboxyl (-COOH) and amide (-NH-CO-) groups could selectively retained Lewis acids (metal cations). For the retention study of heavy metal ions, we prepared cross-linked functional divinylbenzene–ethylacrylate–acrylonitrile/vinyl acrylate copolymers functionalized by: (a) aminolysis with ethylenediamine (EDA) and triethylenetetramine (TETA) or with *N,N*-dimethylaminopropylamine (DMAPA); (b) the carboxymethylation; and (c) alkaline hydrolysis of the copolymer. Additionally, TG, FT-IR, BET and SEM/EDX were performed to fully characterize the ion exchange resins. The retained amounts of Cd^{2+}, Cu^{2+}, $Fe^{2+/3+}$, Ni^{2+}, Zn^{2+}, Pb^{2+}, Mn^{2+} onto different ion exchange resins were investigated, in batch experiments, by Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The ion exchange resins could be successfully used in loading/release of different heavy metal ions, demonstrating the potential use as fillers in columns for water purification.

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137/20.08.2020, *Wastewater Heavy ion metals decontamination with Ion Exchange Resins: TARNița closed mine pollution case* (WHIERTARN), within PNCDI III, and the German research foundation BMBF (Bundesministerium für Bildung und Forschung), project ISOMAT (Project No. 01DS18022).

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YOUNG SCIENTISTS FLASH PRESENTATIONS

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Molecularly imprinted polymers for lipopolysaccharides recognition

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- **Introduction**

In recent years, Gram negative bacteria (GBN) became one of the most challenging worldwide health concerns for both environment and population according to World Health Organization (WHO) list of the drug-resistant bacteria[1]. *Pseudomonas Aeruginosa* ranks second on the WHO list due to its widespread occurrence in on natural waters or wastewaters, even on plants surfaces, from where it can reach the skin. Since GBN infection can be problematic, often leading to endotoxemia (entry of bacterial endotoxins in bloodstream), new methods of detection need to be developed[2]. This work describes the efficiency of molecularly imprinted polymer nanoparticles (MIP-NPs) for recognizing lipopolysaccharides (LPS) that compose the outer membrane of GBN.

Molecular Imprinting Technology (MIT), an efficient, fast and cost-effective solution, also allowing an easy preparation, may be regarded as the epicenter of chemical research due to its importance in certain processes, such as catalysis, separation, and detection. This technique relies on chemical interaction between the used template molecule and functional monomers, resulting in the formation of specific cavities in the polymeric network, when the template is extracted. These cavities are complementary to template, in terms of shape, size and location of functional groups[3].

- **Experimental methods**

In this study, we report the preparation and characterization of MIP-NPs and their non-imprinted (NIP-NPs) counterparts, obtained by combining the MIT with a sol-gel technique, as reported in a similar work[4]. Thus, two solutions were prepared: (1) an aqueous solution containing silane-based monomers, together with the stabilizers, template molecule (LPS from *Pseudomonas Aeruginosa*) and solvent, and (2) a catalytic medium consisting of an ammonium hydroxide- distilled water mixture. The final MIP mixture was obtained by homogenizing the two solutions.

- **Results and discussion**

The obtained MIP-NPs were characterized using modern techniques, such as structural, dimensional, textural, and thermal analyses, aiming at highlighting the successful imprentation, the presence of the monomers and the thermal stability of the particles. The MIP-NPs particles were further tested for LPS recognition from liquid aqueous samples in which case the adsorption capacity and the imprinting factor were determined.

- **Conclusion**

Consequently, the obtained MIPs can be used as recognition units in components of a biosensor for potential electrochemical detection of lipopolysaccharides from *Pseudomonas Aeruginosa*.

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Synthesis and Characterization of Novel Scaffolds based on Citric Acid-functionalized Chitosan containing rGO-TEPA with Nanofibrous Architecture for Application in Wound Dressings

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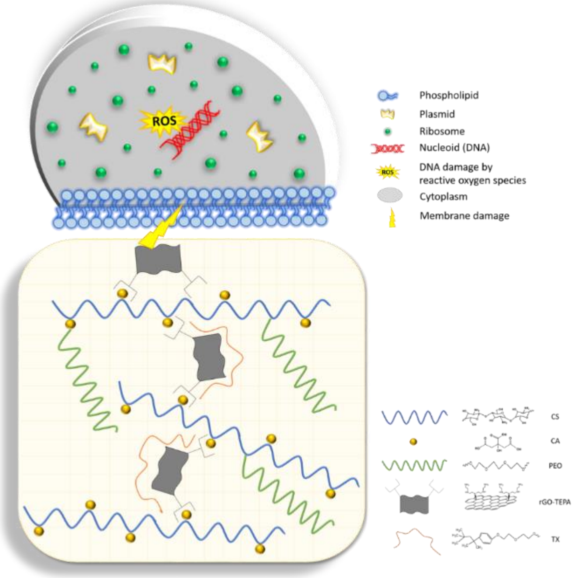
The present research reports the development of novel reduced graphene oxide tetraethylene pentamine-containing citric acid-functionalized chitosan (CsA/rGO-TEPA) based on electrospun scaffolds with nanofibrous architecture. The covalent functionalization of chitosan (CS) with citric acid (CA) was achieved through the EDC/NHS coupling system [1] and was confirmed by NMR spectroscopy. The effect of rGO-TEPA concentration on the viscosity of precursor solutions, and on the morphology, wettability, biocompatibility, and anti-biofilm activity [2] of the nanofibrous scaffolds, was investigated. The formation of bead free nanofibers was correlated to the flow behavior of the polymer solutions through rheology test. FTIR and Raman results exposed the covalent and non-covalent interactions that appeared between the components of the system, and the exfoliation of rGO-TEPA sheets, respectively. SEM microscopy exhibited the nanofibrous structure of scaffolds and the existence of rGO-TEPA sheets entrapped into the CsA nanofibers. The MTT cellular viability test showed that the composite CsA/PG_T2 scaffold possessed the highest cell proliferation level to be considered biocompatible material. The designed nanofibrous structures could have potential applications in antibacterial wound dressings, given that they developed anti-biofilm activity against Gram-negative *P. aeruginosa* and Gram-positive *S. aureus* bacteria.



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Development of thick paste-type inks for 3D printed scaffolds with shape fidelity and integrity

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Configuration of high-performant inks based on well-known biomaterials is a promising approach for the fabrication of 3D scaffolds that closely resemble the native characteristics of targeted tissue. This work has been focused on developing thick paste-type inks as an outstanding strategy to produce complex and geometrically precise engineered scaffolds. The extrusion-based 3D printing of hydrogel or composite precursors has been performed and optimized to fabricate high-resolution 3D printed scaffolds (Fig. 1) for tissue repair or replacing. The approach has been inspired by the preparation of orthopedic cements and accordingly involved the mixing of a solid phase with a liquid phase represented by a 50 wt.% fish gelatin (FG) solution. This concept has been adapted to rapidly prepare

the inks before 3D printing, and to facilitate the fabrication of 3D printed scaffolds with better resolution and without using additional strategies that stimulates shape retention ability.
The high concentration of FG aqueous solution and the substantial incorporation of solid phase have facilitated a highly accurate printability and influenced the *in vitro* stability (swelling behavior, dimensional stability, degradation behavior) and mechanical properties of the printed scaffolds. The protein-containing continuous phase has acted as a binder for dispersed phase, while the solid content has served as a reinforcing additive. The microstructure of the 3D scaffolds has been characterized by scanning electron microscopy (SEM) and micro-CT and the results have indicated the homogeneous distribution of the solid content in the FG-containing matrix.

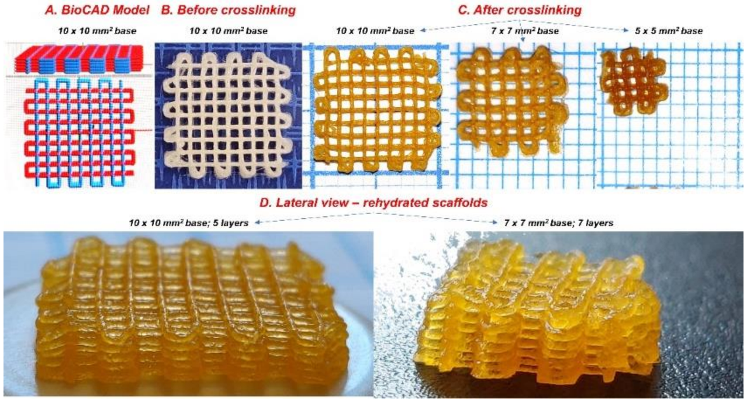

Fig. 1. Representative digital images: A. BioCAD model; B. Front view of uncrosslinked 3D scaffold; C. Front view of crosslinked 3D scaffolds printed using rectangular models with different base dimensions: 10x10, 7x7, and 5x5 mm^2; D. Side view of crosslinked 3D scaffolds[1]

This study reports the formulation of such thick paste-type inks containing natural hydrogel polymers and bioactive components 1) to fabricate 3D scaffolds and satisfy shape fidelity and integrity without using crosslinking strategies during 3D printing, and 2) to facilitate their potential applicability in both soft and hard tissue repair.

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Functionalized POSS as Nano-reinforcing Agents for Naturally-derived Hydrogels for Bone Tissue Regeneration

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- **Introduction**

Providing higher mechanical strength, a more convenient degradation pattern and mineralization capacity, functionalized polyhedral oligomeric silsesquioxanes (POSS) nanoparticles are regarded as one of the best choices in terms of nano-fillers for hydrophilic polymeric networks intended for bone tissue repair[1]. Taking advantage of both naturally derived polymers and nanostructured materials, we propose an innovative strategy to obtain nano-engineered scaffolds that combine two types of nano-fillers, POSS nanoparticles and cellulose nanofibrils (CNF) within a proteinaceous-polysaccharidic matrix composed of methacrylated gelatin (GelMA) and amidated pectin.

- **Experimental methods**

Nanocomposite hydrogels were synthesized and assessed herein by taking advantage of the fast-crosslinking potential of GelMA and amidated pectin. Physical mixing techniques were combined with dissolution in organic solvents while availing the surface chemistry of functionalized POSS compounds. FTIR spectroscopy served as a tool for determining the compositional characteristics of the constructs while the morphology of the scaffolds was investigated focusing on the dispersion of POSS, porosity and geometrical features. The performance of the hydrated structures after photo-cross-linking followed by enzymatic crosslinking was evaluated in terms of mechanical properties and swelling behavior. Pre-osteoblasts were used to perform preliminary in vitro biological tests onto freeze-dried hydrogels. The potential of these novel nanocomposites as 3D printing formulations was studied as well by performing preliminary extrusion tests.

- **Results and discussion**

The structural, chemical and biological properties were considered within a comprehensive study on the influence of polymer and nanoparticle concentration in relation with the chosen synthesis methods. By testing POSS with different functionalities we were able to determine the best approach and ensure that the designed formulation is highly homogeneous. Our results showed that the use of POSS did not hinder the swelling capacities of the freeze-dried scaffold. The mechanical properties proved the great potential of the designed scaffold for hard tissue engineering and the preliminary *in vitro* biological tests performed using pre-osteoblasts showed an optimum biocompatibility. The addition of nano-reinforcing agents yielded a polymeric formulation with shear-thinning properties, good shape fidelity and layer stability. Accordingly, the resulted scaffolds offer essential support for cell adhesion, differentiation, and proliferation through the synergic roles of each wisely chosen component that ultimately emulate the extracellular matrix.

- **Conclusion**

Novel bio-based nanocomposite hydrogels were designed as suitable for bone tissue engineering by using POSS and CNFs as reinforcing agents. Therefore, by means of using different POSS compounds and a controlled polyssacharide:protein ratio, materials with enhanced biomechanical properties and gladdening printability could be obtained. The composition of the bio-inspired materials along with quick and efficient crosslinking properties imply that these scaffolds are noteworthy candidates for the regeneration of mineralized connective tissues.

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Development of hybrid casein-based biomaterials with mineralization potential for bone reconstruction

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- **Introduction**

In recent years, the use of casein in the synthesis of hybrid hydrogels with medical applications has increased due to its multifunctional properties, safety, cost efficiency and commercial availability. Synthetic hydrogels based on (poly(2-hydroxyethyl methacrylate) – pHEMA) and (poly(ethylene glycol) diacrylate – PEGDA) have shown great promise as scaffolds for tissue repair, due to their non-toxic and highly hydrophilic characteristics[1,2]. Casein (Cas) is a well-characterized milk phosphoprotein with its well-constituted structure of porous colloidal particles, consisting of Cas, water and mineral molecules. Its main role is to provide bioactive nutrients, such as calcium and phosphate[3,4]. Casein has the property to offer biocompatibility, biodegradability and bioresorbability in oral administration, this is why it is used as encapsulation matrix[5]. In this work we investigated the potential of Cas to act as mineralization nucleator when embedded in a pHEMA-PEGDA synthetic matrix.

- **Experimental methods**

pHEMA polymers and PEGDA co-monomer embedding various rations of Cas were synthesized through the free radical bulk polymerization of 2-hydroxyethyl methacrylate (HEMA) and poly(ethylene glycol) diacrylate (PEGDA), in the presence of casein powder. Benzoyl peroxide (PBO) and N,N-Dimethyl-p-toluidin (DMPT) were used to initiate the polymerization at room temperature. The potential of the protein to act as biomimetic mineralization promotor was evaluated in biodynamic conditions. For biodynamic testing, the samples were compressed up to two weeks in a biodynamic testing device, with continuous flow of synthetic body fluid, at physiologic temperature. The hybrid hydrogels were characterized by rheology, water affinity and mechanical testing. The distribution of the protein in the matrix was colorimetrically detected. The mineralization occurrence was explored by Fourier Transform Infrared Spectroscopy (FTIR) spectra, Von Kossa staining and Micro-computed tomography (microCT).

- **Results and discussions:**

The distribution in the synthetic matrix and the effect of Cas on the water affinity, mechanical properties and formation of new mineral phase were described.

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Hybrid cryogels with advanced adsorbent properties for sulfadiazine

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- **Introduction**

In recent years natural polymers (chitin and chitosan) gained a keen interest, being used in various industry branches, especially in the medical field (wound healing, excipients for drug administration), due to their great biocompatibility, biodegradability and low toxicity[1]. However, chitosan suffers from low mechanical properties, drawback that in this study was overcome by mixing it with natural clay, i.e., kaolin. Kaolin benefits from lack of toxicity, together with the occurrence of reactive functional groups (such as -OH moieties), fact that renders it suitable for the development of hybrids with advanced adsorbent properties. Silver sulfadiazine (AgSD) is a widely used drug in the treatment of burns and chronic wounds, due to its antibacterial capacity. Nevertheless, its use poses other problems related to water pollution[2]. Hence, it becomes necessary to identify viable means of reducing its pollution effect. Thus, in this study, hybrid cryogels having advanced adsorption properties were developed in the attempt to retain silver sulfadiazine from aqueous samples.

- **Experimental methods**

In order to develop the aimed hybrids, several raw materials were needed as follows: chitosan, acetic acid and water- solvents for chitosan dissolution, crosslinker, kaolin (Acros Organics), the clay; γ-methacryloxypropyltrimethoxysilane (MAPTES, Sigma Aldrich), the silanization (organophilization) agent and silver sulfadiazine (AgSD), the antibiotic. The preparation of this type of hybrids is rather challenging, given the limited compatibility between the components, as there are both inorganic and organic in nature. Therefore, hybrids were prepared within three stages: (i) organophilization of kaolin with MAPTES, (ii) silylated kaolin introduction into chitosan structure and (iii) freeze-drying the resulted gel material.

- **Results and discussion**

In order to confirm the successful organophilization and to confirm that adsorbent materials were obtained, samples were characterized using various modern techniques (FTIR, TGA, SEM, UV-Vis). FTIR spectra confirmed the occurrence of characteristic bands of the involved raw materials. The developed hybrids possess adjustable properties as shown by all the used techniques.

Conclusion:

Innovative hybrids (cryogels) based on natural polymers and clays were successfully prepared. These materials are expected to show a great adsorption capacity, mainly because of chitosan, a well-known swelling material. Furthermore, the use of kaolin is expected to provide improved mechanical properties.

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Silk Fibroin Self-Assembled Architectures Loaded With Anti-neoplastic Drug for Cancer Therapy

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- **Introduction**

Silk fibroin is natural protein biopolymer with remarkable mechanical and biomedical properties that facilities usage for a wide range of biomedical applications and gain the FDA approval for medical uses. Due to its chemical composition and structure, silk fibroin is considered highly biocompatible. Mechanical properties such as excellent mechanical strength or features as high biocompatibility, tunable biodegradability, hygroscopic and low immunogenicity promoted silk fibroin for biomedical applications [1]. Here we report the development of novel drug-loaded self-assembled silk fibroin architectures embedded in a chitosan matrix for cancer management.

- **Experimental methods**

Silk fibroin nanoparticles were prepared by nanoprecipitation method starting from different silk fibroin concentrations (2 and 5 wt. %). The surface of the obtained nanoparticles was further modified by coupling reactions with BOC molecules to reveal amino group. 3D fibroin architectures were obtained by cross-linking assembling via amino groups. Then they were loaded with 5FU and embedded in a chitosan matrix. Morphological and dimensional investigations were performed by SEM and DLS. Drug release behavior was evidenced in a simulated gastro-intestinal tract. In vitro biocompatibility assessment was done on specific tumoral cell lines.

- **Results and discussion**

SEM microphotographs showed the 3D architectures obtained from fibroin nanoparticles with 2 and 5 wt.% silk fibroin concentration. Silk fibroin architectures obtained from nanoparticles with 5 wt. % silk fibroin concentration revealed constitutive nanoparticles with bigger size starting from SF nanoparticles and modified SF-BOC nanoparticles smaller as compared to 2 wt. % silk fibroin concentration. DLS analysis confirm these results. Drug release assay showed that the chitosan capsule protected the 5FU loaded into 3D architectures in the acidic stomach medium. This formulation ensured the release of the drug in the colon as expected (around 40% at colon level).

- **Conclusions**

As a conclusion, we reported here the preparation and complex characterization of an oral formulation based on chitosan capsule loaded with 5FU-silk fibroin nanoparticles as an efficient tool to fight against colo-rectal cancer.

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Scaffolds obtained by 3D Printing based on alginate-clay hybrid nanocomposites

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3D printing is one of the most innovative method used in regenerative medicine for tissue regeneration.

To be used in 3D printing, biopolymers-based inks should accomplish a few essential criteria: biocompatibility, shear tinning behavior, maintain the shape fidelity of the 3D printed scaffolds and mechanical stability. Moreover, the scaffolds should be porous to allow the cells to attach to the matrix, proliferate and regenerate the tissue.

The main goal of this study it was to obtain nanocomposites-based inks feasible for 3D printing process.

In this respect, alginate and different types of layered silicates were used.

Alginate derived from brown algae is one of the most widespread polysaccharides in nature. Alginate is often used in regenerative medicine mostly because it's biocompatible but also because it is an inexpensive biopolymer.

The layered silicates that were used in this study are commercial clays namely, montmorillonite (MMT) and organo modified montmorillonite (OMMT). Montmorillonite is a natural clay, being a major component of bentonite, and presents the following general structure $[(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2{\cdot}nH_2O]$.

Clay improved the rheological properties of alginate-based inks while also inducing enhanced porosity to the nanocomposite scaffolds produced by 3D printing.

Nanocomposite-based scaffolds were characterized structurally (FTIR, XRD), morphologically (SEM, Micro CT), and mechanically (Rheology, Nanoindentation).

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Novel Biomaterials Based on Type II Collagen with 2-Hydroxyethyl Methacrylate and N-Vinyl-2-Pyrrolidone for Tissue Regeneration

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Tissue engineering represents an important component of science that leads to the development of new biomaterials and approaches for regeneration and substitution of damaged or diseased tissue[1]. Type II collagen is the most abundant protein from articular cartilage, and it is frequently used as a natural biomaterial for tissue regeneration[2]. The purpose of this study was to obtain and characterize interpenetration polymeric networks (IPNs) hydrogels as potential biomaterials used in tissue engineering regeneration. The mechanical properties of the biomaterials based on type II collagen were improved using two synthetic polymers. The first one, 2-hydroxyethyl methacrylate (HEMA) is a water soluble and biocompatible monomer with pendant hydroxyl group[3]. The other polymeric component is N-vinyl-2-pyrrolidone (NVP) which represents a biodegradable, hydrophilic and nontoxic comonomer[4].

The new biocompatible hybrid scaffolds based on type II collagen, HEMA and NVP were synthesized by radical polymerization. In order to investigate the structure of the novel hybrid biomaterials, the Fourier-transform infrared spectrometry (FTIR) technique was used. The swelling properties of these hydrogels were evaluated by determining the water absorption degree. Differential scanning calorimetry (DSC) measurements showed different thermal behavior for hybrid scaffolds as compared with scaffolds based on type II collagen. The morphology was evaluated by SEM analysis, the mechanical studies were performed using compressive tests and biological investigations were accomplished by degradation assessments.

The obtained results highlighted the performances of the new hybrid scaffolds based on type II collagen with NVP and HEMA as promising biomaterials for future applications in tissue engineering.

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Tackling the Challenges of Constructing Multifunctional Chitosan-Based Materials

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- **Introduction**

The widening of the raw material base for specialized applications is a constant concern of the studies of the last years, of recovery of the waste of animal or vegetal origin, aiming especially at applications in the medical and pharmaceutical field. A promising perspective is the material sequence chitin-chitosan, which is distinguished by a variety of application structures: micro / nano particles, membranes, sponges, fibers [1-3]. This material has in its native form a series of advantageous properties such as: biocompatibility, biodegradability, haemostatic activity and can be used as a primer in wound healing [4, 5]. In addition, it can be improved by modifying its less desirable features such as weak mechanical properties and a high cost/performance ratio due to its structural-compositional versatility. Being a copolymer from the category of cationic polysaccharides, with different degree of deacetylation, chemical transformation reactionsof grafting typecan be promoted, remedying in the final product some of the deficiencies [6]. Being a natural product, the development of chemical modification is a challenge that must not only elucidate the qualitative-productive experimental technique, but also outline the general framework for correlating process parameters with the nature of the raw material. Against the background of these unknowns, our work comes to propose a new grafting technique, based on saturation with Ce^{4+} ions, not yet used for the transformation of such materials.

- **Experimental Methods**

The experimental methods developed in this study aims on the one hand, for synthesis, the validation of the best technique by differentiating the evolutionary particularities in homogeneous and heterogeneous system, respectively, when promoting grafts on to / from. On the other hand, analytic methods of different types have been used for a very thorough characterization: qualitative methods (FT-IR, UV-Vis, fluorescence spectroscopy), quantitative techniques such as potentiometric titration/conductometry and structural analysis techniques: XRD; SEM/TEM; TGA-MA; DMA; XPS.

- **Results and Discussion**

The results promote the idea of a multicomponent basic material, identifying differences from compositional and structure / superstructure point of view. These specific aspects are the consequence of a transformation whose driving force is the molecular dimension, this sort of chitosan obtained from freshwater crayfish being different from the one obtained, in a previous study by our group, from *Rapana venosa egg* capsules.

- **Conclusion**

Although in an incipient phase, this study demonstrates that the chitin-chitosan copolymers extracted from crayfish shells diversify the application range of this natural material by distinct use of high molecular mass, branched and jealous sequences.

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Corrosion Resistant Hydrophobic Coatings for Metallic Surfaces Protection Prepared by Sol-gel Process

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- **Introduction**

In recent decades, a variety of protective coatings have been developed in order to preserve or slow down the degradation processes of metallic surfaces. The biggest challenge is the inability to stop corrosion, the evolution of which can only be slowed down. The chemical attack is often accompanied by erosion and wear of the metal surface, which involves the physical degradation of the object[1]. Our group developed optimized single- and bi-layer hydrophobic coatings, with simultaneous antibacterial, self-cleaning and anti-corrosive effect to protect metallic surfaces against the action of pollutants or biological attacks with pathogens.

- **Experimental methods**

For the preparation of single-and bi-layer hydrophobic coatings doped with different nanoparticles (Cu, Ag, ZnO), a sol-gel process has been performed. The single-layer coatings consisted of different metallic nanoparticles with antibacterial properties (Cu, Ag and ZnO) embedded in a silica matrix. This layer is directly attached to the metallic substrate and assures a good adhesion. For the bi-layer coatings, a second layer is applied over the first antibacterial layer. This second layer is aimed to increase the hydrophobic character of the coating. Its composition included an optimized amount of zinc oxide particles with flower-like morphology. The obtained coatings were deposited by brushing on different metallic surfaces such as steel, copper and brass. In order to evaluate the corrosion resistance of the coatings, the protected and unprotected metallic surfaces were exposed to the corrosive action of nitrogen dioxide (NO_2).

- **Results and discussion**

The hydrophobic character of the obtained single- and bi-layer coatings was evaluated by contact angle measurements. The morphological characterization was performed using atomic force microscopy (AFM) and scanning electron microscopy (SEM). FT-IR and Raman analysis were also conducted before and after exposure to NO_2 to study the anti-corrosive properties of the obtained coatings. In Fig 1 is shown a comparison between coated (A) and non-coated (B) metallic surfaces (S - steel; Cu - copper and B - brass) after NO_2 exposure.

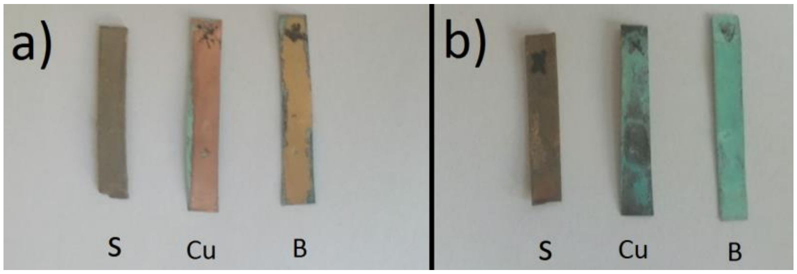

Fig.1. *Image of: a) coated and b) non-coated metallic surfaces after NO_2 exposure*

- **Conclusions**

A simple, fast, cost-efficient sol-gel process was developed in order to obtain single and bi-layer coatings with hydrophobic and anti-corrosive properties for metal surfaces. The obtained coatings are inert, waterproof, transparent, hydrophobic and have a very good adhesion to the metallic substrates.

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Bio-based Epoxy Networks – Comparative Study of Different Curing Systems

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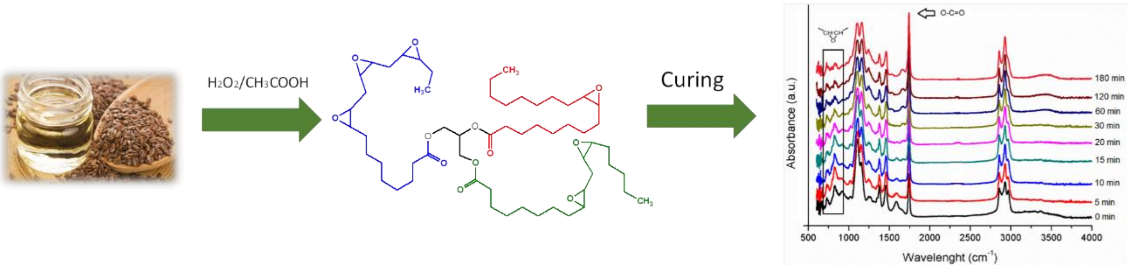
In the last decades there are more and more concerns about the increased pollution, exploring the bio-based raw materials being the facile way to a sustainable industry [1]. In this context, using vegetable oils (VO) as alternative for the conventional petroleum-based chemicals represents a viable strategy, due to their nature, versatile structure, low price and availability [2].

Looking at the macromolecular field, VO's can be easily explored considering the versatile backbone leading to functional monomers suitable for the synthesis of polymeric, composite or hybrid materials [2]. The epoxidation of the VO's double bonds received special attention for technical and industrial use, where epoxy matrices with superior performances were fabricated through different processes [3].

In this regard, the aim of this research study is focused on the development of several bio-based epoxy matrices starting from chemically modified linseed oil (epoxidized linseed oil - ELO), using different natural (citric acid) and conventional (Jeffamine D230) curing systems.

The curing reactions were monitored through differential scanning calorimetry (DSC) and also by means of Fourier transform infrared spectrometry (FTIR). Both techniques were employed to confirm the network formation and to define the curing kinetics.

The relation between the systems feed-composition and their properties will be discussed. Also, the thermal and mechanical properties, water affinity and biodegradability of the developed ELO-based epoxy networks will be presented.



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Methacryloyl Mucin - Based Single and Double Network Systems

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- **Introduction**

Mucin represents the major component of mucus and contains a long polypeptide backbone on which dense brushes of carbohydrate chains are grafted [1]. The complexity of its structure proved to be appealing and mucins have been studied for applications as carriers for bioactive species [2], coatings with improved tribological performance [3,4] or anti-fouling agents [5]. However, its use in the biomedical field is still underexploited. This work presents a two-step procedure of obtaining double network (DN) systems based on methacrylic anhydride-modified mucin (MuMA) by (1) covalent bonding of MuMA methacrylate groups through radical photo-polymerization, leading to single network (SN) hydrogels and (2) hydrogen bonds (H-bonds) formed between the carboxyl side groups of the protein with the hydroxyl groups of tannic acid (TA).

- **Materials and methods**

Following the synthesis and characterization of MuMA, various SN stable hydrogels were prepared using reaction media with different pH values. The SN hydrogels were converted into DN systems through incubation in TA solution. The affinity for aqueous media of both SN and DN hydrogels was assessed and the mechanical properties of the obtained systems were evaluated both at macroscale - through rheology and compression tests and microscale - through nanoindentation tests.

- **Results**

Results on the characterization of the newly obtained product (MuMA) revealed that (i) the mucin protein structure was not altered by the methacrylation and (ii) MuMA maintains the pH dependency of the pristine mucin leading to different folding of the protein chains, as shown by circular dichroism spectroscopy (fig. 1). Following the photo-polymerization of the double bonds of the methacryloyl groups, DN systems were obtained through the incubation of the obtained SN hydrogels in tannic acid (fig. 2, A). The successful formation of a secondary network was demonstrated for all systems by the noteworthy differences in swelling ability, referring to both the time required for attaining the hydration equilibrium, as well as their swelling content (approx. three times higher in SN vs. DN systems) (fig. 2, B). The mechanical tests showed that TA incubation leads to more robust systems that require additional effort to be deformed: the SN hydrogels break around a strain of 30 – 40 %, but are able to undergo higher deformation, while the DN systems require a significantly higher stress to be deformed at the same strain value (around 1.5 ÷ 3 fold for a 30% deformation). While the rheological tests showed that the supplementary reinforcement of the hydrogel brought by the presence of H-bonds was not accompanied by the stiffening of any chain parts, the nanoindentation tests revealed an immobilization of the macromolecular chains on the surface of the synthesized materials which might be beneficial for cells adherence. The registered results demonstrated the ability of MuMA to form robust DN systems with the ability to uptake large amounts of aqueous media without losing their integrity. The high water uptake ability and macro and micro scale mechanical properties, indicate that these systems may find applications in the field of load bearing soft tissue regenerative medicine.

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Thermal stability and graphenic surface influence study of Bovine Serum Albumin through Circular Dichroism

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Protein conformation is a key factor in assessing the connection between protein structure and protein role within a living organism. Thus, a great number of studies have focused on the determination of protein secondary and tertiary structures via various techniques. Circular Dichroism is among the most widely used techniques for the determination of secondary structure content and secondary structure changes of different classes of proteins.

Bovine Serum Albumin (BSA) is an accessible protein, very abundant in blood plasma, with high binding capacity[1] and globular shape. It has been previously used as culture cell media or in the development of biomedical devices such as drug delivery systems, biosensors and so on. BSA structure exhibits a high content of α-helix secondary structure type while the β-sheet structure remains at a relatively low value. Our work focused on assessing the thermal stability of native BSA and the interaction of BSA with various types of graphenic surfaces. We have used different modified graphenic surfaces (egg.: GO, GO-COOH, GO-PEI) in a 1:1 mixture with Bovine Serum Albumin and studied they're effect upon the secondary structure content and thermal stability of the protein.

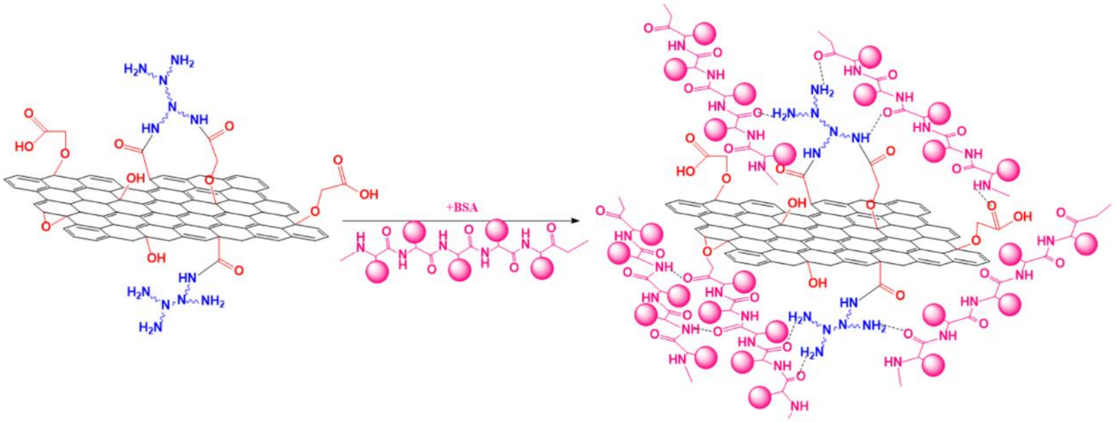

Figure 1. Example of various interactions of BSA chains with one of the modified graphenic surfaces (GO-PAMAM)

The interaction between the protein and the graphenic system has been examined by circular dichroism spectroscopy (CD). The secondary structure content was determined using a Quantitative multivariate analysis software program with a reference data set including 26 proteins[2]. The thermal denaturation studies were on pure BSA revealed the thermodynamic and kinetical parameters of the process and a comparison between pure BSA and BSA after interacting with the graphenic surfaces has been highlighted.

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Thermo-reversible biomaterials for 3D printing

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The three-dimensional (3D) printing technology, has been progressively expanding in many fields like polymer chemistry, pharmaceutical science, medicine and biology. The use of biopolymers as ink for 3D printing has allowed the development of new materials with attractive properties for tissue engineering,

medical devices and drug delivery systems due to fabrication of scaffolds structures which mimics the cellular network to support the cell and to repair and develop the new tissue, organs or to have a newly drug-loaded scaffolds[1,2]. Natural polymers like sodium alginate, hyaluronic acid, chitosan, gelatin and agarose are some of the most widely used in hydrogel fabrication for tissue engineering and drug delivery due to their advantages like biocompatibility, non-toxicity, low cost and high processability than synthetic polymers[3,4,5].

In this work, we report the development of hydrogel bio-inks for 3D printing of scaffolds based on polysaccharides. A mixture of sodium alginate and k-carrageenan was employed and the 3D structure was fabricated through layer-by-layer printing. The crosslinking of the hydrogels was performed after printing the materials, by immersing them in a crosslinking solution of different concentration of $CaCl_2$: KCl =1:1 (volumetric ratio). The shear-thinning properties of the inks were determined by rheological studies. The swelling behavior and structure stability of the 3D printed structure based on sodium-alginate/k-carrageenan ink was conducted in PBS (pH=7,4) at physiological temperature, 37 ^{0}C.

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Biopolymer Assemblies-Synthesis and Characterization

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- **Introduction**

It is well known the fact that substituted polymers with azo chromophores, coupled with aromatic heterocycles have typically high values of electro-optic response. These stable optic effects, found in azo-polymeric materials are a consequence of their internal constitutive properties (free volume of the azo groups, the nature and structure of the polymeric matrix etc.) and of the influence of experimental parameters such as temperature and the type of solvent. Moreover, the length of the conjugation can be increased by the addition of aromatic sequences. These findings have led to the idea that chemically incorporating azo-carbazoles will improve the electro-optic properties and, at the same time, generate new types of interactions that allow the construction of new assemblies, complementary to the natural sequences, which can be used in the detection and treatment of tumours [1-5].

This work includes the synthesis of n-acryloyl morpholine copolymers, with preferential stereochemical catenation, which leads to the enhancement of the properties/anisotropic character. The final desired applications are in bio photonics.

- **Experimental methods**

The validation of synthesized monomers was done by FT-IR and NMR spectra. UV-Vis and fluorescence spectroscopy provides the data necessary for the assignment of photophysical properties.

Excited-state dipole moments of molecules have been estimated from solvent-dependent Stokes shift data using a solvatochromic method based on a microscopic solvent polarity parameter.
The (co)polymers NAM and DNA have been synthesized using precipitation polymerisation, both radical and RAFT types. In order to demonstrate the interaction between the constitutive sequences of the material, the analytical techniques like FT-IR; Raman; XPS; UV-vis; VCD; CDwere used.

- **Results and Discussion**

The proposed compounds, in different solvents have three main absorption and fluorescent bands: the first at *cca.*215-230 nm, which is very intense and corresponds to the π-π* transition; the other two, while not as high, are registered at *cca.* 270-370 nm and are due to the n-π* transitions. The dipole moments have been estimated using the Stokes shifts formulas, based on the absorption and emission bands. The absorption band decreases by increasing the dimension of the molecule complex (HTAB) and/or by increasing the molecular dimension of polymer. The decrease in absorption intensity along with a shift toward longer wavelength can be attributed to staking interaction between the polymer chain and base pairs. These spectral changes can be ascribed to intercalation of planar polymeric chains into the DNA helix, stabilized by π-π stacking interaction at level of phosphorous group such as the VCD analysis suggested. CD spectroscopy is quite often used to identify the backbone distortions in DNA-polymer assembly.

- **Conclusions**

The positions of the absorption peaks are strongly affected by the structure of the compounds, by the length of the π conjugate bridge and by the electronic nature of the substituent groups. The solvent polarity affects the number as well as the intensity of peaks, alongside with the wavelength. It is important to point out the decrease of the absorption/fluorescent maximum when the substituent is not localized on the carbazole sequence. Based on the optical properties, theoretically estimated for these molecules, we are expecting good NLO responses and we further intend to verify these properties by experimental measurements.

ACKNOWLEDGEMENTS:
The authors want to thank to Prof. Ileana RĂU, Prof. Ana-Maria ALBU, Dr. Olivier SIRI's CROMA group, Centre Interdisciplinaire de Nanoscience de Marseille - (CNRS / Aix-Marseille Université), for supplied and valuable discussion and for experimental support.

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Biopolymer hybrids inlayed with graphene oxide as incentive to in vitro osteogenic differentiation and in vivo ectopic osteogenesis

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The study addresses the potential boost of mineral-independent osteoinduction and osteodifferentiation featured by fish gelatin/chitosan (GCs) hybrids per graphene oxide (GO) reinforcement. Standard GCs formulation was referenced against genipin (Gp) crosslinked blend and 0.5 wt.% additivated GO composite (GCsGp/GO 0.5 wt%). Exploratory mechanical investigations were performed before assessing the in vitro osteodifferentiation and the materials' osteoinductive nature in vivo. Osteoprogenitor differentiation was assessed on MC 3T3- E1 pre-osteoblast cell line, while CD1 mice models were used to assess de novo osteogenic potential of the three functional materials by ectopic implantantion in a subcutaneous dorsum pocket of the animals. The ex vivo materials were studied 4 weeks after surgery, regarding biomineralization and morphological changes by means of qualitative (Scanning Electron Microscopy) and quantitative (Micro-Computer Tomography - µCT) architectural inquiry. Also, X-ray diffraction and Fourier-transform infrared spectroscopy underlined the newly-fashioned material structuration by virtue of mineralized extracellular matrix. Specific staining assays revealed collagen formation and Ca^{2+} deposits, validated by µCT. *runx2* and *opn* markers determination stressed on the osteogenic phenotype of the cells populating the ectopically implanted materials. This data supports the GO bioactivity in osteogenesis mechanisms as being self-sufficient to elevate osteoblast differentiation and bone formation in ectopic sites while lacking most common osteoinductive agents.

Keywords: graphene oxide, biopolymer blends, biomineralization, ectopic bone formation, osteoinduction, ex vivo analysis

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Mannose functionalized hybrid nanocarriers for antibacterial drug delivery

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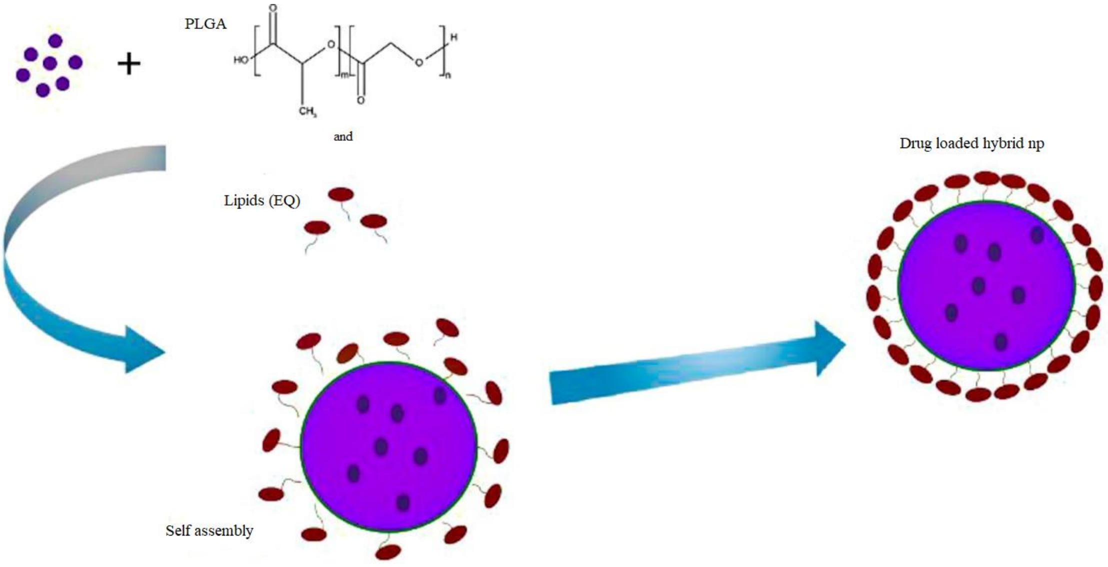
The main objective of this study was to examine the impact of nanocarrier structural properties as well as the mannose modified surface on the efficiency of formulations as lipophilic drug delivery systems.We proposed the synthesis of a type of hybrid nanoparticles with a polymer-vegetable oil structure that will act as a drug delivery system for a controlled release of an antibacterial drug. The materials used to obtain the hybrid nanoparticles were Poly (lactic-co-glycolic) acid and Echium vegetable oil (EQ), implementing Izohidrafural (IHF) as the antibacterial drug with lipophilic behavior. The emulsion solvent evaporation process was used to create all the drug-loaded formulations. Prime parameters such as hydrodynamic characteristics, encapsulation efficiency and the release profiles were evaluated and associated with the compatibility of the drug with the polymer matrix. According to the release profile, the oil integration influenced the nanocarrier's ability to discharge the substance in a more prolonged course.[1][2][3]



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POSTER PRESENTATIONS

Photocrosslinkable polymeric coatings for surface decontamination

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- **Introduction**

The potential danger of chemical-warfare attacks, as well as ecological problems, have led to an increased need for developing new environmentally friendly systems for surface decontamination.[1] Poly(vinyl alcohol) (PVA) is a water-soluble non-toxic polymer, with good physical and chemical properties, that is obtained at large scale and possess excellent filming properties.[2] Thus, strippable coatings based on PVA could potentially be used for decontamination purposes of different surfaces from different chemical, biological, radiological or nuclear pollutants. Although the current solutions are every effective for decontamination, their major drawback is represented by the prolonged curing time of the polymer coatings. Consequently, introducing photocrosslinkable groups (e.g., cinnamoyl) in the PVA could overcome this major issue considering the effective and relatively fast photodimerization[3] reaction which would generate a crosslinked structure in a relatively short time.[3] In the present study, we show that PVA modified polymers with cinnamoyl groups can be successfully used for cleaning of chemically contaminated surfaces. Moreover, the coatings could be applied on a variety of surfaces such as glass, ceramics, and metals.

- **Experimental methods**

PVA modified with cinnamoyl groups (PVA-Cin) was prepared by the esterification of hydroxyl group with cinnamoyl acid chloride in the presence of pyridine using N-methyl pyrrolidone as solvent. Polymeric films were made by casting an aqueous solution of PVA-Cin on different substrates such as glass, ceramic, and metal. The chemical decontamination efficiency was tested against dimethyl methylphosphonate.

- **Results and discussion**

The FT-IR and H-NMR data prove the successful modification reaction of PVA with cinnamoyl chloride. The concentration of PVA-Cin solution was optimized based on its film-forming properties and peel-off characteristics. The aqueous solubility of PVA-Cin decreased with increasing the amount of cinnamoyl groups due to their hydrophobicity. Chemical decontamination experiments indicated that polymer has a high decontamination efficiency of 99.9%.

- **Conclusion**

PVA-Cin was successfully used to obtain flexible polymeric films with good peel-off properties. The PVA-Cin films have shown high efficiency in the contamination removal experiments for the metallic surfaces.

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Porous microparticles based on alginate, chitosan and polyvinyl alcohol with applications in oral administration of active substances

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This paper proposes to develop a solution for the treatment of diseases such as cervical cancer or those involving inflammation of the intestine by designing medical systems with controlled release of active substances.

Over time, people have faced many ailments for which they have not yet found a treatment. One of the most frightening conditions, as a result of which the human psyche produces an unimaginable level of fear is cancer. One of the most important drugs used to treat this type of cancer or to decrease certain causes that later lead to the final condition could be mesalazine.

The problem with active substances arises when they need to be administered. The mode of administration, the residence time, the speed of administration, the place where our active substance operates are just some of the many criteria that we must keep in mind when looking to develop such a device. The development of such a device consists in the following steps:

First step: Choosing the type of device:

Given the differences between the properties of materials at different dimensional scales, we chose to make porous micro-particles consisting of two biopolymers for controlled release of the drug. As we well know, as the size of a particle decreases, its specific surface area increases, which can satisfy an important property, namely the encapsulation efficiency.[1]

Second stage: Choice of materials:

Bioavailability and biocompatibility have always been some of the most important criteria by which certain materials were or were not chosen for certain applications. As a result, we opted for the use of sodium alginate, together with polyvinyl alcohol and chitosan, going on a core-shell structure (one layer inside, another outside), the core being the most protected point, represented by the active substance.

Third step: Choosing the method of obtaining the microparticles:

Having at our disposal several methods by which we could have obtained the desired particles, a more unconventional method was chosen, namely electrospinning, with which we can directly remove the solvent, without needing another separate step.[1]

We`ll use a coaxial electrospinning process. In short, use a needle with two inputs connected to two different syringes (one for each polymer). We mentioned above that at the end some core-shell microparticles will be obtained, so for the inner layer the chitosan is connected to the inside of the needle, and the alginate is connected to the outside, the operating parameters being different between the two solutions. polymer, by applying an electrical voltage between the needle where the dripping will start and the calcium chloride bath where the dripping process will end, we will favor the formation of microparticles with a quasi-spherical shape, loaded inside with medicine.

All the stages described above will be approached and re-evaluated during this paper, together with the interpretation of the characterization analyzes like SEM, TEM, DLS, TGA of the final products and also the conclusions regarding to the final state of these microparticles following the investigations performed. [1]

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Modification of renewable PLA by melt blending with natural additives

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- **Introduction**

Nowadays, biodegradable polymeric materials which are blood compatible have been applied not only confined to biomedical implants and devices, release of drugs, food packagings, but also extended to wound dressings, bone cements and tissue engineering scaffolds due to their environment friendly nature and outstanding physicochemical features [1]. Poly(lactic acid) (PLA) has been the most investigated biodegradable material for high performance for bio-medical applications owing to its remarkable properties that make its commercial and large-scale production [2]. There is a growing concern for hospitalized patients who are at high risk of contracting infections due to biofilms formation [3]. One strategic approach in combating the formation of biofilms include coating the implant with nanocomposite antibacterial thin coatings loaded with antibiotics or other antimicrobial agents. The most common preparation method for polymer-based nanocomposite coatings always includes a liquid media or organic solvents. In consequence, this method usually has restrictions in bio-medical field due to the traces of solvents that remain in material and can induce an inflammatory response. A possible way to effectively overcome this drawback and remove the toxic solvents is the melt-processing method. Thus, the aim of this study is the investigation of the antibacterial activity of PLA based biodegradable nanocomposites obtained by melt-mixing under the influence of the two antibacterial components of different nature.

- **Experimental methods**

Nanocomposites from PLA 4043D (Ingeo, NatureWorks), cellulose nanofibers obtained in-house and two antibacterial agents in the form of a protein (P) and a polysaccharide (PS) were prepared in a Brabender Plasticorder LabStation (Duisburg, Germany) equipped with a 30 cm^3 cell at a temperature of 170 °C for 10 min at a rotor speed of 50 rpm.

- **Results and discussion**

The presence of specific groups of P and PS antibacterial agents in the IR spectra of the modified cellulose confirmed their successful grafting on the cellulose surface. Both types of antibacterial agents have been stable at the melting temperature of the PLA matrix and as such can be used to obtain nanocomposites without thermal degradation during processing as resulted from the TG/DTG curves. A slightly shift of the maximum degradation temperature of PLA nanocomposites containing PS towards slightly higher values was observed as compared with the nanocomposite containing antibacterial agent type P. Antimicrobial activity of PLA based nanocomposites modified with P and PS agents was tested against gram-positive bacteria *Staphylococcus aureus* and gram-negative bacteria *Escherichia coli*.

- **Conclusions**

Antimicrobial films produced from biodegradable PLA through melt-processing can be a sustainable solution for engineered applications which requires non-toxicity in addition to other specific requirements.

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Encapsulation of a mesalazine prodrug used for Inflammatory Bowell Diseases treatment

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- **Introduction**.

Inflammatory Bowel Diseases like Ulcerative Colitis and Crohn Disease are diseases that are located to specific sites in the gastrointestinal tract (GIT), more precisely at colon level. Targeted delivery systems for treatment of IBD are designed to increase local tissue concentrations of antiinflammatory drugs from lower doses compared with systemic administration. Mesalazine is one of the most often used drugs in the treatment of IBD but is only 20% efficient because it is degraded by gastric fluids.

- **Experimental methods**

In order to increase its efficiency, we modified it to obtain a prodrug which in enzymatically activated when it reaches the intestinal level.

The obtained prodrug was encapsulated in acrylic modified clays in order to protect it from gastric degradation and after that, the clays were dispersed in chitosan nanoparticles.

The prodrug fabrication was demonstrated by FTIR an NMR while the nanoparticles were characterized by DLS for size determination, in vitro drug delivery, in vitro biocompatibility and in vivo anti-inflammatory tests.

- **Results and discussions**

The results of the LDH test indicate a low, but slightly higher, toxicity for all composites tested compared to the plastic control. No statistically significant differences were observed between LDH levels released by cells that were in contact with the ten compounds and control, indicating a low cytotoxic effect on the cellular component.

The Live / Dead test is consistent with the results indicated by the MTT and LDH tests, as there is a positive ratio in terms of the number of viable cells and dead cells for all composites. Thus, a similar number of cells were observed that were in contact with MP5 and MP-H5 composites compared to plastic control. In contrast, the number of cells that have been in contact with MP5 and MP-H5 composites is higher compared to MP-M5, MP-MI5 and MP-HE5. This indicates better biocompatibility for the MP-H5 composite than the others tested.

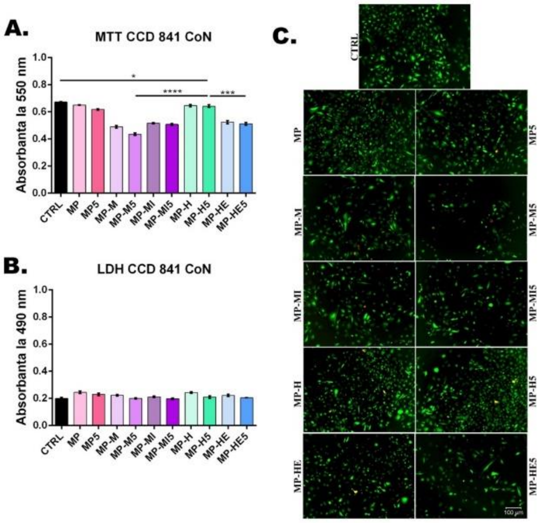

Figure 1. Quantitative evaluation of the viability of the CCD 841 CoN cell line by the MTT test (A); Quantitative assessment of cytotoxicity of materials by LDH test (B); Confocal microscopy images showing living (green) and dead (red) cells (C)

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Design and characterization of GO-COOH decorated hybrid scaffolds based on alginate/gelatin using electrospinning technique

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The main objective of this study is to design novel GO-COOH decorated bicomponent hybrid scaffolds with nanofibrous architecture by rationally embedding into one entity two biobased-derived polymers with biological and biomimetic characteristic (alginate and gelatine) and GO-COOH using electrospinning approach. The underlying principle is based on various types of interactions that can take place between the functionalities of the system's entities and their synergy in improving the structural integrity, mechanical tailor ability and biological performances of the nanofibrous GO-COOH decorated hybrid scaffolds.

The SEM micrographs showed the nanofibrous structure along with the presence of GO-COOH on the surface of hybrid nanofibers. The structural investigations (FTIR, Raman and XPS spectrometry) emphasized the occurrence of different non-covalent interactions (e.g., H-bonding) as well the formation of new chemical bonds between the functionalities of the system ‘components. The biological results (Fig.1) indicate a remarkable cytocompatibility of crosslinked bicomponent SAG scaffolds; the metabolic cellular activity is substantially improved followed the GO-COOH addition, suggesting that GO-COOH can support the cells adhesion, growth and proliferation.

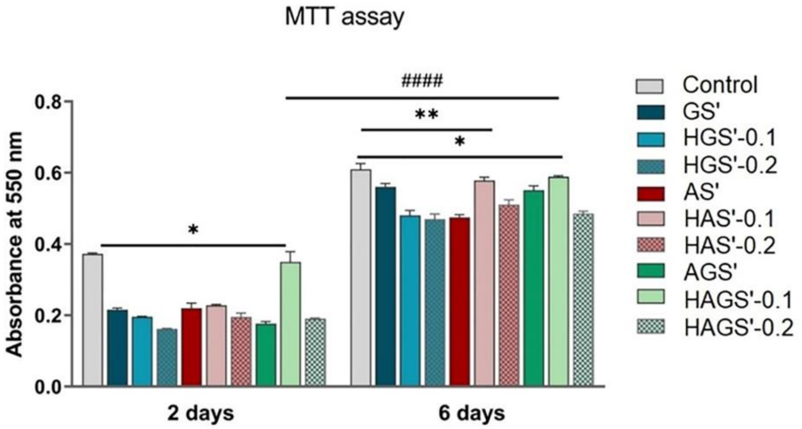

Fig.1. Viability and proliferation of NTC fibroblast seeded with nanofibrous scaffolds determined by MTT assay after 2 and 6 days in standard culture conditions.

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Zinc oxide nanoparticles – amino alcoholic solution for biological decontamination

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The modern decontamination technologies are clearly detached from the classic technologies based on wet spraying-rubbing processes of the decontamination solutions or on dry processes, because they foresee the increase of the efficiency and productivity of the decontamination process. Decontamination operations provided by advanced technologies must be part of a sustained attention and development, in order to ensure the protection of people.

Nanotechnology plays a very important role in developing highly effective nano-based antimicrobial and antiviral formulations. Zinc oxide nanoparticles have proven antibacterial and inhibit the growth of microorganisms by permeating into the cell membrane. The oxidative stress damages lipids, carbohydrates, proteins, and DNA.

The paper presents the biological decontamination of gram-positive bacilli (Bacillus anthracis, Bacillus cereus, Bacillus subtilis), gram-positive cocci (Streptococcus aureus) and gram-negative bacilli (Escherichia coli, Pseudomonas aeruginosa) with an organic decontamination solution enriched with metal oxide nanoparticles.

This newly developed amino-alcoholic based decontamination solution enriched with zinc oxide nanoparticles (ZnO NPs) showed it`s biological decontamination efficiency on several bacilli and cocci.

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Antifouling coatings bearing phosphoryl choline moieties to improve implant body acceptance – a model on synthetic polymer films

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- **Introduction**

An important obstacle during the implantation of a biomaterial is the activation of a "foreign body" reaction enabling a host-immune response which is notably characterized by an inflammation and a fibrotic development around the implant. The deposition of an antifouling coating on biomaterials intended for implantation may act as a defensive line against host-immune reactions by preventing the adhesion of proteins and activation of platelets, limiting thus foreign body reaction and allowing the body to focus on healing.

The antifouling behavior of poly(ethylene glycol) (PEG) and PEGylated derivatives has been valorized on the market for more than 20 years, resulting into their translation as vital ingredient in everyday products, surfactants and a serious of medical applications. Nevertheless, various reports have shown that PEGylated products can cause immunological response, hypersensitivity or antibody generation [1-3]. Zwitterionic polymers such as phosphoryl cholines (PC) attracted a lot of attention once the discovery of zwitterionic lipid phosphatidylcholines as the major component of the external layer of erythrocytes known to be non-thrombogenic. Thus, they are considered as antifouling candidates, possessing a native bio- and haemocompatibility [1-4]. Furthermore, over the years, PC-based substrates or coatings have been shown to possess superior antifouling properties, high resistance to biofilm formation and bacterial adhesion, making them promising candidates for biomedical applications such as hernia or cardiovascular implants, biosensing, contact lenses and many other. In the present study we aim at the development of a natural polymer derivative tethered with PC moieties by using a method previously developed in an initiative to obtain antifouling coatings possibly able to enhance implant-body acceptance.

- **Experimental methods**

Briefly, PC grafted biopolymer was synthesized by first grafting azide moieties onto its backbone, that subsequently facilitated the introduction of PC moieties *via* an azide-alkyne “click reaction” in the presence of an alkyne-terminated PC compound. The obtained derivative was purified by dialysis and freeze-dried. A 1mg/mL solution of thus freeze-dried derivative was further used to obtain PC-tethered coatings on synthetic films and their antifouling properties were investigated against BSA and IgG model fluorescent labelled proteins by fluorescence microscopy. Basic characterization methods such as FTIR, UV-VIS, SCA, etc, were used over the study.

- **Results and discussion**

A simple two-step synthesis path involving an initial azidation step and a subsequent click reaction to incorporate PC moieties onto the backbone of a biopolymer was applied to obtain PC-polymer derivatives. Thus, obtained derivatives were used as potential antifouling coating on synthetic polymer films with known hydrophobic. Significant reduction in BSA and IgG protein adsorption was seen in the case of films coated with PC-based derivatives compared with pristine films (without a coating). In addition, an influence of the presence of a plasma treatment before coating application was seen, where plasma treated surfaces presented a more homogeneous coating and therefore an increase in antifouling behavior.

- **Conclusion**

Antifouling properties were proven to be enabled by PC-tethered natural-based polymer coatings, which opens new opportunities in using such derivatives as alternatives for PEG-based coatings and/or in biomedical applications.

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Investigation of crosslinked hydrogels based on Salecan biopolymer

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Polysscaharide based hydrogels have attained great interest in recent years thanks to their low toxicity and biocompatibility. In particular, a series of salecan containing semi-synthetic interpenetrated systems were investigated, where salecan proved excellent rheological property and biological activity[1,2].

In order to expand the potential use of salecan, the possibility to obtain crosslinked solely salecan hydrogels was investigated. The influence of salecan concentration on the final properties of crosslinked hydrogels was followed.

FTIR, SEM and BET analyses were employed to determine the morphology and structure of the synthesized salecan based materials. Thermo-mechanical behavior of the hydrogels was investigated using nanoindentation, DMA and TGA analyses. Moreover, equilibrium water content, swelling and degradation of the crosslinked hydrogels in phosphate buffered saline, were performed.

Salecan based crosslinked hydrogels were successfully prepared. The change of Salecan content obviously affected the swelling behavior and morphology of the composite hydrogels. Moreover, thermo-mechanical behavior of the crosslinked salecan based materials was influenced by the increased salecan concentration.

The obtained salecan based crosslinked hydrogels could serve as promising candidates in tissue engineering but also as carriers for drug delivery applications.

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A Composition Study of Some Plant Oils Used in the Development of Lipid Nanotransporter (NLC)-based Hydrogels for the Efficient Treatment of Varicose Veins

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- **Introduction**

In recent years, the importance of plant oils obtained by cold pressing has increased not only for their fat content but also for their frequent use in the pharmaceutical and cosmetic industry. The purpose of the paper consisted in carrying out a composition study for a series of plant oils in order to correlate it with their antioxidant activity, following their use in the development of hydrogels based on lipid nanotransporters (NLC) which have a therapeutic effect on varicose veins.

- **Experimental methods**

Plant oils were obtained by cold pressing the seeds of pumpkin, castor, evening primrose, wheat germ, organically grown grape seeds, imported jojoba oil. The determination of fatty acids was performed by gas chromatography coupled with mass spectrometry (GC-MS). In order to identify the peaks corresponding to the analyzed compounds, the NIST spectrum library was used. Antioxidant activity was established by the FRAP (Ferric Ability Reducing of Plasma) method.

- **Results and discussions**

The chromatograms obtained highlight the richness of saturated and unsaturated fatty acids present in the selected plant oils, the table showing the percentages of saturated and unsaturated fatty acids and the antioxidant activity of each type of plant oil studied.

No.	**Oil Name**	**Total saturated fatty acids [%]**	**Total unsaturated fatty acids [%]**	**Antioxidant activity [mg Fe/g sample]**
1.	Pumpkin seed	21,0	78,0	1100,3
2.	Castor oil	2,5	97,0	890,5
3.	Evening Primrose	6,8	93,0	560,7
4.	Wheat germs	18,7	80,3	950,4
5.	Grape seed	11,0	88,0	780,9
6.	Jojoba	0,5	75,0	690,5

Due to the disadvantages of conventional therapy, there is an obvious requirement for the development of new alternatives based on nanostructured topical formulations containing natural active principles and leading to a coupled action: of high therapeutic performance and improved safety profile for the treatment of varicose veins.

Fatty acids in plant oils are contained in cellular and neuronal membranes, being useful for supplementing and normalizing unbalanced diets in adults and children and frequently used in pharmaceutical and cosmetic techniques as carriers of various active substances.

- **Conclusions**

From the plant oils studied we ended up choosing to develop hydrogels based on lipid nanotransporters (NLC) from pumpkin oils and wheat germ oils which besides their high percentage of unsaturated fatty acids, also have high antioxidant activity. These oils will be used in cosmetic products which have a therapeutic effect on varicose veins.

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Development of New Collagen/Clay Composite Biomaterials

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The fabrication of collagen scaffolds for use in skin implants offers many challenges to tissue engineers[1]. Type II collagen represents the most abundant protein from articular cartilage and it is commonly used as a natural biomaterial for tissue regeneration. The clay particles are remarkable because they are recognized to be biocompatible, nontoxic, and biodegradable[2]. Composite materials represent an interesting route to provide collagen-based matrices with enhanced properties originating from a controlled morphology of mineral particles arranged in three-dimensional structures[3].

The purpose of this study was to obtain and characterize new composite biomaterials based on collagen and several types of clays.

The prepared composite scaffolds were characterized by FTIR, XRD and SEM. DSC and TGA measurements showed different thermal behavior for hybrid scaffolds as compared with scaffolds

based on type II collagen. The swelling ratio, biodegradation ratio and mechanical properties of composite scaffolds were also studied.
The obtained results highlighted the performances of the new collagen based composites as promising biomaterials for future applications in biomedical field.

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Mechanism of polymer particles formation during the soap-free emulsion terpolymerization of styrene - acrylic acid – N -(isopropyl acrylamide) for photonic crystals fabrication

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- **Introduction**

Photonic crystals (PCs) are a continuously fascinating research field due to their capacity of light modulation on one or multiple directions, according to Bragg's law[1]. The aim of this study was the synthesis of a novel temperature and humidity responsive material, obtained in a single polymerization stage, presenting PNiPAM on the surface of polymer colloids with self-assembly properties for possible thermal and humidity responsive optical drug delivery polymers.

- **Experimental methods**

This study presents the synthesis and characterization of a styrene (ST), acrylic acid (AA), and N-(isopropyl acrylamide) (NiPAM) terpolymer obtained by a soap-free emulsion process. The optical properties of the colloids were investigated by UV-Vis, SEM, and optical microscopy. The existence of two polymerization mechanisms dependent on the substrate composition is supported by the UV-Vis, kinetics, TEM and XPS analyses. LCST values between 33 - 44 °C were evidenced through DSC analyses.

- **Results and discussions**

Our study aimed also the influence of AA/NiPAM ratio on the reaction mechanism and the reaction kinetics. The polymerization rate increases with the increase of NiPAM concentration in the substrate. The obtained polymer colloids permitted the fabrication of photonic crystals (PCs) in all four cases, regardless of the substrate composition. A micellar polymerization mechanism in the case of AA rich substrates and a heterogeneous mechanism for NiPAM rich substrates were ascertained using the UV-Vis, DLS, TEM, and XPS analyses. As the NiPAM concentration increased in detriment to AA, the particle formation mechanism leads to the formation of two distinct types of polymer particles. The zeta (ζ) potential values confirmed the latexes stability in all cases. The humidity responsive characteristics were evaluated as an application for the obtained PCs.

- **Conclusions**

The polymer particles present the capacity to form photonic crystals structures through self-assembly. The mechanism is predominantly micellar in the case of substrates rich in AA, while the mechanism is predominantly heterogeneous for NiPAM rich substrates. The materials obtained using high NiPAM concentrations exhibit a reversible opaque to transparent transition under high humidity. The presence of carboxylic groups allows the possibility for further functionalization with active ingredients/components/medicines of the polymer colloids.

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Synthesis and characterization of novel polyethyleneimine bio-based benzoxazine resins

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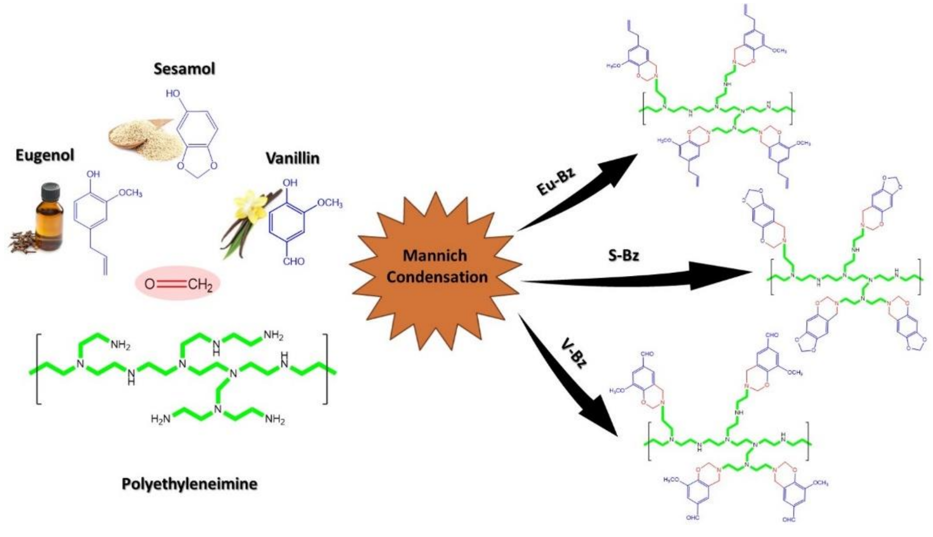
There is an emerging demand in the industrial sectors for the synthesis of easy to handle, yet high performance thermosets with less harmful impact on the environment for coatings, electronic devices or aerospace industry [1]. Three novel polybenzoxazine resins have been synthesized by using sesamol (S-Bz), eugenol (Eu-Bz) and vanillin (V-Bz) as bio-based pheolic resources. The benzoxazine formation has been developed starting from branched polyethyleneimine (PEI) bearing primary amine functionalities. The PEI structures used in the design of the complex bio-based benzoxazine provides the benefits of a non-toxic reactant including the formation of a high crosslinked structures by decorating the amine backbone with benzoxazine rings that will be subsequently polymerized for the formation of novel thermosets.

The molecular structure of the benzoxazine monomers was confirmed using Fourier transform infrared (FT-IR) and nuclear magnetic resonance spectroscopy (1H- and 13C-NMR). The polymerization temperature and curing behavior of the Bz monomers was studied using differential scanning calorimetry (DSC). The thermal stability of the final polybenzoxazine thermosets was investigated by thermogravimetric analysis (TGA) in order to establish the influence of phenol type on the thermal performance of bio-based polybenzoxazine. The Limiting Oxygen Index (LOI) value, which is characteristic for flame retardancy capability of materials was calculated by employing the char yield value from TGA.



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Ethanolamine, a novel linker for the covalent functionalization of cellulose acetate membranes

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Surface functionalization of polymeric membranes has emerged as a novel, promising technology for the production of multifunctional materials with applications in industry (e.g. water purification) or in the biomedical field. Cellulose acetate, in particular, is preferred for membranes production due to its high availability, versatile solubility in polar aprotic solvents, environmental friendliness and biocompatibility [1, 2]. In order to functionalize cellulose acetate membranes, 3-aminopropyltriethoxysilane (APTES) is frequently used as a linking agent between the membrane and the active molecule [2], however its high price raises certain issues when it comes to the mass production of the materials. Ethanolamine, an organic compound containing a primary alcohol and an amine group, could successfully replace APTES in the functionalization process, this leading to the attainment of a cost positive final product.

This study contains preliminary data about the potential of ethanolamine to be used as a novel, low cost linker for the attachment of various molecules on the surface of cellulose acetate membranes. For this purpose, commercial cellulose acetate membranes were hydrolyzed in the presence of sodium hydroxide and ethanolamine was covalently immobilized on their surface. The newly synthesized functional membranes were characterized by different techniques such as X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (FT-IR), Raman spectroscopy and thermogravimetric analysis (TGA/DTG). It was demonstrated by hi-res XPS onto C1s and O1s that the polymeric membranes were covalently functionalized.

Potential applications for covalently immobilized ethanolamine onto cellulose acetate membranes include binding of molecules with high complexing capacity for the retention of heavy metals or biomolecules for the improvement of biological processes such as osseointegration or hemodialysis.

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Strippable polymeric nanocomposite coatings for radioactive decontamination

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This work comprises an extensive study performed for the investigation of the decontamination efficiency of novel eco-friendly, water-based, strippable polymeric nanocomposite coatings developed for the decontamination of radioactive hazardous materials. For this purpose, eight different types of film-forming decontamination solutions, containing different types of complexing agents were prepared. The chelating agents were selected based on their structure, their capacity of complexing metals and their biodegradability. Besides the classical complexing agents (ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), 1,2-dihydroxybenzene and sodium gallate), three types of eco-friendly „new generation chelators" (iminodisuccinic acid (IDS), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) and ethylenediamine-N,N'-disuccinic acid (EDDS)) were employed, in order to compare their decontamination efficacy. Poly(vinyl alcohol) (PVA) was chosen as polymeric matrix in the decontamination formulations due to its high solubility in water, non-toxicity, biodegradability and also due to its excellent film forming and adhesive properties. The nano-clay fillers, bentonite (BT) and saponite (SP) were used herein not only for the improvement of the mechanical and thermal properties of the nanocomposite coatings, but especially for their outstanding ability to adsorb radioisotopes. Glycerol was introduced as plasticizer, to ensure the ease of strippability of the nanocomposite coatings. This decontamination method is based on the following principle: the decontamination solution is placed on the contaminated surface, the contaminant is entrapped into the nanocomposite matrix and when the coating is completely dried, it can be exfoliated, thus obtaining a clean, decontaminated surface.

To perform the decontamination tests, common types of surfaces found in contaminated areas (galvanized metal sheets (GMS), painted metal (PMe), ceramic tiles (CT) and plastic material (PMa) from the gas masks) were contaminated with a standard radioactive solution, consisting of ^{60}Co, ^{133}Ba, ^{137}Cs and ^{241}Am radioisotopes, with a well-known radionuclide volumetric activity. The decontamination factors obtained indicated that all the decontamination solutions can successfully be used to remove ^{137}Cs (DF>95%) from all the types of surfaces subjected to analysis. Also, for the other radioisotopes, high decontamination factors were obtained, as follows: DF ≈ 95% (^{133}Ba), DF ≈ 91% (^{60}Co) and DF ≈ 91% (^{241}Am). These new strippable polymeric nanocomposite coatings proved their efficiency for radioactive decontamination, while maintaining a minimal environmental impact because the biodegradability of the decontamination formulations prevents the generation of secondary wastes.

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Sol-gel synthesized silver-silica materials to obtain hybrid thin films on glass surfaces

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• Introduction

Sol-gel hybrid films have attracted attention of technological and scientific community due to the possibility of improving the properties of different materials for a variety of applications such as solar panels, solar collectors, video display screens, photochromic glasses[1,2].

The aim of this work was to synthetized the silver-silica materials by sol-gel process in order to realize the hybrid thin films on glass surfaces. The structural, optical and morphology properties of prepared silver-silica materials were characterized by FT-IR and UV–Vis spectroscopy, TGA and AFM analysis.

• Experimental methods

The sol-gel silver-silica solutions were prepared by mixing two silane precursors that contain various functional groups (methyl and glycidyl) with different solutions of $AgNO_3$, in the presence of titanium(IV) isopropoxide as cross-linking agent. The syntheses were conducted in acidic medium, at room temperature. The final samples were characterized both as powders (obtained after solvent evaporation) and as hybrid thin films (deposited on glass substrates) in order to investigate the structural, optical and morphology properties.

• Results and discussions

The functional groups present in the silver-silica materials were identified by FT-IR spectroscopy. The Si–O–Si characteristic modes (1000–1200 cm^{-1}) were found in all samples (asymmetric stretching). Thermogravimetric analysis was employed in an N_2 atmosphere to evaluate the thermal stability of the sol-gel silver-silica materials. To determine several significant effects, the weight loss was studied over three temperature intervals: 0–200 °C, 200–500 °C and 500–700 °C. The transmittance and diffuse reflectance of the hybrid thin films deposited on glass substrates were measured using a UV-visible spectrometer. The UV-visible spectra reveal that all hybrid films were highly transparent. The AFM results indicated that the surface morphology can be changed as function of $AgNO_3$ solution added during the formation of silica matrix.

• Conclusions

Silver-silica materials were prepared by acid-catalyzed sol-gel process, using silane precursors with various functional groups (methyl and glycidyl) and different solutions of $AgNO_3$. FTIR spectra indicated that the sol-gel silica materials have been successfully modified with organofunctional groups. The thermal stability of the sol-gel silver-silica materials, measured in an N_2 atmosphere, showed that the weight loss occurred stepwise. AFM analysis confirmed the formation of silver nanoparticles on the silica surface. The obtained silver-silica materials via sol-gel process could be used for improving the efficiency of the solar cell.

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Development of Bacterial Cellulose/Chitosan Membranes tailored with core-shell polymeric nanoparticles For Wound Dressing Applications

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- **Introduction**

The healing process represents a dynamic and complex interaction between cells, growth factors, blood, or extracellular matrix. Dermal wounds such as ulcers or burns which do not easy heal are a worldwide problem that demands clinical care. Without a clinical care or an improper management of such wounds can lead to delayed wound healing and wound infection. The wound dressing requires improvement of tissue repair, regeneration, and a growth process [1]. The study aims to develop novel wound dressing support which can overcome the classic wound dressing models by targeting a complex therapy management.

- **Experimental methods**

The management complexity is assured by the synergistic effect of the bacterial cellulose/chitosan membrane support and drug-loaded polymeric particles. In this regard, the study involved development of the membrane support with various compositions according to bacterial cellulose-chitosan ratio. At the same time, core-shell poly(N-isopropylacrylamide) (PNIPAM) nanoparticles were synthesized and loaded with silver sulfadiazine, an antimicrobial agent for skin infections. Finally, bacterial cellulose/chitosan membranes loaded with PNIPAM nanoparticles entrapped with silver sulfadiazine were prepared. PNIPAM nanoparticles were subjected to physico-chemical characterization and drug release test in specific media. Morphology of the membranes, PNIPAM particles and the final bacterial cellulose/chitosan membranes tailored with drug loaded PNIPAM particles was investigated by SEM. DLS was used to evaluate the size and Zeta potential of the obtained polymeric nanoparticles. The rheological measurements were performed by a Kinexus Pro Malvern rotational rheometer equipped with temperature control unit. The tests were performed on samples of 20 mm diameter with parallel plate geometry in a frequency range 1 to 20 Hz.

- **Results and discussion**

The morphological characterization revealed the structural and dimensional information both for PNIPAM nanoparticles and BC/chitosan membranes. Internal structure information with core-shell nanoparticles was evidenced by TEM analysis. DLS of PNIPAM nanoparticles was performed in order to reveal the dimensional differences between nanoparticles obtained with different recipes. The drug release profiles of antibacterial silver sulfadiazine were obtained for several encapsulation carriers: PNIPAM nanoparticles, drug entrapped BC/chitosan membranes and membranes loaded with drug loaded PNIPAM nanoparticles.

- **Conclusion**

As a conclusion, we reported here the preparation and complex characterization of a potential wound dressing design based on drug loaded PNIPAM nanoparticles entrapped in a bacterial cellulose/chitosan membrane support.

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Mechanical Behavior of Reinforced Silicone Rubber for Biomedical Applications

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Introduction

Silicone rubber is a widely used material in various applications, due to a large degree of flexibility, chemical stability, low surface tension, high permeability, oxidative resistance and a very good biocompatibility[1]. The major drawback of the silicone rubber is the modest mechanical properties[2]. The aim of this work is to study the influence of inorganic fillers with different hydrophobicity, such as hydrophilic nanosilica and hydrophobic nanosilica on the mechanical behavior of silicone rubber. The tensile strength and modulus of the nanosilica/silicon composites films were studied before and after aging by flexural tests and immersion in Phosphate Buffered Saline (PBS) and Simulated Body Fluid (SBF) environments[3]. In addition, the mechanical properties of silicon sample before and after *in vivo* study were characterized.

Experimental methods

Elastosil LR 3003/40 (Wacker, Germany) was used as an elastomer matrix and hydrophilic nanosilica (HDK N20, Wacker) and hydrophobic nanosilica (HDK H18, Wacker) as fillers. Different concentrations of nanosilica (1, 3, 5, 7%) were used in the composites. After the homogenization of the components in a laboratory mixer, the mixture was poured into metal frames of different thicknesses (0.6, 1 and 2 mm) and crosslinked into a laboratory press (165°C, 50 atm, for 5 minutes). For post-crosslinking, the pressed films were placed in the oven at 200°C for 4 hours.

Results and discussion

The results highlighted the influence of the filler content on the mechanical properties of the silicone rubber. The mechanical parameters (J - Young modulus, E - elongation at break and TS - tensile strength) increased progressively with the addition of inorganic fillers, especially with the addition of hydrophobic nanosilica (Fig. 1a). The hardness also increased after the addition of the hydrophobic nanosilica as observed in Fig. 1 b). The tensile properties were found to increase with the concentration of nanosilica up to 3 or 5%, depending on the thickness, while a further increase of the filler content to 7% lead to a decrease of some mechanical properties, due to poor homogenization.

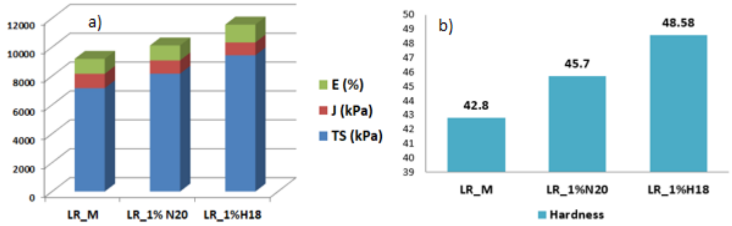

Fig 1. Tensile properties a) and hardness b) of neat silicone, silicone rubber with 1% N20 and silicone rubber with 1% H18.

Conclusions

Overall, the tensile properties increased with the addition of hydrophobic nanosilica. Immersion in PBS and flexural tests did not change significantly the mechanical properties, showing that the material is sufficiently stable in different environmental conditions. The hydrophobic nanosilica confers superior mechanical strength compared to hydrophilic nanosilica, due to its better compatibility with silicone, which is a hydrophobic matrix.

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Boron complexes of beta-diketones embedded in hybrid silica coatings with enhanced optical and thermal properties for textile fabrics

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- **Introduction**

Knowledge of natural compounds, on the one hand, and non-covalent interactions, such as hydrogen bonds, π−π stacking and electrostatic bonds, on the other hand, has led to the development of a new domain, the chemistry of supramolecular compounds. Thus, numerous systems, synthetic materials or platforms have been developed, for different applications, such as those of intelligent materials, catalysis, switches, antennas, detection and nanomedicine. Many of them have the support of natural or synthetic textile materials, being used in different fields such as filters, medical materials, clothes and covers. All of these hybrid materials are aimed at improving human living conditions and protecting the environment. [1-4]

- **Experimental methods**

In this study are presented experimental data regarding the manufacture of some compositions using sol-gel processes by appropriate selection of some boron complexes of beta-diketone dyes and silane components. Compositions were applied onto the surface of textile materials by pad-dry method and properties of coated textile fibers were analyzed.

The host matrix was obtained by generating of hybrid silica networks modified with aromatic groups by the hydrolysis / condensation of tetraethoxysilane : organosilanes precursors in molar ratio 1: 0.1-1: 2, in acid catalysis. The β-diketone complexes have been immobilized in hybrid silica matrices by sol-gel processes and deposited on textile materials by impregnation followed by thermal cure.

- **Results and discussion**

The dyeing of the textile fibers in the sol-gel system provided intense and uniformly colored materials. The coated textiles were characterized by FTIR spectroscopy, color measurements in CIEL*a*b* system, fluorescence spectra and thermogravimetric analysis. The spectrophotometric measurements revealed that colored textiles preserve the original properties of the chromophores, which are influenced by the interactions between the dye and the host matrix.

- **Conclusion**

Following the functionalization of textile materials with hybrid systems containing β-diketone complexes, were obtained and studied coatings having enhanced optical and flame retardancy properties.

ACKNOWLEDGMENT: 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-2017-0395/SECURE-NET, PNCDI III (70PCCDI/2018)

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Valorization of Rabbit Skin Glue to Produce Antimicrobial and Biocompatible Nanofibers

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This paper assesses the extraction of rabbit glue from rabbit skin by-product for use as a raw material for producing of antimicrobial and biocompatible nanofibers by electrospinning. Collagen glue was associated with different antimicrobial agents such as ZnO NPs, TiO_2 NPs doped with nitrogen and AgNPs and chitosan. Conventional antimicrobial agents such as quaternary ammonium salts, metal oxide NPs, metal salt solutions and antibiotics are widely applied to control bacterial infections. However, their use is limited due to the toxic nature and reduced activity of antimicrobial agents[1].

The electrospun nanofibers were subsequently characterized using scanning electron microscopy (SEM), Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FT-IR) and X-ray dispersion (XRD). Antimicrobial activity was performed against gram-positive and gram-negative bacteria and pathogenic fungus. The biocompatibility of electrospun nanofibers was investigated to determine the cell viability by the MTT test assays using the cell line of mouse fibroblast (NCTC clone 929).

Nanofibers obtained by the electrospinning process showed a diameter in the range of 42.66 nm - 114.6 nm, pores with a diameter of about 100 nm, and indicated P1 (rabbit collagen), P3 (rabbit collagen loaded with TiO_2-AgNPs) and P4 (rabbit collagen loaded with chitosan) variants as suitable for the cell proliferation (Figure 1). Antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus* and fungal activity against *Candida albicans* prove that the electrospun samples can be explored for production of medical wound dressing.

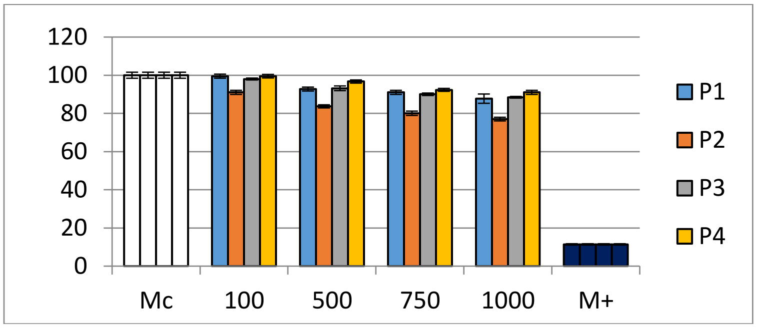

Figure 1. Cell viability of NCTC clone L929 fibroblast cells cultivated in the presence of nanofibers for 48 h, evaluated by MTT assay. All samples were reported to the Mc (untreated cells) and positive martor (M+).

The results recommend the potential use of antimicrobial and biocompatible nanofibers for non-active dressings, wound healing and tissue engineering.

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Recovery of Chitosan from Unexploited National Ecosystems - Dimensional - Compositional Characterization

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- **Introduction**

It is already documented that the antibacterial activity of chitosan depends on its characteristics such as solubility in acid media or in aqueous solutions, as well as on the particulars of the studied subtypes [1]. It has already been proven that low molecular chitosan is recommended to be used in applications that involve antimicrobial, antioxidant, antiviral activity, as well as in food protection [2]. If enhancing the antimicrobial activity implies forming intermolecular bonds, associated with a higher swelling degree [3]; the antifungal activity relates to the activity of the amino groups, with a positive charge that bind to the phospholipids from the cellular walls of mushrooms, which are negatively charged. Through this electrostatic interaction, a polymeric film is generated at the surface of the membrane, which alters the permeability and limits the nutrient income. In addition, this film can further alter the structure of the membrane by penetrating the cellular walls and reducing the DNA/RNA activity or the protein synthesis [4]. Out of these considerations, this study aims to compare and characterize the chitosan obtained from crayfish shells (*Astacus leptodactylus*) and from *Rapana venosa egg* capsules. The objective of this study is to define the uses of this natural extract, obtained from recycled food waste.

- **Experimental methods**

The methods used in this study are analytic ones such as FTIR, UV-Vis, fluorescence spectroscopy, potentiometric titration, offering information about the composition, and techniques such as SEM, XRD- which allow a morphological perspective, highlighting the texture of the structure; along with viscometry, that determines the dimensional size of the compounds and rheometry, which describes the flow behaviour.

- **Results and discussion**

The results obtain from FTIR and UV-Vis spectroscopy confirm the fact that the material that has undergone demineralisation and deproteinization processes is a type of chitosan. Moreover, in comparison with the chitosanobtained by our group from *Rapana venosa* egg capsules, these samples have a higher molecular mass. The separation parameters as well as the deproteinization and deacetylation techniques have a clear influence on the molecular mass, on the deacetylation degree and on the structure of the samples.

- **Conclusion**

The results demonstrate that food waste, which include crayfish crab shells represent a valuable source of chitosan, which enlarges the market of raw materials for specialised applications in the medical field and packaging industry.

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New developed magnetic nanoparticles as drug delivery systems for bone cancer

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Nanotechnology can offer a solution to alleviate the side-effects that may appear after chemotherapy by using magnetic nanoparticles (MNPs) as carriers for active substances. Unfunctionalized MNPs has been successfully obtained through the co-precipitation method, encapsulated in polymeric microspheres through the ultrasound-mediated solvent evaporation method, and functionalized with anti-tumor substances (carboplatin - Carbo@ $Fe_3O_{4,}$ doxorubicin - Dox@Fe_3O_4 and gemcitabine - Gem@F_3O_4). The anti-proliferative efficiency of these systems was analyzed after 48 hours of incubation with G292 osteosarcoma cells using *in vitro* tests to estimate the cell viability, alkaline phosphatase (ALP) activity and the level of reactive oxygen species (ROS). The cell number decreased for all drug nanosystems with a higher percent compared to pure drugs. These novel nanosystems induced the generation of ROS and decreased the ALP activity in human osteoblasts, which confirmed their cytotoxic effect. Further, a higher degree of Dox@Fe_3O_4 accumulation was visualized in the cytoplasm and nuclei of osteoblasts in comparison with pure doxorubicin. These functionalized MNPs can represent new efficient cancer treatment options throughout their anti-proliferative capacity against osteosarcoma.

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The Nanomechanical and Tribological properties of Polypropylene/Fly-ash/Glass fiber composites

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- **Introduction**

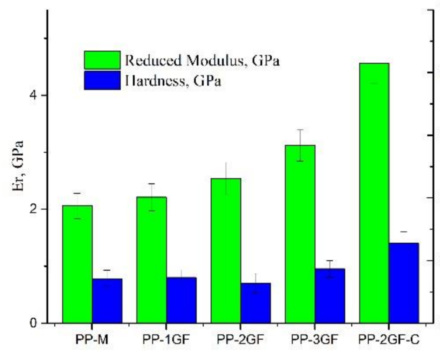
Automobile manufacturers face great challenges as regulations of automobile fuel consumption and CO2 emission become stricter year by year. Glass fiber-reinforced polymers are still considered as an main solution material for lightweight automobile parts, such as body panels, doors, roofs, frame segments, and seating systems. The addition of fly-ash into the system provided a cheaper filler for the final product thus reducing the cost of the car part and also provides usefulness to a waste material. Nanoindentation and nanoscratching technique can be used in order to measure a wide range of local mechanical properties (hardness, stiffness, reduced modulus, friction coefficient, etc.) for homogenous and heterogenous materials[1][2][3]. The purpose of this paper was to study the possibility of replacing a certain percentage of glass fiber with fly-ash, without decreasing the nanomechanical and tribological properties of polypropylene/fly-ash/glass fiber composites.

- **Experimental methods**

In dynamical conditions, by melt processing method, composites based on commercial polypropylene (PP), 5 wt. % fly-ash (C) and 20, 25 and 30 wt. % long glass fiber (GF) were obtained. The nanoindentation and nanoscratch tests have been performed at room temperature on a TI Premier system (Hysitron Inc., USA) using a three-side pyramidal Berkovich tip.

- **Results and discussion**

The results showed an increase of the reduced modulus and the hardness with the increase of the glass fiber content. The addition of 5 wt. % fly-ash in PP with 25% glass fiber had the effect of increasing both the reduced modulus and the hardness with 79.5% compared to PP with 25% glass fiber and with 46% compared to PP with 30% glass fiber (Fig.1). The contact depth was also reduced for the composite with fly-ash (Fig. 2), which was in correlation with the overall increased nanomechanical properties of this composite.



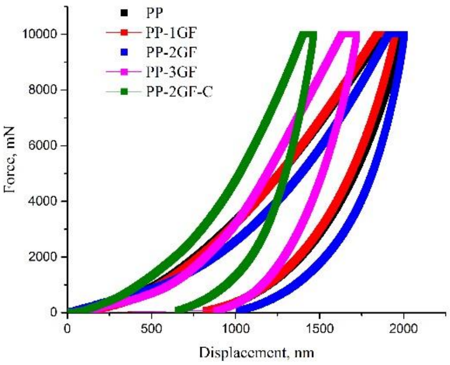


Fig 1. Reduced Modulus and Hardness; Fig 2. Force vs Displacement

- **Conclusion**

The glass fiber content of PP composite can be reduced by the addition of fly-ash. The addition of fly-ash greatly increases the nanomechanical properties of a polypropylene/glass fiber composite, as a result of achieving a synergistic effect between the components. Further applications could consider this synergistic effect between components in order to provide a material with improved properties for automotive industry.

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The nanomechanical behavior of Polyamide/Layered double hydroxide-melamine composites with flame retardant properties

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- **Introduction**

For automotive materials good flame retardancy, next to good wearing properties and other surface properties are often required. For improving flame retardancy of the polyamide matrix,either layered double hydroxides (H) alone or melamine (M) as fillers were reported [1][2]. In this study new materials were investigated based on the combination of two. Nanoindentation and nanoscratching techniques were used in order to measure a wide range of local nano-mechanical properties (hardness, stiffness, reduced modulus, roughness, friction coefficient). The nanomechanical and tribological properties highlighted directly the influence of the fillers on materials surface and in indirectly the interaction between fillers and polyamide matrix.

- **Experimental methods**

A commercial polyamide 6 (PA) was used as the polymer matrix having compounded with different content of H and M. Sample names represents the different weight ratios of M or H in the PA matrix. All samples were obtained in dynamical conditions by melt processing method (extrusion-injection).

All nano-mechanical tests have been performed at room temperature on a TI Premier equipment (Hysitron Inc., USA) using a Berkovich probe.

- **Results and discussion**

The obtained results showed an increase of the reduced modulus and the hardness, with the addition of M or M and H compared to the neat PA. The highest values were achieved with the addition of 5 wt.% M in PA (Fig.1). However, all M+H PA composites showed improved properties in comparsion with neat PA. The contact depth is also reduced for the composite with M and M+H in comparison with PA (Fig. 2), which is in correlation with the increased nanomechanical properties of this composite.

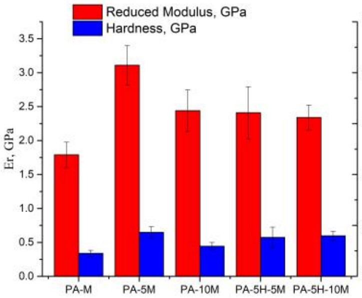

Fig1. Reduce Modulus and Hardness

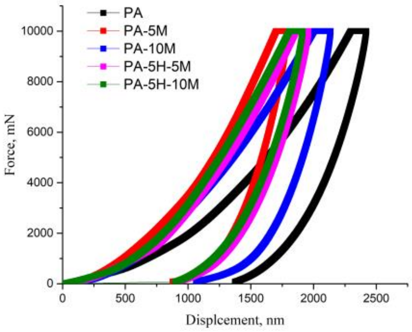

Fig2. Force vs Displacement

- **Conclusion**

The addition of M and H improves the nanomechanical properties of neat polyamide 6, due to the combined effect between the components. However, the best result was obtained with the addition of only 5% M in the polymer matrix. In comparsion with the initial PA all materials were proven as possible candidates to improve the existing profile of PA.

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Evaluation of alginate-based formulations suitable for the removal of radionuclides and heavy metals from the contaminated surfaces

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This work comprises different alginate-based formulations suitable for the removal of radionuclides and heavy metals from the contaminated surfaces. The goal of this study was to evaluate the influence of sodium alginate (SA) on the final properties of the film-forming gels. Sodium alginate is an anionic biopolymer with exceptional properties (biodegradability, biocompatibility), possessing the ability of forming hydrogels via divalent cations cross-linking. Being especially designed for surface decontamination applications, these alginate-based formulations possess a unique combination of features: homogenous film-forming ability, ease of strippability, mechanical resistance, high decontamination efficiency, biodegradability. The decontamination solutions were obtained by using polyvinyl alcohol (film-forming polymer), nanosized hydrophilic bentonite (due to its remarkable adsorption capacity), and SA. These formulations can be customized for the removal of hazardous metals by introducing sodium alginate because this biopolymer can easily form hydrogels through the entrapment of the contaminants, by using them to form the crosslinking bridges between the polymer chains. Different concentrations of SA (0.25%, 0.5%, 0.75% and 1%) were employed in the decontamination solutions, in order to establish the appropriate composition for this type of application. The results of this study showed that SA could improve the physical and mechanical performances of the film-forming gels, but it could also have a significant contribution on their decontamination performances and their biodegradability. By employing SA in the decontamination solutions, we can reduce the amount of synthetic polymer, thus minimizing the problems encountered due to solid waste subsequent disposal.

ACKNOWLEDGEMENTS: The authors would like to thank for the financial support provided by the National Authority for Scientific Research from the Ministry of Education, Research and Youth of Romania through the National Project PN-III-P2-2.1-PTE-2019-0400, ctr. No. 49PTE/2020 and PN-III-P2-2.1-PED-2019-4222 ctr. No.427PED/2020. Authors are also grateful to Lanxess for donating the complexing agent BAYPURE® CX 100.

Polymer particles with applications in the administration of active substances

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- **Introduction**

Chitosan is a natural, biocompatible, biodegradable, nontoxic and easily available polymer that can be used to prepare nanoparticles. Chitosan nanoparticles can be widely used in pharmaceutical industries as an antimicrobial agent or as drug delivery vehicle [1]. In medicine, chitosan is useful in bandages to reduce bleeding and as an antibacterial agent can also be used to help deliver drugs through the skin. It is also used in the development of chitosan drug control releasing systems including chitosan sponges, chitosan film, chitosan beads, chitosan microbeads (microspheres) and chitosan nanoparticles [2].

The purpose of this study is to promote the development of a hybrid drug control release system.

- **Experimental methods**

Chitosan nanoparticles were prepared by ionic gelation method, chitosan polysaccharide is dissolved in aqueous acidic solution to obtain the cation of chitosan. Then the sodium tripolyphosphate solution is added drop by drop in the solution of chitosan. Due to the complexation between opposing charges (positive/negative), chitosan undergoes ionic gelation and precipitates to form spherical nanoparticles. The nanoparticles were characterized by UV-Vis spectroscopy, FTIR (Fourier transform infrared spectroscopy), DLS (Dynamic Light Scattering), X-ray photoelectron spectroscopy (XPS).

- **Results and Discussion**

Results revealed that the size of the prepared alginate and chitosan nanoparticles varied. Furthermore, increasing either sodium tripolyphosphate or chitosan concentration increased the size of their nanoparticles [3].

- **Conclusion**

Chitosan nanoparticles were successfully prepared by ionic gelation method.

ACKNOWLEDGMENT: The authors acknowledges Executive Agency for Higher Education and Research Funding (UEFISCDI) and National Research Council (CNCS) for the financial support through the PN III research project 'Smart materials for medical applications-INTELMAT' no. 39PCCDI/2018. The DLS analyses on (Malvern Zetasizer Nano ZS90) were possible due to European Regional Development Fund through Competitiveness Operational Program 2014-2020, Priority axis 1, Project No. P_36_611, MySMIS code 107066, Innovative Technologies for Materials Quality Assurance in Health, Energy and Environmental - Center for Innovative Manufacturing Solutions of Smart Biomaterials and Biomedical Surfaces – INOVABIOMED.

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Physical and Barrier Properties of Clove Essential Oil Loaded Potato Starch Edible Films

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In this work, nanoemulsion of Clove essential oil (CEO) was loaded in potato starch edible films and the effect of different parameters (polymer, plasticizer, and CEO concentration) on the film properties were analyzed and optimized. Mechanical properties were studied in terms of puncture and tensile tests. Thermal stability of the films was investigated by differential scanning calorimetry (DSC). Films morphology was observed by optical polarized microscope. Their color was characterized by CIELAB parameters. Water vapor permiability and water vapor transmission rate are measured by gravimetric method using W3/031 (Labthink, China) instrument. The gas permeability properties of films towards oxygen (O_2) and carbon dioxide (CO_2) were determined as reported by Nascimento da Silva[1] and according to ASTM D1434[2]. Films were characterized with white color and high opacity. The results of polarized microscopy showed uniform incorporation of nanoemulsions into the edible film. The loaded CEO improved water and gas barrier properties of the films. The obtained results suggested that the new multicomponent films may be used as food active packaging.

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