

**12-13 JUNE 2024 RIMINI**  
**MACROGIOVANI24**



# BOOK OF ABSTRACTS

**UNDER THE PATRONAGE OF**



ALMA MATER STUDIORUM  
UNIVERSITÀ DI BOLOGNA

DEPARTMENT  
OF INDUSTRIAL CHEMISTRY  
"TOSO MONTANARI"



ALMA MATER STUDIORUM  
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DEPARTMENT  
OF CIVIL, CHEMICAL,  
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**MACROGIOVANI 2024**

RIMINI (ITALY), 12<sup>TH</sup>-13<sup>TH</sup> JUNE 2024

# BOOK OF ABSTRACTS

**Macrogiovani 2024**

June 12<sup>th</sup> -13<sup>th</sup>

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## PRELIMINARY STUDIES ON THE SUITABILITY OF POLYMERIC MATERIALS FOR THE REALIZATION OF SUSTAINABLE, FLEXIBLE AND ACTIVE PRIMARY PACKAGING (PR-FESR BIO4SUSPACK PROJECT)

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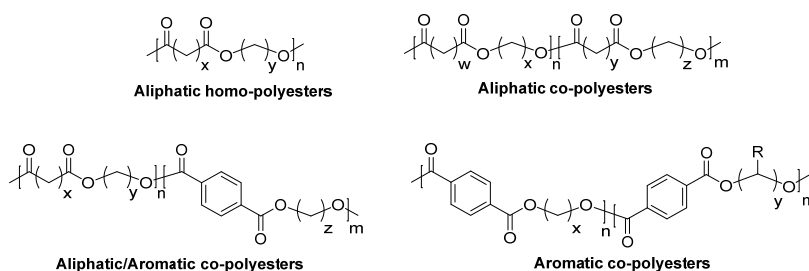
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### Abstract

The research for new, renewable, and high-performant materials is one of the most appropriate strategies to reduce environmental pollution, greenhouse gas emissions and to accelerate the transition from fossil fuels dependency to a circular and carbon-neutral economy. The need for optimization is even more evident in the production processes of raw materials, as they are responsible for the generation of large volumes of materials synthesized from non-renewable sources and without a designated sustainable end of life.<sup>1</sup> The food industry uses plastic on a large scale and is therefore the sector where the most critical issues are concentrated. More than 80% of the food packaging industry is currently based on flexible materials, reflecting the potential of this strategy, in terms of a drastic reduction in plastic volume, lower costs for production, transport and end-of-life waste disposal. The growth drivers for bioplastics are bio-based and/or biodegradable materials, that can be further modified with natural fillers to achieve similar performance and functionalities as oil-based materials.<sup>2</sup> By-products and/or agri-food wastes can also be used to obtain active additives: with cellulose nanocrystals (CNCs), for example, it is possible to obtain flexible, light and resistant packaging, replacing fossil-based raw materials with cost-effective, sustainable, innovative and bio-based ones. Agri-food by-products can be either employed to improve mechanical and barrier properties, but also as antimicrobial agents to extend the shelf-life of packaged foods. Accordingly, as part of the BIO4SUSPACK project, some bio-based, biodegradable and food-grade commercial polymers (Figure 1) on the European market were selected, and subjected to thermal, mechanical gas barrier, and surface characterization.

The more suitable polymers will be further improved in terms of their overall properties, with the ultimate aim of replacing the commercial solutions of the companies involved in the project with more sustainable studies will be carried out to confirm the sustainability of the new materials. The project results will make it possible to promote, through dissemination plans and/or digital platforms, the transition of companies from the Emilia Romagna region operating in the food sector to the circular economy and sustainable production/product models.



**Figure 1.** Chemical structures of the commercial polyesters

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## MULTIPOTENT PRECURSORS AS IMMOBILIZATION STRATEGY FOR CONJUGATED POLYMERS WITH COMPLEMENTARY ELECTRONIC PROPERTIES

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### Abstract

Indubitably, conjugated polymers played a significant role in the rise of organic electronics in the past decades, contributing dramatically to the development of technologies such as OLEDs, OPVs, and flexible electronics. The success of these materials, which comprise a fully conjugated backbone where the carbons are all sp<sup>2</sup> hybridized and electron wavefunctions can span several units, is to be ascribed to the combination of appealing semiconducting and redox properties with their high processability in solution processes precluded to silicon. However, their inherently flat structure and tendency to form aggregates, can lower their solubility, resulting in complex issues during device fabrication or even the synthesis of high-molecular weight well-characterized materials. At the same time, addition of solubilizing side chains can make the materials too soluble, complicating the device design when steps with orthogonal processes are necessary.

To avoid these limitations and investigate new fabrication possibilities, we are developing a novel approach based on solution-processable polymeric precursors that can be employed for the immobilization of high-molecular conjugated polymers characterized by different structures and properties. In particular, during this presentation, I will introduce the concept of highly-processable polymeric precursors as a solution to prepare high-molecular weight conjugated polymers with the absence of solubilizing chains and discuss an example of two different semiconducting materials characterized by complementary electronic properties but originating from the same precursor. Notably, such transformations are achieved by different chemical treatments, which can also be applied orthogonally and on the solid state, thus generating different phases on a single substrate.

We characterized the systems proposed and show several examples of how this methodology can be applied for the fabrication of OFETs, redox polymers, and multicolored electrochromic displays.

**Acknowledgements.** This study was carried out within the POLiBATT project – funded by European Union – Next Generation EU within the PRIN 2022 PNRR program (D.D. 1409 del 14/09/2022 Ministero dell'Università e della Ricerca).



## DEVELOPMENT OF POROUS STRUCTURES TO REMOVE MICROPLASTICS

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### Abstract

Microplastics (MPs) are defined as plastic fragments typically less than 5 mm in size, partially passing through wastewater treatment plants. They can enter marine ecosystems, posing risks to marine life<sup>1</sup>. Currently, multiple technologies for MPs removal have been developed including physical, chemical, and biological approaches. Among the different tools proposed to remove MPs there are filtration technologies, adsorption removal, coagulation treatments, magnetic removal, bioremediation methods and chemical oxidation treatments. Most of them, are obtaining high removal efficiencies but some technologies are not totally “green”<sup>2</sup>.

This work is focused on the development of foams, hierarchical porous systems, based on bacterial cellulose, BC, naturally formed during Kombucha fermentation, and poly (vinyl alcohol), PVA, a biodegradable polymer, to be used for the removal and adsorption of MPs from wastewater coming from the washing of synthetic clothes. Foams were obtained through an eco-friendly preparation method able to generate a pore structure by entrapping air into the polymer/filler aqueous dispersion during a high-speed mixing. Foam with different compositions were prepared by modulating BC and PVA phases. The thermal properties of the realized foams were obtained by using differential scanning calorimetry and thermogravimetric analysis, foam morphologies were assessed through scanning electron microscopy (SEM), interaction among the phases were detected by Fourier transformed infrared analysis, moreover mechanical properties were examined.

**Acknowledgments.** This research was supported by the project PRIN2022 “Production of bacterial cellulose from agrifood residues by Kombucha culture: enhancing cellulose productivity and tailoring its techno-functional properties for advanced applications - BACK APP” funded by European Union – Next Generation EU, C.I. 2022AEXJL7 - CUP B53D23005780006,

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## NEW SUSTAINABLE RECYCLING PROCESSES FOR CHROME-TANNED LEATHER

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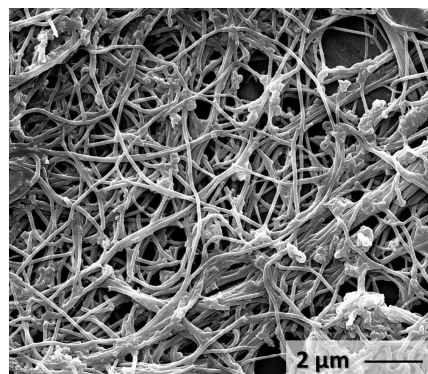
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### Abstract

One of the oldest and most widespread manufacturing sectors in the world is leather production. To produce finished leather, animal hides and skins are chemically treated with tanning agents to change the collagen's macromolecular structure and prepare them for application as sports equipment, furniture, clothes, and bags<sup>1</sup>. The most common tanning process involves the use of trivalent chromium, which is easily oxidised into hexavalent chromium, a highly soluble and carcinogenic metal ion. Thus far, the end of life of leather waste has typically been in landfills, resulting in serious environmental problems and health risks. New technologies for leather scraps recycling are divided into two categories: direct and indirect methods. Using direct techniques, leftover leather is recycled to create new composite materials without undergoing any chemical changes. Indirect methods require laborious steps to separate and recover collagen and chromium and then recycle each one separately. In this research, a direct and sustainable mechanical recycling method has been developed. Leather scraps were grinded in a cutting mill and/or in a planetary ball mill, testing the effect of both dry and wet (in presence of water) milling conditions on the morphology of leather (Fig.1). Polymer composites were obtained by combining the grinded leather with various polymers, either in the form of aqueous solutions/suspensions or by melt mixing. The polymer matrices selected for different applications include thermoplastic polyurethane, cellulose acetate, polyvinyl alcohol, polylactic acid, polybutylene succinate adipate, waterborne polyurethane and polyacrylate suspensions. Surface and bulk morphologies of the prepared materials were examined by scanning electron microscopy (SEM); thermal and mechanical properties of the samples were also assessed by differential scanning calorimetry, thermogravimetry and tensile tests. Results demonstrated the suitability of the proposed process for the recycling of chrome-tanned leather waste.



**Figure 1.** SEM micrograph of wet ball-milled leather.

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## SYNTHESIS AND CHARACTERIZATION OF POROUS POLYMERIC MATERIALS FOR ENVIRONMENTAL REMEDIATION

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### Abstract

The 21<sup>st</sup> century has been referred to as 'the century of the environment',<sup>1</sup> highlighting the profound global concerns related to increasing pollution resulting from human activity. The concept of "environmental remediation" is at the centre of this discussion. It involves a comprehensive approach to dealing with hazardous substances in the environment, including their removal, treatment, and containment across various environmental settings.

Among the various removal strategies, adsorption stands out as one of the most feasible, versatile, and cost-effective methods.<sup>2</sup> This process involves physical and/or chemical interactions between targeted molecules and the adsorbing substrate.

Accordingly, the present project focuses on the synthesis and characterization of porous polymeric materials designed for adsorption purposes. The goal is to optimize the materials features that are crucial for the maximization of the adsorption process. Among others, a high surface area, tailored pore structures, and suitable surface chemistry are key parameters in determining the final adsorption capacity of the developed materials. To do so, a fine tuning of the materials- and process-related parameters is essential. As preliminary part of this work, the study of the crosslinking step by which the porous polymeric structure is obtained has been addressed. It represents a crucial phase, as it is responsible for the balance between mechanical/chemical stability of the materials and the availability of active sites, that are necessary to ensure a high adsorption capacity. As a result, different crosslinking agents were investigated, paying particular attention to safety and sustainability in their selection. The polymer/crosslinker ratio and crosslinking conditions were varied, in order to find the optimal trade-off of the targeted properties.

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## DRESALIZATION AND OPTIMIZATION OF PVDF MEMBRANE FOR REMOVAL OF MICROPLASTIC RELEASED FROM TEXTILE

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### Abstract

This study investigated the development of porous hydrophilic membranes using polyvinylidene difluoride (PVDF) to be used for the removal of microplastics of fibrous shape released to water during washing of synthetic clothes<sup>1</sup>. The membranes were prepared via the Non-Solvent Induced Phase Separation (NIPS) technique, where the polymer solution was cast onto a suitable substrate (glass) and subsequently immersed in a coagulant bath containing the non-solvent<sup>2</sup>. Dimethyl isosorbide was employed as biobased non-toxic solvent and three different coagulant baths were used to induce polymer precipitation and to study their effect on the final membrane morphology and properties: H<sub>2</sub>O, H<sub>2</sub>O-NaCl, and H<sub>2</sub>O-Isopropanol (IPA). Moreover, various porogen agents were added into the polymeric casting solution with the aim to modulate the membrane pore size, thus achieving optimal porosity for the specific application of interest. In detail, three different porogenic agents, i.e., Pluronic F-127, Triton X-100 and Span 80 were selected and their impact on membrane morphology and performance was evaluated. The obtained membranes were characterized through morphological and thermal analysis, porosity, thickness and contact angle measurements, mechanical tests and pure water permeability. The obtained results showed that membranes prepared with Pluronic F-127 as pore former agent and coagulated into the H<sub>2</sub>O bath exhibited the most promising properties to be used to remove microplastics released to water during washing of synthetic textile, offering high microfibers retention capacity. This study provided a fundamental basis for the development of efficient and sustainable PVDF membranes for filtration applications during washing processes.

**Acknowledgments.** This research was supported by the Horizon Europe Project REMEDIES “Co-creating strong uptake of REMEDIES for the future of our oceans through deploying plastic litter valorization and prevention pathways” Grant agreement ID: 101093964.

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## CARDOON BIOMASS EXPLOITATION FOR BIOPLASTICS DESIGN

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### Abstract

Poly(3-hydroxybutyrate) (PHB) is a totally biobased and biodegradable polyester, produced by microorganisms, representing a valid alternative to conventional plastics. It presents several drawbacks such as a "narrow temperature window of processability" and high crystallinity. Many strategies have been proposed to solve PHB drawbacks such as the use of plasticizers or blending with other biopolymers. This work is part of "CARDIGAN project", (CARDoon valorization by InteGrAted biorefiNery), a collaborative project financed by the Italian Ministry of Research, in a context of integrated biorefinery and circular economy, in which we enhance all cardoon fraction to produce innovative bioplastics. In this work PHB is produced by fermentation using Inulin extracted from Cardoon roots as carbon source. Moreover, oil extracted from cardoon seeds is used for a double purpose: i) it is subjected to an epoxy mechanism, improving reactivity, to be used as green and biodegradable PHB-plasticizer; ii) it has been tested as substrate for *Pseudomonas resinovorans* in order to produce medium-chain length PHA (mcl-PHA). PHB, epoxy cardoon oil (ECO) and mcl-PHA have been mixed in physical blends with the aim to develop PHB based films with optimal thermal, mechanical, and physical properties. The ternary blend, in which the PHB polymer matrix was added with mcl-PHA and epoxidized cardoon oil, evidenced a synergic effect of both additives in modulating PHB structural and thermal properties, promoted by the physical interaction occurring among the components.<sup>1</sup>

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**CELLULOSE BASED HYPER-CROSSLINKED NANOFIBRILS FOR WATER REMEDIATION**

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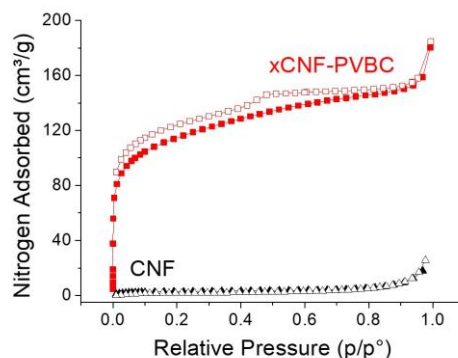
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**Abstract**

Physical adsorption stands out as a particularly advantageous method for water remediation due to its spontaneous, reversible, and eco-friendly nature as well as minimal energy and economic costs<sup>1</sup>. A microporous structure is essential for this process to take place; thus, hyper-crosslinked resins (HCLRs) emerge as particularly promising candidates in current research. HCLRs have a micro/mesoporous structure, high specific surface area and exceptional chemical and thermal stability, all while offering high tailorable morphology, porosity, and functionality<sup>2</sup>. In this work, HCLRs were exploited to enhance the adsorption capabilities of cellulose, a highly sustainable material. Cellulose nanofibrils (CNF) were chosen for their high specific surface area and eco-friendly attributes, then grafted with poly(vinylbenzyl chloride) to improve their adsorption properties. Through Friedel-Crafts alkylation, the resulting material was hyper-crosslinked, resulting in cellulose nanofibrils grafted with a highly microporous shell (xCNF-PVBC), characterized by a specific surface area of 409 m<sup>2</sup>/g (Figure 1), with cellulose content of approximately 70 wt%. The functionalized xCNF-PVBC, tested for adsorption of 2,4-dichlorophenol (DCP) from water at 298 K, exhibit very good adsorption capabilities, with adsorption capacity of 284 mg/g at the initial DCP concentration of 1000 mg/L. Thermodynamic analysis was carried out to elucidate the adsorption mechanism of the synthesized material, showing the exothermic nature of the process. Results highlight the potentiality of this approach to develop bio-based alternatives to conventional fossil-based adsorbent materials.

**Acknowledgements:** We acknowledge financial support under the National Recovery and Resilience Plan (NRRP), NextGenerationEU, PRIN Project PHOTOPAD, code P2022FP2W4, 2023-2025, CUP B53D23027540001.



**Figure 1.** CNF and xCNF-PVBC nitrogen adsorption/desorption isotherms at 77 K (adsorption in full symbols, desorption in empty symbols).

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## BLENDING OR BONDING? BENZOTHIOXANTHENE DERIVATIVES AS EMITTERS IN LUMINESCENT SOLAR CONCENTRATORS BASED ON POLY(METHYL METHACRYLATE) FROM RECYCLED SOURCES

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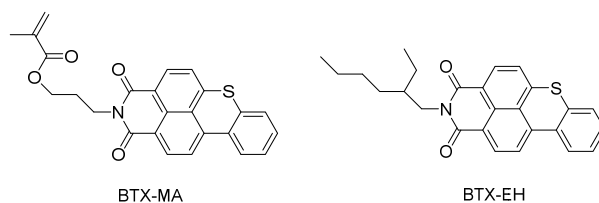
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### Abstract

Many conjugated planar fluorophore structures used for the preparation of poly(methyl methacrylate) (PMMA) Luminescent Solar Concentrators (LSC) face concentration quenching due to the presence of free dye molecules that phase separate from the host polymer matrix, even at relatively low concentrations.<sup>1</sup> One potential strategy to mitigate this effect without diminishing the fluorophore quantity is the covalent integration of dye into the polymer chain through co-polymerization with a monomeric unit functionalized with the fluorophore molecule. Benzothioxanthene (BTX) imides have shown promising emitting properties in solution<sup>2</sup> and comparable to commonly used perylene diimides (PDIs). Also, considering the mono-substitution, they are the best candidate since they prevent cross-linking during the polymerization process. Notably, two BTX derivatives were synthesized as fluorophores: i) BTX-EH, dispersed within the PMMA matrix; ii) BTX-MA, containing a methacrylic group suitable for co-polymerization with MMA. All devices were based on PMMA manufactured through free-radical polymerization of chemically recycled methyl methacrylate (r-MMA), and exhibits properties similar to PMMA slabs produced from virgin methyl methacrylate but with a lower environmental impact. LSCs with varying fluorophore concentrations (from 100 to 550 ppm) were obtained with a high quantum yield (QY up to 85%), and the internal ( $\eta_{\text{int}}$ ) and external ( $\eta_{\text{ext}}$ ) photon efficiencies were determined as well.<sup>3</sup> The results obtained are promising in defining the bonding method as a valid strategy to emphasize the emission properties of BTX imidic derivatives.



**Figure 1.** BTX imidic derivatives structure.

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## MOLECULARLY IMPRINTED POLYMERS WITH BIO-BASED MONOMERS TO ADSORB CARBAMAZEPINE FROM WASTEWATER

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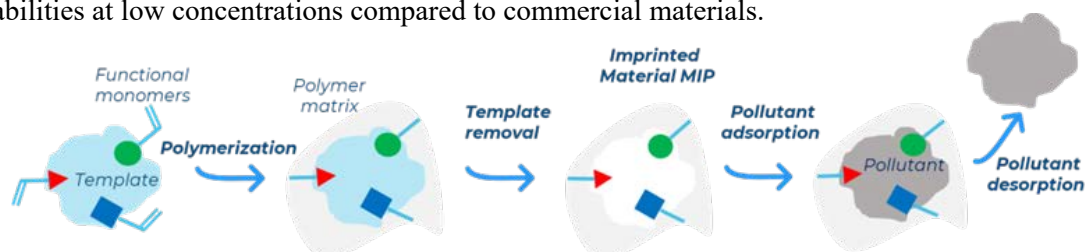
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### Abstract

In aqueous effluents, the presence of pharmaceuticals is becoming increasingly relevant day by day. These compounds are viewed as contaminants of emerging concern (CEC) due to their lasting presence and harmful effects even in low concentrations. Presently, conventional wastewater treatment plants struggle to fully eliminate them. One of the most detected drugs globally is carbamazepine, primarily used in psychiatry as an anti-epileptic medication.

This study introduces novel resin materials aimed at removing carbamazepine from wastewater. These materials, known as molecularly imprinted polymers (MIPs), possess the ability to selectively capture specific target molecules through a combination of structural effects and non-covalent interactions (Figure 1). Previous research has identified selective MIPs capable of removing carbamazepine, many of which utilize methacrylic acid as a monomer and ethylene glycol dimethacrylate as a cross-linker. In this investigation, six polymers were synthesized using radical polymerization, employing a trifunctional cross-linker, trimethylolpropane triacrylate, and six different bio-based monomers: methacrylic acid, eugenol, p-coumaric acid, 3-(2-furyl) acrylic acid, fumaric acid, and ferulic acid. The choice of cross-linker aimed at producing more stable and rigid materials, particularly suitable for future applications in adsorption columns. The selection of monomers aimed at examining the interaction between carbamazepine and various functional groups, with many containing aromatic rings to facilitate  $\pi$ -stacking interactions. For preparing the materials, bulk polymerization has been selected to minimize the amount of solvent involved: the reaction conditions and reagents ratio between template, monomer, and cross-linker have been optimized.

Characterization of the polymers included FTIR analysis to confirm successful reaction occurrence and thermogravimetric analysis to assess thermal stability, while their adsorption capacity was evaluated using UV-vis and UPLC by introducing carbamazepine into a real treatment plant effluent to consider matrix effects. Adsorption isotherms were plotted for different concentrations of carbamazepine for each material. The adsorption performances of the MIPs were compared with two industrial resins: activated carbon (NORIT) and Amberlite XAD16N. Results indicate that all materials remain stable up to 280°C, and the polymers prepared with eugenol and p-coumaric acid demonstrate superior adsorption capabilities at low concentrations compared to commercial materials.



**Figure 1.** Outline of the process for preparing a molecularly imprinted polymer.

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## VITRIMERIZATION OF EPOXY-BASED COMPOSITES FROM THERMOSETS

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### Abstract

Epoxy-based thermosets are a class of materials with a wide range of applications, mainly related to their high mechanical and chemical resistance. However, due to their crosslinked nature, epoxy resins cannot be reprocessed at their end of life, raising an important global challenge. One possible strategy relies on the production of vitrimers, i.e. polymers characterized by a three-dimensional structure containing dynamic covalent bonds that allow the material to be reprocessed through exchange reactions.<sup>1</sup> When dealing with epoxy-acid/anhydride curing systems these reactions are based on a transesterification process that can be initiated at high temperature by a transesterification catalyst or, alternatively, by -OH rich species.

Using this approach, it is possible to incorporate a transesterification catalyst into the initial formulation of the dynamic network to obtain a cross-linked system that inherently has the ability to be recycled. Alternatively, it is possible to act on the cured post-consumer product through a vitrimerization process, i.e. the conversion of a permanently cross-linked network into a dynamic, exchangeable one. For this latter purpose, a chemo-mechanical process is carried out in the presence of an external transesterification catalyst, such as Zn-based organic salts, followed by a hot pressing step.<sup>2</sup> As a substitute di Zn salts, cellulose fibers can be used as feedstock for external hydroxyl groups during functionalization by ball milling, obtaining vitrimeric composites. This strategy has great potential, as it represents a cost-effective, environmentally friendly and scalable method for the valorization of epoxy resin waste.<sup>3</sup> Inspired by the approach described above, the present work aims to obtain reprocessable composites by utilizing biobased fillers as catalyst for the vitrimerization of epoxy resins. A commercial epoxy resin, the diglycidyl ether of bisphenol A (DGEBA) is crosslinked with hexahydro-4-methylphthalic anhydride (4-MHHPA), using 1-methylimidazole (1-MI) as initiator. Vitrimerization is then achieved through ball milling process followed by hot pressing in presence of Zn(AcAc)<sub>2</sub> as a catalyst or, alternatively, of pulverized natural fibers. The influence of the epoxide/anhydride ratio, the nature and amount of the catalyst/filler, and the grain size, on both the reprocessibility of the starting material and the properties of the final composite is evaluated. The results demonstrate the high potential such recycling technology thus addressing the pressing global challenge of epoxy thermoset waste and contributing to the advancement of eco-friendly and scalable solutions in materials science and engineering.

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**BIOINSPIRED MULTIFUNCTIONAL COATINGS FOR MARINE HULLS**

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**Abstract**

The project aims to develop a groundbreaking epoxy resin/silicone coating for marine hulls with antifouling, slippery and self-healing capabilities, driven by the pressing ecological need for sustainable and efficient solutions in marine transportation. Despite their adhesive strength and corrosion resistance, traditional epoxy resin/silicone coatings face challenges such as limited biofouling resistance (especially in static conditions), complex formulations (usually requiring 3 or more different layers), and vulnerability to mechanical damage, resulting in increased fuel consumption, and corrosion risks.<sup>1</sup> The idea of my PhD project aims at designing a bioinspired multifunctional coating to enhance vessel surface longevity, performance, and environmental sustainability while reducing maintenance requirements and extending overall vessel lifespan. In the first part of the project, the focus has been providing the coating with antifouling properties. Marine fouling poses a significant challenge for marine vessels, leading to issues such as biocorrosion, increased frictional forces, compromised safety protocols, and the introduction of invasive marine species. Conventional paints contain metal oxides, whose toxicity may offset their efficacy. To overcome this limitation, the possibility of integrating natural biocidal agents (capsaicin, piperine, quercetin and succinic acid) is explored. This approach draws inspiration from the defensive mechanisms observed in different plants and organisms in nature. By utilizing chemical compounds, it aims to either deter or restrict the attachment of microorganisms to surfaces. First, the antifouling efficacy of the active molecules have been assessed. Capsaicin was identified as a promising molecule against marine microorganisms. PDMS coatings with different capsaicin concentrations (1%, 3% and 5% w/w) and curing agent ratios were hence prepared to investigate the biocide release patterns in marine water. Further analyses have focused on the wettability of biocide-containing coatings, revealing a slight reduction in the water contact angle in the presence of capsaicin. Finally, analyses using UV-Vis spectroscopy is being used to examine the release kinetics of biocide from the coatings in marine environment. Once the antifouling properties will have been optimized, the durability and ease of application of the eco-friendly coatings will be addressed. The idea is resorting to surface tension gradient systems and reversible chemical bonds to provide the coating with self-stratifying and self-healing properties.<sup>2,3</sup>

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**SYNTHESIS AND NANOSTRUCTURATION OF THIN AND CONDUCTIVE PEDOT FILMS BY LIQUID-PHASE POLYMERIZATION**

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**Abstract**

Conductive polymers (CPs) have represented a key research topic in the field of organic electronic devices, as alternatives to silicon-based technologies. Among them, poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most used and investigated materials because of its good and tailorable electrical properties, transparency to visible light and environmental stability. For all these reasons, PEDOT has found applications in organic solar cells, supercapacitors, organic light-emitting diodes and nanostructured devices.

In this project, we studied the synthesis of this polymer using a liquid-phase polymerization process.<sup>[1]</sup> This process involves the sequential deposition of an oxidant solution (vanadium pentoxide) and a monomer solution (EDOT) onto a glass substrate treated with piranha solution. The resulting film is washed with a solvent to eliminate the excess monomer and then subjected to annealing heat treatment.

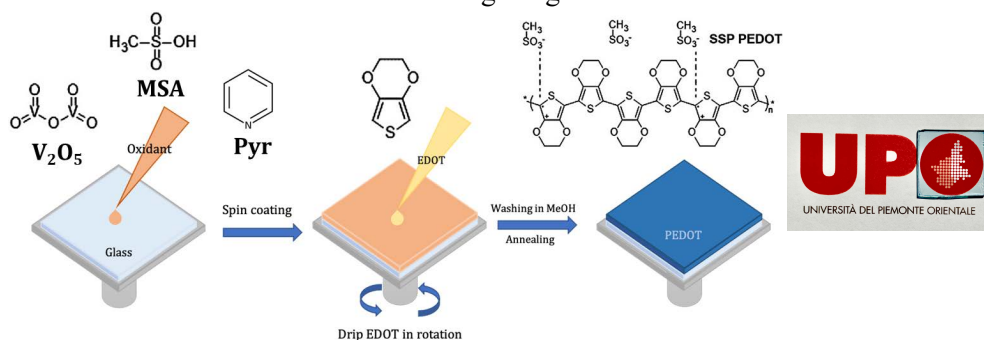
To enhance the properties of the polymeric film, we varied the deposition time of the oxidizing solution, the rotation speed and the concentration of the oxidizing solution.

The analysis showed that the thickness of the polymeric film is primarily influenced by the deposition time of the oxidant solution.

Additionally, the concentration of the oxidant slightly affects the polymer thickness due to the varying viscosities of more and less concentrated solutions. We determined the morphology and thickness of the samples using optical profilometry and measured the conductivity of the samples with the Van der Pauw method using a 4-point probe in electrical contact with the polymeric film. A direct current is applied between the outer test leads, while a voltage drop is measured between the inner leads, providing the sheet resistance ( $R_s$ , measured in  $\Omega/\square$ ).

We studied the nanostructuring process of the films using nanosphere lithography. To improve the deposition of nanospheres on the PEDOT layer, a silica one was applied to the film. This layer facilitated the formation of a monolayer of polystyrene particles, which was subsequently reduced using reactive ion etching (RIE).<sup>[2]</sup>

The resulting mask enabled the precise nanostructuring of the PEDOT films. By optimizing this process, we achieved PEDOT nanostructures with a high degree of order.



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## EFFECTS OF DIFFERENT LAYERED NANOFILLERS IN THE ANIONIC POLYAMIDE 6: A COMPREHENSIVE CHARACTERIZATION

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### Abstract

Polyamide 6 (PA6) in-situ anionic polymerization is an attractive method for producing thermoplastic nanocomposites with high mechanical and functional properties.<sup>1</sup> The objective of this research is to examine the thermomechanical characteristics of anionic PA6-matrix (aPA6) nanocomposites, establish a relationship with microstructural characteristics such as the degree of crystallinity and the dispersion of nanofiller, and explore feasible options for enhancing them for high-end applications.

The nanocomposites were prepared in a lab-made small-scale polymerization plant as follows. Caprolactam (CL)(AP-Nylon, Bruggeman S.A.), was melted at 110 °C in a round-bottom flask under nitrogen flow, followed by the addition of a commercial initiator and activator (C10 and C20P, Bruggeman S.A.) in variable concentrations and the layered nanofiller (different organomodified nanoclays and expanded graphite nanoplatelets (xGnPs)) in proper amount. The stirred mixture was then injected into a preheated mold at various temperatures (140-170 °C) through a thermoplastic resin transfer molding (tRTM) facility, and left to polymerize for 20 minutes.

The mechanical properties of the nanocomposites were found to be influenced by the processing parameters such as the temperature and the concentration of the initiator and activator,<sup>2</sup> mostly due to the profound impact of these parameters on the matrix crystallinity.<sup>3</sup> Tensile tests on the PA6 samples showed optimal mechanical properties at intermediate polymerization temperatures (150-160 °C) and low initiator and activator concentrations. All the investigated nanocomposites presented a high degree of conversion with little (<2%) residual caprolactam, as investigated by thermogravimetric analysis. While all the investigated nanofillers mostly increased the elastic modulus, the quasi-static properties at break and the impact properties resulted in being strongly affected by the nanofiller type and dispersion. A more polar organomodified nanoclay was better dispersed and intercalated by the monomer, leading to nanocomposites which retained the tensile ductile behavior showed by the matrix. The use of a compatibilizer between the matrix and the nanoplatelets and the ultrasonication of the reactive mixture during the production process was found to be effective in order to improve the xGnPs dispersion.

This study provides valuable insights into the properties and behavior of thermoplastic nanocomposites based on aPA6. While the results suggest that these nanocomposites have potential for use in various applications where improved mechanical, thermal, and electrical properties are required, further research is needed to fully characterize the interfacial interactions between the fillers and the matrix and to improve the filler dispersion, also considering surface functionalization.

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**SEARCH FOR THERMOPLASTIC ELASTOMERS WITH BIOLOGICAL OR RECYCLED CONTENT**

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**Abstract**

Due to their lightweight and flexibility, plastics are among the most widely used materials in the automotive manufacturing.<sup>1</sup> Polymer end of life is one of the objectives of this period. In the elastomer field two ways can be considered. The first one is to use recycling polymers to minimize the problem of environmental pollution.<sup>2</sup> The second way is to use thermoplastic elastomers (TPEs) instead of thermoset ones. These last materials consist of an elastomeric part, as the soft fraction, and a non-elastomeric material as the hard segment.<sup>3</sup> Because of this structure they can be reprocessed and reformed as a thermoplastic polymer.<sup>2</sup> The aim of this work is the characterization of thermoplastic elastomers with high recycled content, to evaluate their performance in comparison with virgin materials. The materials analyzed cover both exterior and interior automotive applications such as body seals, hoses, floor mats and cupholders. The samples are made with TPS (Thermoplastic polystyrene elastomer) provided by a specialized supplier. To evaluate the mechanical properties of the samples tensile and tear resistance, hardness, compression set were analyzed. The chemical characterization of materials was made with Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC). In order to understand the resistance of materials to external agents, they were also subjected to aging tests. Further mechanical and chemical tests will be performed in the future. The study of suitability of large-scale use of green TPEs could decrease the amount of waste and complete the life cycle of materials, reducing dependence on virgin resources and CO<sub>2</sub> emissions related to production.

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**HYBRID JUNCTIONS - OPTIMIZATION OF THE LATTICE SUBSTRATE****ANDREA CORRADO<sup>1</sup>, MATTEO PERINI<sup>2</sup>, ALESSANDRO PEGORETTI<sup>1</sup>, MATTEO BENEDETTI<sup>1</sup>**<sup>1</sup>*Department of Industrial Engineering, University of Trento, Trento, Italy*<sup>2</sup>*ProM Facility, Rovereto, Italy.**Email: andrea.corrado@unitn.it**Role: PhD student, 1<sup>st</sup> year***Abstract**

The history of aviation has always placed a great amount of effort in the research of weight reduction of components, to enhance the overall performance of the vehicle but also for reducing fuel consumption.<sup>1</sup> For this reason, composite materials have been the heart of the design process, especially for Carbon Fiber Reinforced Polymers (CFRP), known for their high stiffness to weight ratio.<sup>2</sup>

However, in many cases, composites must interface with other metallic components, such as inserts or other brackets. The junction between these two different materials is usually made by rivets, bolts or glue. In response to many issues with these methods,<sup>3,4</sup> a new interface has been analysed.

To increase the degrees of freedom in the design process, the 3D printing of metals has been chosen. Taking advantage of this technique, the surface next to the CFRP material can be optimized to have an interlocking mechanism between the two.

This approach involves studying how a lattice structure interacts with the epoxy resin of the CFRP. The idea is to co-laminate the composite material above the lattice surface thus, increasing the adhesion between the two and reducing the number of steps in the manufacturing process.

Single lap specimens with different Simple Cubic unit cells of the lattice substrate were simulated and tested, achieving great results.<sup>5</sup>

Based on those obtained results, an all-new Finite Element optimization has been carried out, using different types of unit cells. In particular, the following have been analysed: Simple Cubic (SC), Octet Truss (OT), Auxetic (AUX), Truncated Octahedron (TCO). The optimization of the variables included the minimization of both internal stresses and deformations of a Ti6Al4V structure when shear and tear-out loads are applied.<sup>6</sup> The variables of the minimization are the three independent measures of the volume that include the unit cell and the diameter of the single struts.

Among the four different cells, for a load of 10 kN applied on both X and Z axis on a surface of 25×35 mm, the optimum Ti6Al4V infilled unit cell is the Simple Cubic one.<sup>6</sup> The dimensions along X, Y, Z axis are 0.45×1.7×0.5 mm respectively with a strut diameter of 0.4 mm.

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## ON THE DEVELOPMENT OF FUNCTIONALIZED POLYLACTIC ACID POROUS FILMS

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### Abstract

The porous polymer substrates, which hold high porosity, suitable mechanical properties as well as specific functionality, can be employed in various fields for their retention capacity. The extension of their applicability to the biomedical context also requires additional features related to biodegradability and biocompatibility.<sup>1</sup>

The aim of the present study was to design and develop porous, biodegradable, biocompatible, highly functionalized, and easy-to handle polymer films. Furthermore, in order to ensure an easy and scalable production method, the non-solvent induced phase separation (NIPS) technique was selected.<sup>2</sup> The polymer matrix, based on polylactic acid (PLA), was supplemented with another biopolymer, polycaprolactone (PCL). In particular, a PCL with star-shaped geometry, controlled molecular mass and maleic end groups (PCL-COOH) was prepared *ad hoc* in order to obtain a system characterized by a high concentration of acid end groups.

Morphological analysis performed using FE-SEM revealed that the preparation technique used, namely NIPS, ensured a uniform distribution of PCL-COOH domains within the polymer matrix. Moreover, the thermal and mechanical properties of the films were investigated by means of differential scanning calorimetry and thermogravimetric analysis, and mechanical tensile tests.

Adsorption and time-controlled release tests were carried out using pararosaniline hydrochloride, a positive charged dye, as a model molecule. These experiments demonstrated the possibility of modulating the retention capacity by adjusting the PCL-COOH concentration and the pH of the system.

Furthermore, the porous film containing the highest concentration of PCL-COOH was tested for the retention and release of doxorubicin, a commonly used chemotherapeutic agent. The results showed that the developed system exhibited remarkable adsorption capacity and controlled drug release, highlighting its effectiveness as a potential drug delivery system.

Finally, the biocompatibility of the films, which proved to be enzymatically degradable, was investigated through cell viability and hemocompatibility tests.

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**TUNING OF ALTERNATIVE SUSTAINABLE FILLERS FOR ELASTOMER COMPOSITES****CARLO DIBERNARDO<sup>1</sup>, CAMILLA NOÈ<sup>1</sup>, MASSIMO MESSORI<sup>1</sup>**<sup>1</sup>*Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi n.24, 10129, Turin, Italy**Email: carlo.dibernardo@polito.it**Role: PhD student, 1<sup>st</sup> year***Abstract**

Elastomer composites are an example of technical material produced in tons scale on a yearly basis, with tire manufacturing alone accounting for 29.2 million tons in 2018. This production ties closely to carbon black (CB), which more than 92% of the worldwide production is intended for rubber manufacture.

Typically, elastomer composites result from formulations where rubber is blended with a series of additives and fillers, imparting unique mechanical and rheological properties. CB has emerged as one of the most effective fillers in tire production, yet its fossil-origin poses significant ecological challenges. In fact, its production involves the incomplete combustion of hydrocarbons, typically derived from fossil fuels, leading to the release of greenhouse gases (GHGs) such as carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>). These emissions contribute to climate change and air pollution.<sup>1</sup>

Among alternative filler materials, biomass has proved to be a valuable raw material source. In particular, waste biomass derived from agricultural or food production has already been explored as a sustainable alternative to CB as reinforcing filler in rubber composites with promising results. Although limited to academic proof-of-concept, bio-fillers proved to have promising reinforcing abilities; their commercial implementation faces challenges such as inefficient dispersion and limited compatibility with the matrix, crucial parameters for reinforcement.

Addressing these challenges requires mechanical, thermal or chemical approaches. Our work has focused on the chemical method to enhance the filler-matrix interaction. Chemical functionalization marks a viable strategy for bio-filler tuning with possibilities of increasing hydrophobicity, dispersion and filler-matrix interaction. However, solely relying on chemical grafting may not suffice to achieve satisfactory reinforcing abilities, as it may have limited effects on parameters like the overall surface area and particle size.

Efforts to mitigate the ecological impact of CB in tires include exploring chars from pyrolysis. Biochar, a biomass-derived char with CB-like structural features, constitute a potential alternative filler with similar reinforcing abilities and potentially lower environmental impact.<sup>2</sup> Therefore, this study aims to comprehensively understand how different parameters affect the reinforcing abilities of bio-based fillers. To reach this goal, we will explore different agricultural waste tuning possibilities and compare them with pyrolysis-derived fillers.

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**TREATMENT OF DECOMMISSIONED WIND TURBINE BLADES FOR GLASS FIBER RECYCLING**ELEONORA DI FRANCESCO<sup>1</sup>, MAILA CASTELLANO<sup>1</sup>, DARIO CAVALLO<sup>1</sup>, SILVIA VICINI<sup>1</sup><sup>1</sup>*Dipartimento di Chimica e Chimica industriale, Università di Genova, Genova, Italia**Email: eleonora.di.francesco@edu.unige.it**Role: PhD student, 1<sup>st</sup> year***Abstract**

Wind energy technologies have advanced significantly in the past twenty years, becoming more efficient and cost-effective, establishing wind power as a leading renewable energy source. However, the early commercial wind turbines are nearing the end of their operational life, posing a significant environmental challenge due to the disposal of non-recyclable turbine blades. By 2050, it is estimated that nearly 43 million tons of waste will be generated globally from wind turbines. Around 10% of a wind turbine's material is constituted of wind blade, which are primarily made of glass and carbon fiber reinforced polymers. This composite includes about 20% thermoset polyester, epoxy, or a combination of the two resins. Since fibers make up about 65% of the composite, developing methods to effectively recycle them is crucial for environmental sustainability.

Chemical treatments as solvolysis, with sub/supercritical water or acid/base catalysis, have low carbon impact and allow to obtain clean fibers that maintain virgin fiber's mechanical properties. One problem connected to these methods is the low versatility, considering that the wind blade is a mixture of different materials (for example balsa wood and metals), moreover, these processes are difficult to scale up, they typically require long times, high pressures, and therefore high costs.<sup>1</sup>

For industrial purposes, thermal recycling seems to be the most promising method. Pyrolysis is the most studied procedure. This process permits to take advantage of the organic component, obtaining syngas or energy from its combustion, but it also results in a damaged fiber covered by char and with a "fluffy" aspect, unsuitable for reuse.<sup>2</sup> Pyrolysis products can be treated with chemicals or other thermal steps to remove the char, but at added cost. This project aims to find a scalable treatment that better preserves the integrity of the fibers. Induction heating has been brought into focus, since compared to pyrolysis it seems to be reproducible, safe and more energy efficient, maintaining the advantage of versatility and the ability to work with big volumes of sample.<sup>3</sup>

Future developments aim to solve the post-treatment challenges, assuming the possibility to use the char coming from pyrolysis or induction heating process as a conductor for electrochemical cleaning.

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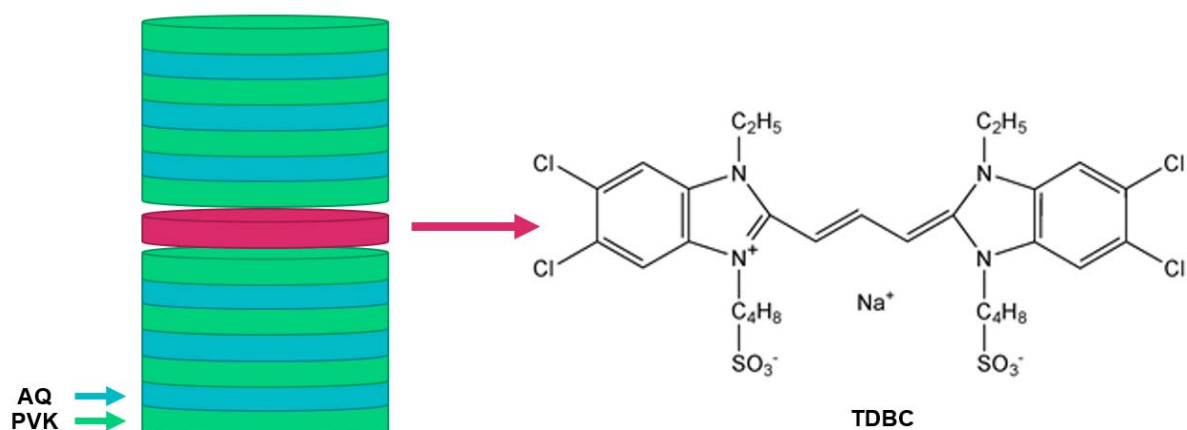
## ENHANCING OPTICAL MICROCAVITIES WITH TDBC J-AGGREGATES

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## Abstract

This study demonstrates the integration of a J-aggregate into all-polymer microcavities. J-aggregates are increasingly researched thanks to their peculiar optical properties characterized by sharp and intense absorbance and photoluminescence signals.<sup>1</sup> To this end, we exploit a class of planar one-dimensional photonic crystals, known as distributed Bragg reflectors (DBRs), as building blocks of the microcavity architecture. These structures consist of a periodic stacking of dielectric materials' bilayers with different refractive indexes that give rise to light frequencies whose propagation is forbidden within the structure. These frequencies take the name of photonic bandgaps.<sup>2</sup> Introducing an engineered defect layer within the lattice generates cavity modes, specific frequencies within the photonic bandgap where light propagation is allowed.<sup>2</sup> An example of the structure is reported in Figure 1. In principle, when a dye is embedded into the microcavity defect, its photoluminescence cannot propagate at the photonic bandgap's wavelengths, and all photons are redistributed within the cavity mode.

In this work, we report on the effect of spun-cast poly(*N*-vinylcarbazole) (PVK) – Aquivion® (AQ) microcavities on the emission properties of TDBC (Figure 1) which results in highly emissive optical structures with enhanced spectral selectivity with respect to those fabricated with standard organic emitters. These results offer new promising opportunities for improving the performances and versatility of photonic devices. Indeed, the ease of spectral tuning of the microcavity optical properties makes them promising tools for a variety of technological applications including sensing, lasing, and optical communication.



**Figure 1.** Left: Schematic of a PV:AQ microcavity embedding a defect layer of TDBC (1,1'-disulfobutyl-3,3'-diethyl-5,5',6,6'-tetrachlorobenzimidazolylcarbocyanine sodium salt) (right).

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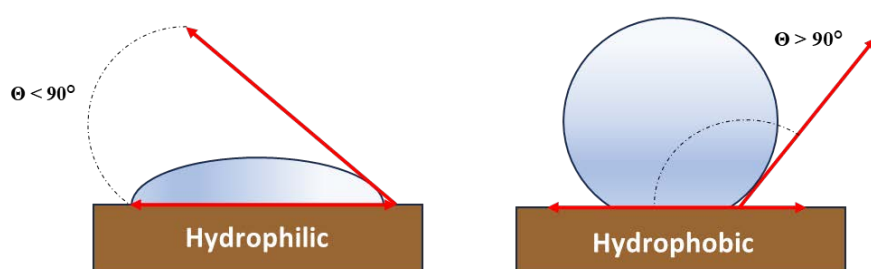
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**BIO-BASED HYDROPHOBIC COATINGS DEVELOPMENT FOR SUSTAINABLE CELLULOSE PACKAGING**ANGELICA GIOVAGNOLI<sup>1</sup><sup>2</sup>*Department of Industrial Chemistry “Toso Montanari”, University of Bologna, Bologna, Italy**Email: angelica.giovagnoli2@unibo.it**Role: PhD student, 1<sup>st</sup> year***Abstract**

The biggest issue correlated to the use of fossil-based packaging is the end-of-life management, it means that due to waste disposal difficulties, the ecosystem is being destroyed and all the correlated consequences are affecting negatively our lives. In 2019, the global food packaging market was valued at \$303.26 billion, with a growth potential of \$60.33 billion between 2020 and 2025. If the current manufacturing trends and plastic waste management persist, it is estimated that 12000 million tons will accumulate on landfills and environment by 2050 polluting soils,<sup>1</sup> water and all the connected production chains with toxic substances released. The replacement of conventional packaging with sustainable alternatives that easily and safely degrade, is a vital solution to decrease disposal of plastic wastes in landfills, rivers, and marine environments.<sup>2</sup> Cellulose, starch, chitosan and polylactic acid can be considered as promising alternative materials to conventional food packaging ones.<sup>1</sup> Their use, can be exploited only after a careful search for additives and green coatings to be introduced inside the bio-polymeric matrices to improve their thermal, mechanical and barrier properties.

With the aim to face this real issue with sustainable solutions, in this project, new hydrophobic fatty acid based additives have been developed to be applied as functional coatings for cellulose packaging. By esterification reactions of several polyols with fatty acids, linear and star-shape molecules have been synthesized. All the structures and properties have been investigated by spectroscopic and thermal analysis. Moreover, by preliminary additive applications (e.g. dip coating, spray coating), the actual hydrophobicity has been verified by water contact angle measurements (WCA).

The results obtained have highlighted the strict correlation between the molecular structures and the final hydrophobic properties of the additives.



**Figure 1.** Different WCA values for hydrophilic and hydrophobic surfaces.

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## HYDROPHILIC POLYTHIOPHENES FOR LOW ENVIRONMENTAL IMPACT ORGANIC SOLAR CELLS

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### Abstract

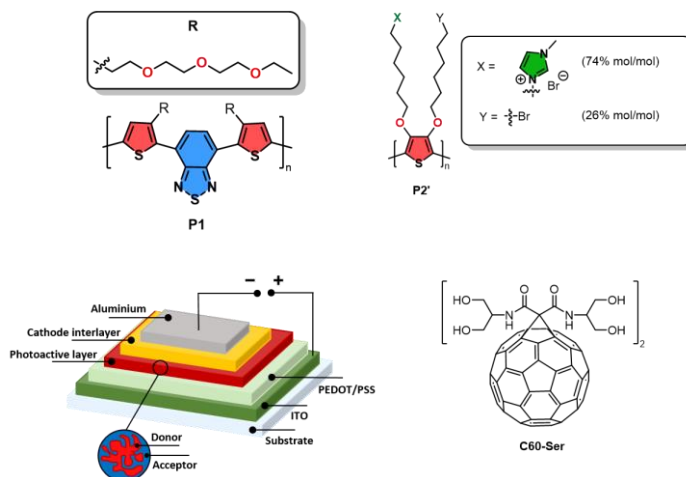
Nowadays, organic semiconductor materials are extensively studied and employed as inorganic counterparts in many applications such as organic photovoltaic devices (OPVs), light-emitting diodes (OLEDs), and thin-film transistors (OFETs). In addition to display easily tunable and promising electrical characteristics, intrinsically conjugated materials/polymers (ICPs) also present cost-effective production and potential recovery through solvents.<sup>1</sup>

To achieve optimal efficiency in converting light into electricity, the design and synthesis of new materials with tailored features is thus necessary. These features which include a low band gap, high charge mobility, and strategically positioned frontier orbitals, could be obtained by incorporating electron donor/acceptor groups alternately along the polymer's main chain.<sup>2</sup>

Moreover, as an emerging necessity to fulfill in the advancement of ICPs is to guarantee their solubility in environmentally friendly and non-toxic solvents, the research is now widely focused on developing electroactive polymers that can be processed by water or alcohol.<sup>3</sup>

Two new and highly polar thiophene-based materials have been therefore successfully synthesized and investigated. **P1** is soluble in alcohol and features both electron-donor and -acceptor groups within its main chain: starting from 4,7-bis(3-(2-(2-(2-ethoxyethoxy)ethoxy)ethyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole as a monomer, **P1** was synthesized through palladium-catalyzed Suzuki cross-coupling reactions. The polymer **P2'**, which is soluble in water and incorporates ionic groups into its side chain, was obtained from the post-functionalization of poly-3,4-bis((6-bromohexyl)oxy)-2,5-dimethylthiophene, synthesized via oxidative polymerization using FeCl<sub>3</sub>.

The newly synthesized polymers underwent characterization using standard analytical methods, including <sup>1</sup>H-NMR, gel permeation chromatography (GPC), UV-vis spectroscopy, and cyclic voltammetry (CV). All derivatives were finally tested as photoactive components in completely halogen-free OPVs, investigating their role as active layer and/or cathode interlayer.



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## SPINNABILITY OF MONOFILAMENTS FOR SELF-REINFORCED COMPOSITES

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### Abstract

Polymer composites are a class of materials made of a polymeric matrix and a reinforcing phase, often in the form of short/long fibres, fibres mats or textiles. Their exploitation is steadily increasing in different application fields, e.g., aerospace and automotive industries, because of improved material performance and cost-effective production, together with a very low density. However, due to the bi-component essence of these materials, they present two mayor limits. On one hand, the interfacial adhesion between the fibers and the matrix has to be maximized to well-distribute the stresses and thus achieve high mechanical performance. On the other hand, because of the difficulty in the separation of the matrix and reinforce phases, composites suffer from a poor recyclability.

Self-reinforced composites (SRCs), a relatively recent class of composite materials, have been introduced as a potential solution to the aforementioned challenges. Being constituted by the same material for both the reinforce and the matrix, they can ensure perfect interfacial adhesion, resulting in high strength and stiffness, excellent impact resistance at low density, as well as ideal recyclability.<sup>1</sup> According to the rule of mixtures, such materials need to be made of high modulus polymeric fibres to achieve satisfying mechanical performance. This is typically obtained by acting on the crystallinity of the fibers, working on both the fine tuning of the process parameters (e.g., spinning speed, draw ratio) and the molecular weight and molecular weight distribution, as they heavily affect the melt spinnability and, in turn, the physical and mechanical properties of the resulting fibers.<sup>2</sup> In the field of SRCs, those based on polypropylene (PP) are by far the most widely studied. However, all the commercially available products are made of virgin PP,<sup>3</sup> while the use of recycled polypropylene (rPP) has not been yet explored in literature, neither as matrix nor for the fibres. This strikingly contrasts with the amount of plastics on the market, in which PP is the most abundant.

With respect to virgin PP, the main challenges in the use of rPP for the production of fibres are related to the unavoidable drastic reductions in average molecular weight and the broadening of the molecular weight distribution, as well as the presence of impurities that can severely compromise the spinnability of the melt. Because of these severe limitations, the study and optimization of fibres from rPP is still a poorly investigated field. The present project intends to fill this gap, aiming at the development of SRCs partially or even fully based on recycled PP which possess properties suitable for the application in the automotive and sport industry. As first part of the work, preliminary analyses are performed to identify the materials- and process-related parameters that play a key role in the production of polymeric fibres.

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**PORPHYRINS-ENHANCED CRYOGELS AS DUAL-FUNCTION MATERIALS FOR HEAVY METAL DETECTION AND REMOVAL IN WATER**GIUSEPPE PROIETTO SALANITRI<sup>1,2</sup><sup>1</sup>*CNR-IPCB, Via Paolo Gaifami 18, 95126, Catania, Italy*<sup>2</sup>*Department of Industrial Chemistry "Toso Montanari", University of Bologna, Viale Risorgimento 4, 40136 Bologna, Italy**Email: giuseppe.proietto3@unibo.it or giuseppe.proietto@ipcb.cnr.it**Role: PhD student 1<sup>st</sup> year***Abstract**

Cryogels have been mainly studied in the last decade as they can be successfully applied to the energy, biomedicine, and water treatment fields. Compared to similar polymer structures, their structural versatility, macroporous morphology, and tunable elasticity can improve an extensive list of functional properties such as adsorption.<sup>1</sup> One of the significant advantages lies in the formation of rapid water diffusion pathways, made possible by the interconnected pore architecture that allows complete access to active functional sites in less time, increasing the yield of the desired result. From this perspective, synthesizing polymer-polymer hybrid cryogels incorporating porphyrin moieties can effectively harness both the inherent properties of the cryogels and the distinctive features of the porphyrin ring.<sup>2</sup> As known, porphyrins are a class of macrocycles whose chemical and optical properties change depending on their aggregation state, metal-based adducts, and lateral substituents. In particular, including porphyrins in macromolecular systems can achieve these molecules' unique chelating and chromophore properties with the durability and stability of a polymeric material.<sup>3</sup> In this work novel hybrid cryogels containing porphyrin-based methacrylate units were synthesized to obtain freestanding materials for removing and detecting mercury ions. Functionalized aminoethyl methacrylate (AEMA) with the soluble porphyrin meso-tris (N-methyl-4-pyridyl) mono(4-carboxyphenyl) porphine trichloride (PORPH) was polymerized with 2-hydroxyethyl methacrylate (HEMA) in ratios from 5% to 20% w/w. These cryogels were tested for the adsorption of Hg<sup>2+</sup> and novel organic pollutants. The materials showed potential as Hg<sup>2+</sup> sensors, changing color upon adsorption. At neutral pH, Hg<sup>2+</sup> was efficiently chelated, with the 20% porphyrin cryogel achieving a maximum adsorption capacity (Q<sub>e</sub>) of 56.4 mg/g. Diclofenac and SDS were effectively removed, while paracetamol remained in solution. Furthermore, its chromophoric capacity was evaluated for potential use as a detector laying the groundwork for the development of devices that capture and detect metal ions, such as mercury.<sup>4</sup>

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**DESIGN OF A SUCCESSIVE SELF-NUCLEATION AND ANNEALING (SSA) THERMAL PROTOCOL FOR THE ASSESSMENT OF THE IMPACT OF MANUFACTURING PROCEDURES ON THE MOLECULAR STRUCTURE OF BIOMEDICAL UHMWPE**RIGHETTI MATTEO<sup>1</sup>, GIANOGGIO LUCA<sup>1</sup>, BRACCO PIERANGIOLA<sup>1</sup><sup>1</sup>*Department of Chemistry, University of Torino, Torino (TO), Italy**Email: matteo.righetti@unito.it**PhD student, 1<sup>st</sup> year***Abstract**

Characterizing various UHMWPE formulations pre- and post-implantation is often crucial to understanding their clinical performance. The technique of Successive Self-Nucleation and Annealing (SSA), developed and introduced by Müller et al. in 1997,<sup>1</sup> is now a well-established thermal fractionation technique that exploits the molecular segregation capacity exhibited by semicrystalline polymeric systems when they are isothermally crystallized or annealed. SSA is conceptually based on the sequential application of self-nucleation and annealing steps to a polymer specimen. SSA has shown excellent results in characterizing and differentiating various LDPE and LLDPE. On the contrary, UHMWPE, like HDPE, is a challenging material to fractionate, due to its high linearity and minimal presence of molecular defects.<sup>2</sup>

To evaluate the effect of oxidation and that of irradiation and remelting procedures on the morphology of UHMWPE, a Successive Self-Nucleation and Annealing (SSA) thermal protocol was developed, and the resulting thermal fractionation profile of virgin UHMWPE was compared with those of oxidized, irradiated, irradiated and remelted, irradiated and annealed UHMWPE specimens. All samples came from the same batch of ram-extruded GUR 1050. The extent of oxidation was monitored by Micro FTIR (Perkin Elmer) analysis and quantified in terms of Oxidation Index (OI) values. Differential Scanning Calorimetry have been used to perform Self-Nucleation (SN) and SSA experiments using a DSC 250 equipped with an RCS40 Refrigerated Cooling System (TA Instruments).

Each sample was heated to 170°C and held in the melt for 3 min to erase thermal history, then it was cooled, at a constant rate of 20°C/min, to 40°C, in order to allow the crystallization of the material. An ideal  $T_s$  (the lowest  $T$  at which the sample is only self-nucleated and not annealed) of 139,5°C was determined through SN experiment, as described by Rojas de Gáscue et al.<sup>2</sup> An SSA thermal protocol was developed employing a total of 9 annealing steps, a 5°C fractionation window and a 5 minute isotherm at each  $T_s$  explored. The same SSA protocol was applied to all samples.

The thermal fractionation profile of irradiated UHMWPE samples revealed that the use of  $\gamma$ -rays does not significantly alter the lamellar thickness distribution but reduces the amount of the most stable crystalline fraction that the material can develop. Following the remelting and annealing processes, the materials show negligible level of oxidation and the thermal fractionation profile revealed that combination of irradiation and thermal treatments can generate changes to the UHMWPE molecular structure that reduce the overall crystallinity and broadened the lamellar thickness distribution.

The SSA technique has preliminarily proven to effectively discriminate between different formulations of UHMWPE. Subsequently, we intend to assess its efficacy in characterizing other formulations, for instance those containing additives such as Vitamin-E at different concentration.

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## SMECTIC LIQUID CRYSTAL MEMBRANES FOR WATER CONTAMINANT PURIFICATION

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### Abstract

Design of novel strategies for the removal and reduction of contaminants in wastewater, ensuring clean water and averting severe damage on human health and aquatic ecosystems, is one of the mayor challenges for a sustainable society.<sup>1</sup>

Of particular concern are emerging pollutants like pharmaceuticals, pesticides, and endocrine disruptors, which pose significant risks even at minute concentrations. Employing adsorbent materials shows promise in selectively removing these pollutants and facilitating their photodegradation into less harmful substances.

In this framework, we will present the preparation of new adsorbent based on liquid crystalline network with smectic organization. Starting from a blend of liquid crystalline (LC) monomers, we synthesized porous adsorbents featuring a 2D smectic lamellar structure. These polymers offer a large surface area for pollutant sequestration, and selectivity towards specific contaminants depending on their charge and molecular size.<sup>2</sup>

The materials have been prepared by photopolymerization of a mixture of reactive mesogens containing carboxylic groups, which can be used during the wastewater treatment for the removal of cationic compounds. Moreover, insertion of photocatalytic TiO<sub>2</sub> nanoparticles have been attempted to achieve a second functionality to the materials, namely the degradation of pollutant under UV light.

The preliminary adsorption test conducted on Methylene Blue indicates that the proposed smectic liquid crystalline polymers exhibit remarkable efficacy in the sequestration of the dye, chosen as a model molecule to simulate an organic pollutant. Moreover, the maximum adsorption capacity of these materials substantially overcome that of conventional adsorbents described in literature.

Future investigations will be undertaken utilizing real pollutants, with a focus on also implementing the photocatalytic degradation under UV or visible light towards a possible recycling of the adsorbent materials.

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## CHITOSAN-BASED GO & rGO HYBRID MATERIALS FOR WATER PURIFICATION

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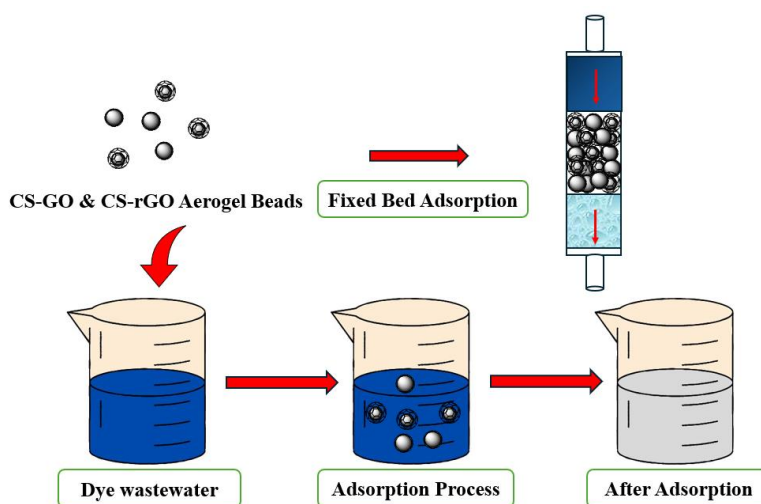
*Role: PhD student, 2<sup>nd</sup> year*

### Abstract

The persistent contamination of the ecosystem by industrial pollutants creates a global hazard to both native species and humans. One of the most effective and popular method for removing the pollutants from water is adsorption<sup>1</sup>. With this regard, the synthesis of an environmentally friendly adsorbent that can absorb a wide range of contaminants from water is still a challenging task<sup>2</sup>. Thus, to address this issue we synthesized chitosan-graphene oxide (CS-GO) and chitosan-reduced graphene oxide (CS-rGO) hybrid aerogel beads.

X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) were used to examine the structural characteristics and thermal stability of the aerogels. The adsorption capacity of CS-GO and CS-rGO hybrid aerogels was evaluated using two model dyes, methylene blue (MB) and indigo carmine (IC), which have cationic and anionic charges, respectively shown in Fig. 1. We evaluated the efficacy of mixed beads CS-GO and CS-rGO in various ratios (25/75, 50/50, and 75/25) with respect to IC and MB adsorption.

Due to the oxygen-containing functionalities on the CS-GO surface, the adsorption capacity of MB (102.56 mg/g) was found to be larger on the CS-GO hybrid aerogel, whereas IC dye (63.46 mg/g) was more efficiently adsorbable on CS-rGO because of the  $\pi$ - $\pi$  interactions between IC and CS-rGO. The adsorption kinetics and isotherms exhibited the best association with the pseudo-second-order model and the Freundlich isotherm, respectively. These mixed beads were then used as a column packing for assessing the adsorption efficiency towards MB in a continuous setup. Overall, this work presents a facile, cost-effective, and ecologically safe technique for conjugated, cationic, and anionic dye adsorption, offering an expanded approach to the remediation of dye pollutants.



**Figure 1.** Graphical Abstract, the adsorption of IC and MB on CS-GO and CS-rGO.

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**SOLID STATE COOLING BY NATURAL RUBBER: EVALUATION OF THE EFFECT OF CROSSLINKING DENSITY ON THE ELASTOCALORIC PERFORMANCE**

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**Abstract**

Elastocaloric cooling is recognized as a promising alternative to current vapour compression cooling systems, which often rely on environmentally hazardous refrigerants. Natural Rubber (NR) stands out among elastomers exhibiting elastocaloric behaviour due to the combination of several favourable characteristics, such as nontoxicity, low cost, sustainability, softness, long-life fatigue and high caloric potential<sup>1</sup>. Despite these properties, research on the refrigeration potential of NR is still in its early stages, and several aspects require attention. This work investigates, for the first time, the effect of crosslinking density on the elastocaloric properties of NR. Samples with three different crosslinking densities ( $2.9$ ,  $4.0$  and  $5.2 \text{ mol} \cdot 10^{-4} / \text{cm}^3$ ) were produced by internal compounding and hot pressing and thermo-mechanically characterized. The assessment of the elastocaloric effect of the produced samples revealed that reducing the crosslinking degree significantly enhanced the elastocaloric performance, obtaining a coefficient of performance (COP), evaluated as the ratio between extracted thermal energy and deformational work per unit volume, of  $2.4$  with the least cross-linked sample. These results underscore the significance of crosslinking density as one of the primary factors to be considered to enhance the refrigeration potential of NR.

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**BIOACTIVE GLASS-DOPED ALGINATE METHACRYLATE COMPOSITE  
HYDROGEL AS A NOVEL BIOINK FOR 3D BIOPRINTING**

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**Abstract**

Three-dimensional (3D) bioprinting has emerged as a promising technique for the fabrication of reliable biological models, by the co-deposition of cells and biomaterials (i.e. bioink), in a specific 3D architecture. Alginate methacrylate (AlgMa) hydrogel is widely recognized as a good starting material for 3D bioprinting applications, owing to its high biocompatibility and the possibility to tune its stiffness, by exploiting both ionic and covalent crosslinking. Bioglasses (BGs) are bioactive glassy materials mainly used in tissue engineering applications to promote the growth and regeneration of bone tissue. Upon contact with body fluids they slowly release active ions, particularly calcium and phosphate. This process leads to the formation of a layer of hydroxyapatite (HA) on the glass surface, which is the main mineral component of bone. Moreover, BGs can be loaded with the so-called 'therapeutic ions', to promote the healing process both in soft and hard tissues<sup>1</sup>. Hydrogels doped with bioglasses combine the tailorable rheological properties and water retention characteristic of hydrogels with the bioactive properties of bioglasses. This makes these composite materials promising for a wide range of biomedical applications, including bone regeneration, and the biofabrication of bone tissue models. In this work, AlgMA was doped with BGs to develop and validate a 3D bioprinted model through a fine optimization and characterization of the BG/AlgMA hydrogel. The synthesis of AlgMa was carried out by following a known alginate methacrylation process<sup>2</sup> and the degree of substitution was confirmed by means of <sup>1</sup>H-NMR and MALDI measurements. A novel bioglass composition, containing strontium, magnesium and alkali oxides, was used to obtain AlgMa hydrogels doped with different ratio of BGs. Firstly, to better understand which were the most performing formulations in terms of mechanical and biological properties, various parameters were considered, such as (i) CaCl<sub>2</sub> concentration for ionic crosslinking (ii) BG concentrations, (iii) intensity and exposure time of UV light for chemical crosslinking. Since rheological properties are the physicochemical parameters with the largest influence on hydrogels printability, an accurate rheological characterization was performed on the hydrogel formulations. Results demonstrated the influence of BG concentration on the mechanical properties of BG/AlgMa hydrogels. Subsequently, *in vitro* mineralization tests were conducted to study the behavior of BG/AlgMa hydrogels when exposed to simulated body fluid (SBF). Scanning electron microscopy (SEM) allowed to assess the variation of materials porosity according to the different hydrogel's composition and hydroxyapatite development. Also, SEM-Energy Dispersive Spectroscopy (EDS) and X-Ray Diffraction confirmed the formation of hydroxyapatite. Moreover, the mineralized hydrogels showed enhanced mechanical properties, closer to those of bone tissues. These findings highlight the promising potential of BG/AlgMa composite hydrogel in 3D bioprinting for the biofabrication of 3D bone models.

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**GREEN NEUTRALIZATION OF POLY(ETHYLENE-CO-METHACRYLIC ACID) WITH SODIUM HYDROXIDE IN AQUEOUS SOLUTION**

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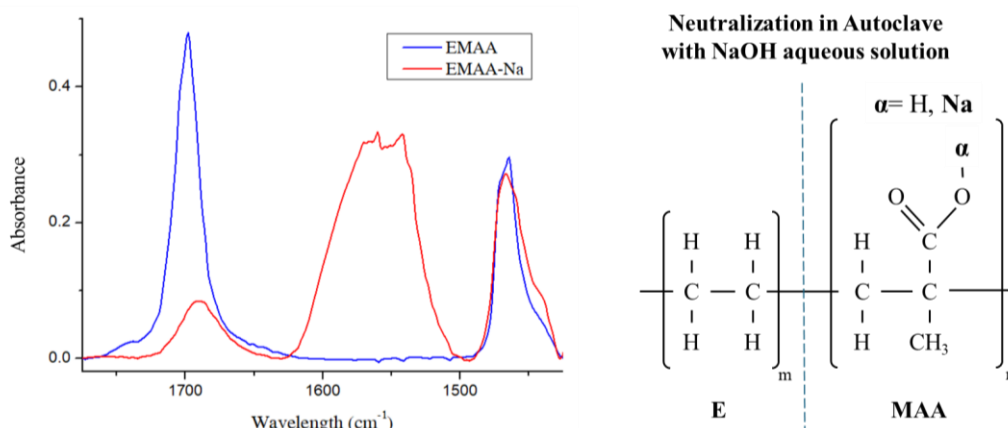
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**Abstract**

Following the guidelines of the project Made in Italy Circolare e Sostenibile (MICS) funded by Next Generation EU, a green approach for the production of ionomers based on ethylene (E) – methacrylic acid (MAA) copolymers (EMAA) is investigated. These ionomers are used in the packaging industry for their toughness and low sealing temperatures.<sup>1,2</sup> EMAA can be bulk-neutralized with different counterions in a melt compounder at temperatures above 150 °C. Then, ionomer films are obtained by extrusion.<sup>2,3</sup> The second option consists of preparing an EMAA solution with organic solvents like tetrahydrofuran or mixtures of toluene and alcohol. The neutralization is conducted in the solution by adding the desired base, and then thin films or coatings are prepared by casting.<sup>1</sup>

In the present study, EMAA with 12wt% MAA is neutralized in an aqueous solution of NaOH 1M for 1 hr at 130 °C, employing a hydrothermal reactor with magnetic stirring. Chemical characterization is performed with FTIR Spectroscopy. First, a thin film of neat EMAA is prepared by hot pressing using an especially prepared mold at 130°C for a few minutes. The carbonyl functional groups absorb IR light at 1700 cm<sup>-1</sup> due to the formation of carboxylic acid dimers. After processing in NaOH solution, its intensity decreases and a red-shift down to 1680 cm<sup>-1</sup> is observed. At around 1550 cm<sup>-1</sup> a new peak related to sodium carboxylate appears: its absorbance increases with the degree of neutralization (DN). These results are in agreement with the literature and confirm the partial neutralization of the copolymer precursor.<sup>1</sup> DN is estimated equal to 90±4%, obtaining the ionomer EMAA-0.9Na. The adopted protocol prevents the formation of anhydrides in EMAA. Finally, thermal characterization is carried out, showing that neutralization leads to a decrease in the melting temperature of the polymer.<sup>2</sup>

**EMAA-Na Ionomers: a green approach for neutralization**



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## CELLULOSE HYDROPHOBIZATION FOR FOOD PACKAGING APPLICATIONS

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### Abstract

Cellulose<sup>1</sup> is being explored as a low-cost and sustainable alternative to synthetic plastics in single-use items, with the aim of reducing environmental pollution. However, its industrial application in food and beverage packaging is limited by the fact that, unlike conventional thermoplastics, it cannot be processed. Moreover, its inherent hydrophilic nature makes cellulose not suitable for such packaging applications. The first technological challenge was overcome by the Italian company Sacmi, which has successfully developed a new technology for shaping dry cellulose fibres, enabling the fabrication of complex objects such as cellulose-based bottle caps.

The next challenge to be tackled is, therefore, the hydrophobization of cellulose fibres. Focusing on the scalability and sustainability of the process, the application of drying oils is investigated to achieve a hydrophobic coating on cellulose fibres.

Drying oils present a series of conjugated carbon-carbon double bonds in its fatty acid chains and harden to a tough, solid film through a process of oxidative polymerization. In our approach, the oxidative polymerization, that naturally occurs under atmospheric conditions over several days, was accelerated by applying specific thermal treatments or exposing the reactive system to atmospheric pressure plasma. Differential Scanning Calorimetry (DSC) analyses were explored to monitor the exothermal enthalpy of reaction<sup>2</sup>, while Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) spectra were carried out to evaluate the auto-oxidation and the disappearance of double bond signals, closely related to the degree of curing.

Cellulose fibres treated with drying oils and exposed to high temperatures were found to be hydrophobic with low water absorption.

**Acknowledgments.** The PhD project is supported by the Italian company Sacmi and NextGenerationEU (PNRR).

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**BALANCING PERFORMANCE AND ENVIRONMENTAL SUSTAINABILITY OF MATERIALS AND PROCESSES FOR TIRE PRODUCTION**

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**Abstract**

With almost three billion tires produced worldwide in 2019 the tire sector is claimed to be of ecological importance due to its intensive consumption of natural resources, both in terms of raw materials and energy use during the production process.<sup>1</sup> Among the tire life cycle phases, the raw material extraction phase has been evaluated as burdensome in terms of environmental impact.<sup>2</sup> This means that carefully choosing the materials used in the tire composition can be crucial for assessing the overall sustainability of the product. On the other hand, determining the composition of materials also dictates the tire performance, both in term of processability of the compound and behaviour of the end product. Ensuring safety and efficiency while driving plays a key-role in tire design, and the choice of innovative materials can lead to durability enhancement and improved performance. The real difficulty is finding the right balance between performance and sustainability. The tool that can help in this decision-making phase is Life Cycle Assessment (LCA) analysis, which points the way to more sustainable practices and identifies key strategies aimed at optimizing performance while minimizing environmental burden. By quantifying factors such as energy consumption, emissions, resource use, and waste generation, LCA provides a detailed understanding of a product environmental footprint.

This work aims to provide a comprehensive overview of the performance-sustainability relationships of model elastomeric compounds relevant for tread applications, prepared and vulcanized in lab-scale equipment. Such model formulations are composed by styrene-butadiene rubber, silica, silane as compatibilizing agent, plasticizers, antioxidants, activators and curatives.

An LCA analysis was conducted to evaluate the environmental impact of the raw materials and of the mixing process. Scanning Electron Microscopy and analysis of the torque-time mixing curves were carried out to assess the efficiency of the process, and tensile properties were correlated to resistance and durability performance of the tire. The obtained results were weighed up to enable an objective and holistic decision-making process.

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**CYCLODEXTRIN-FUNCTIONALIZED POLYSACCHARIDE SYSTEMS FOR CURCUMIN INCAPSULATION AND DELIVERY**

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**Abstract**

Curcumin (CUR) is a molecule with antibacterial, antioxidant and anticancer properties but poor solubility in aqueous environment<sup>1</sup>. The development of curcumin delivery systems is therefore highly desirable. Cyclodextrins (CDs) are able to host hydrophobic molecules within their toroidal cavity, they therefore can improve the solubility and stability of poorly water-soluble compounds and increase the bioavailability of some drugs. In this study,  $\beta$ -CDs-CUR inclusion complexes were prepared and investigated. However, it was verified that the drug encapsulation was very low (2-3%) and the release was high. Indeed, as the host-guest inclusion complex formation is governed by weak interactions<sup>2</sup>, the thermodynamic equilibrium can easily shift towards breakdown of the complex with uncontrolled release of the host molecule. Many studies have suggested increased host-CDs affinity and diffusion-controlled drug release when CDs are part of supramolecular structures<sup>3</sup> such as those formed with various types of polymers including polysaccharides. In addition, polysaccharides have functional groups in their backbone that make them easily modifiable both by chemical reactions and physical interactions with a number of different molecules. In order to be conjugated with chitosan (CS), through the formation of amide bonds,  $\beta$ -CDs were functionalized with succinic anhydride (S) or maleic anhydride (M). The two obtained conjugated systems were named CD\_S\_CS and CD\_M\_CD. After fabricating three-dimensional matrices (scaffolds) by freeze-dried process, they were loaded with CUR. It was verified that the drug encapsulation efficiency in these systems was quite high (70-80%). However, since CS does not possess dimensional stability in aqueous medium, a cross-linking reaction using two different procedures was carried out. In particular, a physical crosslinking with tripolyphosphate (TPP) was used for both scaffolds, while a chemical crosslinking with ethylene glycol dimethylacrylate (EGDMA) was employed for the CD\_M\_CD\_CUR sample. The systems were characterized by spectroscopic (UV-VIS, FT-IR, <sup>1</sup>HNMR) and thermal techniques (TGA, DSC) as well as by swelling measurements in phosphate buffer (PBS, pH=7.4). Finally, the kinetic release of CUR in PBS/EtOH solution and the antioxidant power of the developed systems were evaluated.

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COVALENT ADAPTABLE NETWORKS BASED ON  $\beta$ -AMINO ESTERS FOR SELF-HEALING

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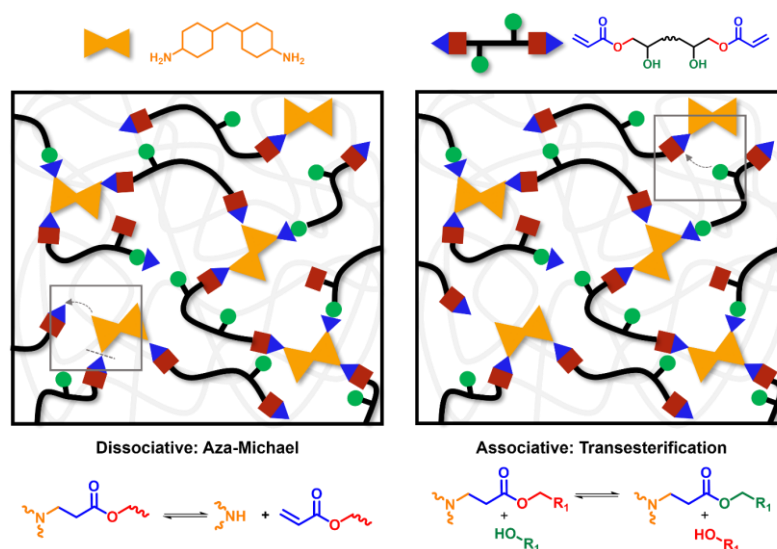
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Abstract

In the age of plastic -where the environment is heavily burdened by human waste- covalent adaptable networks (CANs) can be a relevant alternative to classical thermosets and thermoplastics. CANs present the mechanical performances of the former with the ease in reprocess and recycle of the latter. This new class of materials was first introduced in 2011 and have gained relevance with every passing year. Their applications ranging from enhanced recyclability, self-healing, composites, and hydrogels.<sup>1</sup>

In this framework, a novel CAN based on  $\beta$ -amino ester chemistry is presented.<sup>2</sup> Preliminary model studies were performed to establish reaction kinetics and side reactions on different substrates. Bulk material curing was then achieved *via* aza-Michael addition -one of the most exploited acrylates click reactions- between an amine and an acrylic reaction partner. Thermal characterisation showed good thermal stability and glass transition temperature ( $T_g$ ) near 50 °C. Such materials can easily be thermoformed and thermally reprocessed, their dynamicity originating by both the retro aza-Michael addition and transesterification reaction in presence of hydroxy functionalities (Figure 1).



**Figure 1.** Display of dual network rearrangement *via* dissociative retro aza-Michael reaction and associative transesterification.

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**REFRACTIVE RESILIENCE: ENHANCING MECHANOCROMIC DBRs THROUGH A NEW FABRICATION APPROACH.**

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**Abstract**

Mechanochromic materials have proven to be invaluable tools for visual strain sensing in various fields, from personal health monitoring to soft robotics.<sup>1</sup> However, conventional strain sensors often rely on external power sources and connections for signal processing, which limits their versatility.<sup>1</sup> Inspired by nature's dynamic coloring mechanisms that enable seamless communication in different environments, researchers have turned to photonic crystals because of their immediate response to mechanical strain. This is possible thanks to the periodic structure of photonic crystals, which consist of two materials with different refractive indices periodically arranged to form a dielectric lattice extending in 1, 2 or 3 dimensions.<sup>2</sup> In this research, we focus on 1D photonic crystals, also known as distributed Bragg reflectors (DBRs), which consist of a series of thin layers that form the dielectric lattice.<sup>3</sup> In our quest to improve mechanochromic DBRs, we present a new fabrication approach that promises to improve the quality and performance of these materials by reducing fabrication time and material waste. Using a novel solution-based deposition method, we produce mechanochromic DBRs with unprecedented precision and control. This innovative approach not only improves the reproducibility and reliability of the resulting materials, but also expands their application possibilities. Our focus is on using thermoplastic elastomers (TPEs) and perfluoropolymers with different refractive indices to develop DBRs capable of exhibiting dynamic spectral shifts in response to mechanical stress. These materials, known for their good processability and rubber-like elasticity, offer a unique combination of versatility and performance that enables the development of highly sensitive and adaptable strain sensors. By systematically characterizing the DBRs we produce, we aim to elucidate their optical response under different loading conditions. By correlating these results with standard stress-strain curves, we aim to determine the spectral sensitivity of our system to applied stress/strain units and thus gain valuable insights into its practical utility. Furthermore, we explore the potential applications of these advanced mechanochromic DBRs in optomechanical photonics and envision a future where these innovative materials play a central role in revolutionizing sensor technology and beyond.

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## BLOCK COPOLYMERS AS SMART MATERIALS WITH REVERSIBLE SHAPE-MEMORY PROPERTIES

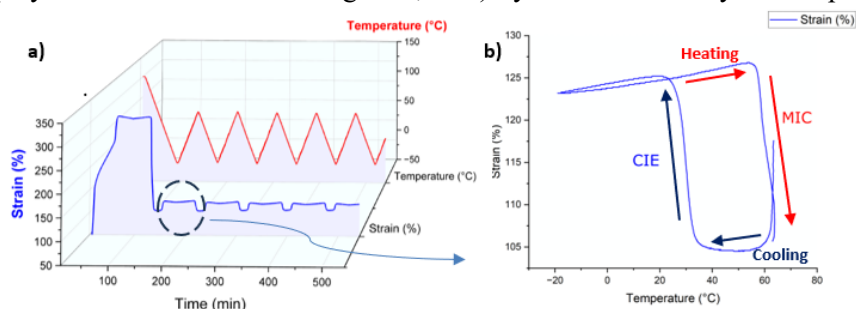
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## Abstract

Stimuli-responsive materials manage to change some of their properties when exposed to a proper trigger, and between them, Shape-memory polymers (SMPs) are known for their ability to retain one or more temporary shapes, after a programming process, and to switch from one to another by applying the right stimulus. SMPs are characterized by permanent and temporary netpoints in their structure, and with the cleavage of the temporary netpoints, the original shape-changing is achieved. In SMPs, glassy or crystalline domains often represent the temporary netpoints; thus, SMPs usually exhibit thermo-sensitive features and a temperature variation is the most common trigger;<sup>1</sup> stating on SMPs molecular structure and the applied programming process they can show reversible or irreversible shape-memory mechanisms. This work presents a novel SMP based on block copolymers of polycaprolactone (PCL) and polybutylene succinate (PBS), both sustainable and biodegradable polymers. Methacrylate triblock copolymers PCL-PBS-PCL undergo to a cross-linking process, obtaining a final polymeric network with two distinct crystalline phases (with melting at about 50 and 85°C) near the thermal transitions of the two homopolymers. The presence of chemical crosslinking between the chains is mandatory in order to form permanent netpoints inside the multicrystalline network. The rigid and high-melting PBS domain represents a skeleton for the more flexible and low-melting PCL's semicrystalline phase that acts as temporary netpoints. These semicrystalline networks show a reversible shape memory effect (SME) after an appropriate thermo-mechanical programming cycle consisting of heating above the melting temperature of the PBS domain, exerting external stress to deform the material, and cooling while maintaining the applied stress.<sup>2</sup> Indeed, when re-heated at the so-called activation temperature, the melting just of the PCL phase occurs, obtaining a contraction of the material (Melting-Induced Contraction, MIC); when cooled down, PCL-orientating crystallization is induced (Crystallization-Induced Elongation, CIE) by the stretched crystalline phase of PBS, further elongating the sample. A cyclic variation in temperature between PCL phase's melting and crystallization leads to a reversible change in the macroscopic shape of the sample (figure 1).



**Figure 1.** a) thermo-mechanical programming and SME b) MIC-CIE due to PCL phase.

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**BIO-BASED ELASTOMERIC COMPOUNDS FOR SUSTAINABLE TIRE  
MANUFACTURING**

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**Abstract**

In the tire industry, while past efforts predominantly focused on enhancing safety and performance, a growing interest exists nowadays towards environmental sustainability aspects. One of the recent trends is increasing the use of bio-based ingredients to replace traditional petroleum-based materials.<sup>1</sup> However, integrating bio-based components into complex elastomeric mixtures is highly challenging due to the intricate physical and chemical interactions among the numerous constituents of a typical tire compound. A thorough understanding of compatibility, processing requirements, and potential interactions with other components is essential for achieving effective dispersion of the solid and liquid phases within the elastomeric matrix during the mixing process.

In this study, the processability and mechanical performance of a series of model tread compounds containing bio-based components were investigated, taking traditional petroleum-based formulations as a reference. Experimental tests and theoretical models were exploited to study the miscibility of the components, which is crucial for obtaining the desired set of performance. In particular, differential scanning calorimetry, dynamic-mechanical analysis, and broadband dielectric spectroscopy were used to study the compatibility of the plasticizers with the other tire compound constituents, focusing on shifts in the glass transition temperature and other relaxation phenomena of the polymer chains under mechanical and dielectric stimuli. These analyses were complemented by transmission and scanning electron microscopy investigations to collect microstructural information and quantify the degree of dispersion of reinforcement fillers and other additives. The obtained results were related to an experimental and theoretical evaluation based on the Hansen solubility parameters, which allow for predicting the compatibility of two or more chemical compounds. Finally, life cycle assessment methodology was also employed to evaluate the sustainability of the selected green additives, correlating any sustainability improvements with variations in tire compound performance.

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## EXPLORING MULTIVARIATE DYNAMICS IN MIXED PLASTIC WASTE RECYCLING THROUGH PRINCIPAL COMPONENT ANALYSIS (PCA)

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### Abstract

The imperative for recycling polymeric materials has never been more pressing, with environmental concerns and resource scarcity driving the search for sustainable solutions. Pyrolysis-based chemical recycling stands out as a promising technique, offering the potential to recover valuable resources from mixed plastic waste while minimizing environmental impact.<sup>1</sup>

In our study, we explore the intricate dynamics of pyrolysis-based chemical recycling, aiming to maximize resource recovery and promote circularity in the plastics industry. By analyzing large datasets derived from the recycling process, we seek to identify key variables that influence the quality and efficiency of resource recovery.

Central to our analysis is Principal Component Analysis (PCA), a powerful statistical tool for uncovering hidden patterns and relationships within complex datasets.<sup>2</sup> By integrating PCA into our analysis framework, we obtain valuable information about the interaction between process parameters and the quality of the products obtained. This allows us to optimize recycling strategies and improve process sustainability.

We also explore the potential integrability of pyrolytic oil in the petrochemical sector, particularly in co-feeding with virgin naphtha in steam cracking processes. Our ongoing research and tests aim to evaluate the feasibility and benefits of this process integration approach.

This abstract illustrates our research efforts, which contribute to the advancement of sustainable practices in the plastics industry, aligning with the principles of circular economy and environmental stewardship.

### Acknowledgements.

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## HYBRID INTERCALATED POLYMERIC-BASED STRUCTURES FOR DYES ABSORPTION FROM WASTEWATER

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### Abstract

Water pollution from industrial waste poses significant concerns due to its detrimental impacts on natural ecosystems and human health. Industrial waste, through various forms, contributes substantially to the contamination of water resources. The simultaneous presence of organic and inorganic pollutants in the wastewater has claimed the need for multiple pollutant removal. One technique used for this purpose is the adsorption process using adsorbent materials like clays or polymeric-based composites. In particular, special attention is focused on hybrid materials that, combining an inorganic matrix (host) with functional compounds (guest), have shown enhanced sorption properties and selectivity for heavy metals and hazardous dyes adsorption from wastewater. In this context, cellulose-based adsorbents are considered promising as low-cost, easily available, biodegradable and nontoxic materials for the removal of contaminants.<sup>1</sup>

In this work, we developed a hybrid host-guest system for the absorption of dyes from water. As inorganic matrix (host) was used a family of synthetic swelling fluorophlogopite ( $\text{Na}_y[\text{Si}_6\text{Al}_2]\text{Mg}_6\text{O}_{20}\text{F}_4 \cdot \text{XH}_2\text{O}$ ) (Micas), in particular Na-2-Mica and Na-4-Mica, containing respectively two and four sodium atoms.<sup>2</sup> The guest material consisted of cellulose nanocrystals (CNCs) extracted from date palm sheath fibers. A commercial polysaccharide, carboxymethylcellulose (CMC), was also tested as a guest compound to compare the adsorption of the composite materials obtained with CNCs. ATR-FTIR and Raman spectroscopy, X-ray diffraction analysis (XRD) and Thermogravimetric analysis (TGA) were conducted to study the formation of intercalated hybrid structures. The adsorption experiments were conducted on a solution of Methylene blue (MB) (3,7-bis(dimethylamino)-phenothiazin-5-ium chloride), a thiazine cationic dye extensively used to dye textiles, such as cotton, cellulose, wood, and silk. The results showed that the intercalation of polysaccharides (both CNC and commercial CMC) in Na-4-Mica structure permitted to obtain the highest absorption of MB, reaching a value of 86%. On the contrary, the hybrid cellulose-Mica composites obtained with Na-2-Mica showed a decrease in absorption, even compared to the pristine mica. This behaviour could be attributed to the different host structure and starting porosity of the Mica, which can influence the final absorption properties of the hybrid materials.

<i>Sample</i>	<b>Na-2-Mica</b>	<b>CNC-M2</b>	<b>CMC-M2</b>	<b>Na-4-Mica</b>	<b>CNC-M4</b>	<b>CMC-M4</b>
<i>Absorption</i>	70%	60%	58%	42%	86%	84%

**Table 1.** Absorption of MB with pristine Micas and hybrid materials in 24h.

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**SYNTHESIS AND APPLICATIONS OF MAIN-CHAIN LIQUID CRYSTALLINE ELASTOMERS PREPARED BY MICHEAL'S ADDITION**MARCO TURRIANI<sup>1,2</sup>, DANIELE MARTELLA<sup>1,3</sup>, CAMILLA PARMEGGIANI<sup>1,3</sup><sup>1</sup>*LENS (European Laboratory for Non-Linear Spectroscopy), University of Florence, Sesto Fiorentino, Italy*<sup>2</sup>*Department of Physics, University of Florence, Sesto Fiorentino, Italy*<sup>3</sup>*Department of Chemistry, University of Florence, Sesto Fiorentino, Italy*

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Role: PhD student, 2<sup>nd</sup> year**Abstract**

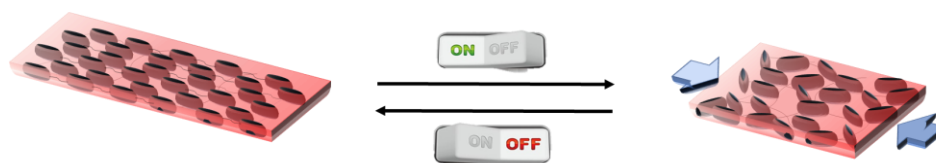
Liquid crystalline elastomers (LCEs) are smart materials consisting of rubber-like polymers made by slightly crosslinked liquid crystalline networks. These materials have aroused great interest because they combine the entropic elasticity of classic elastomers with the orientational order at the molecular level and sensitivity to different external stimuli of Liquid Crystals.<sup>1</sup>

Liquid crystals, if left free, spontaneously self-assemble in micrometric domains in which mesogens are aligned along the same director. If those liquid crystals have polymerizable groups, they can react and give a polydomain liquid crystal elastomer (PD-LCE).<sup>2</sup>

The liquid crystalline monomers, in the nematic state, can be aligned along a single direction by applying an external electrical, magnetic or shear field or through an aligning surface. In these conditions, when crosslinked, an LCE with a macroscopical alignment is obtained and is called monodomain or single crystal LCE (SC-LCE).

SC-LCEs respond to an increase of the entropy, given by an external trigger, in the system with a macroscopic and reversible contraction that can be traduced in different movements or tension (Fig. 1). For this reason, SC-LCEs find applications in literature in different fields like micro-robotics or microfluidics. The ability to rapidly generate tension, with an opportune external trigger, can be exploited to mimic the contraction of biological muscles.<sup>3</sup> Bearing in mind these considerations a palette of different SC-LCEs has been synthesized exploiting Michael's addition which is a powerful and versatile tool to obtain main-chain LCEs starting from commercial diacrylate mesogenic monomers. This reaction is extremely versatile and characterised by the absence of byproducts and side reactions.<sup>2</sup>

This work has received funding for the European Union's Horizon 2020 research and innovation programme under grant agreement No. 95216 (REPAIR)



**Figure 1.** Scheme of SC-LCEs actuation.

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## HIGH QUALITY GLASS, SILICON AND METALS FROM END-OF-LIFE PHOTOVOLTAIC PANELS

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### Abstract

The energy transition towards renewable sources is essential to reduce the use of fossil fuels and their environmental impact. Photovoltaic technology plays a fundamental role in the production of clean energy as it is one of the most mature and widespread technologies for electricity production from solar energy.<sup>1</sup> In the coming decades, a significant increase in installed PV capacity is expected due to the growing energy demand. The recovery and reuse of materials (glass, silicon, metals) and polymers from end-of-life photovoltaic panels (EoLPV) is very important to reduce the use of resources that are running out and to promote the installation increase of solar power or the use of these materials in other production chains. Therefore, it is necessary to develop PV recycling processes that are sustainable for companies.<sup>2,3</sup> This work aimed to improve an operating process to treat first-generation EoLPV. In particular, some critical issues such as selectivity of the mechanical separation step was upgraded. The new process involves an initial phase consisting in manual removal of the junction box (1.1% wt) and cables (0.9% wt). Subsequently, the frame is removed via a framing machine and then sent to a blade crusher to obtain the aluminium fraction (9.4% wt). The photovoltaic panel, without frame, is then subjected to a new mechanical operation, which allows the selective removal of the backsheet (4.7% wt), glass (73.9% wt) with a light layer of Ethylene-Vinyl Acetate (EVA) wt), and a powder composed of EVA, cells and electrical contacts (10% wt). To remove EVA layer from glass a tumbling machine was used thus obtaining a high-quality pure glass (73 % wt). Finally, the crushed material containing EVA, cells and metals is sieved (< 1 mm) to separate the electrical contacts (0.4% wt) from the rest of the fraction. This last fraction corresponds to 9.6% by weight of the panel, of which approximately 5.8% is EVA and the remaining 3.8% is Si and metals used in the cell (Al, Ag, Zn, Pb, Sn, Cu, Fe). The recovery of precious metals and silicon can be carried out by chemical or thermal processes. The electrical contacts, however, can be treated to recover the metals (Ag and Cu) or sold as such. Therefore, from 1 ton of EoLPV it will be possible to obtain 730 kg of pure glass, 94 kg of pure Al, 47 kg of backsheet, 11 kg of junction box, 9 kg of cables, 4 kg of electrical contacts, 58 kg of EVA, 38 kg of Si and metals and 9 kg of non-recoverable EVA as it is mixed with glass.

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## EVALUATION OF AGING EFFECT ON THE DURABILITY OF ANTIBACTERIAL TREATMENTS APPLIED ON TEXTILE MATERIALS FOR THE AUTOMOTIVE INDUSTRY

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### Abstract

The automotive industry is always seeking novel solutions to improve the durability and the performance of textile materials used in vehicles. Indeed, especially after the coronavirus pandemic, antibacterial treatments have gained interest for their potential of ensuring cleanliness and safety toward microbial contamination within vehicles. This study gives a panoramic view of the durability of antibacterial treatments applied on textile materials in the automotive industry, focusing on their performance after experiencing accelerated aging processes. Two different textile materials, a fabric and a synthetic leather, both treated with antibacterial agents, were tested according to ISO 22196 and ISO20743 standards, respectively, using two model microorganisms, *Escherichia coli* and *Staphylococcus aureus*. The impact of mechanical, thermal, and solar aging on the antibacterial properties has been evaluated. In addition, scanning electron microscope (SEM) analysis was performed to investigate the surface morphology of the materials before and after aging. Furthermore, contact angle measurements were conducted. The results suggest that neither mechanical nor thermal aging processes determined diminished antibacterial action. It was determined, instead, that the most damaging stressor for both textile materials was UV aging, causing severe surface alterations and a reduction in antibacterial activity.



## TRANSPARENT, MULTIFUNCTIONAL, AND FULLY BIO-BASED CHITOSAN/TANNIN HYDROGEL FILMS FOR WOUND HEALING APPLICATIONS

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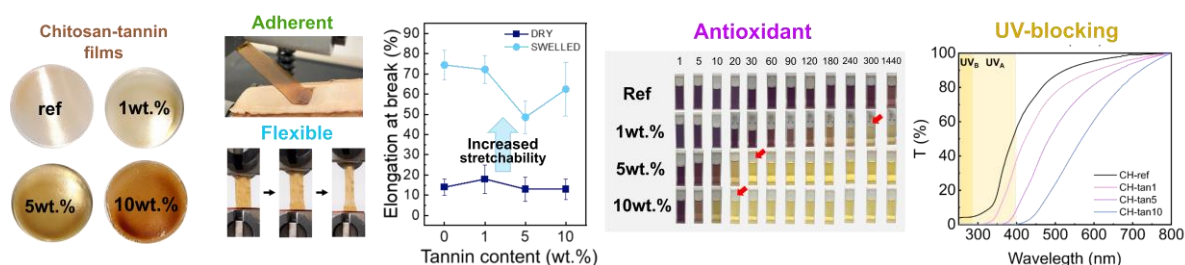
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### Abstract

In the last decade, natural polymers have gained considerable attention in fabricating hydrogels aimed at promoting wound healing management. Among them, chitosan, a linear amino polysaccharide derived from crustacean exoskeleton, insect cuticles, or fungi, exhibits attractive properties being biocompatible, non-toxic, highly hydrophilic, and hemostatic.<sup>1</sup> Moreover, most of the research is currently focusing on the transition from passive wound dressings to smart multifunctional materials that actively promote the wound-healing process. This is typically achieved by incorporating active molecules/particles into the polymeric matrix, leading to a bio-multiactive hydrogel that can provide all-in-one advanced functions. In this work, novel hydrogel films based on chitosan and multifunctional *Castanea Sativa* wood-tannins were developed. Specifically, chitosan/tannin (CH-tan) hydrogel films were prepared at increasing tannin concentrations (0, 1, 5, 10 wt%) through the solvent casting method, where the use of formic acid allowed their homogeneous distribution into the polymer matrix. The obtained films exhibited excellent swelling ability (swelling degree >2000%), thus great capacity of wound exudates absorption. Moreover, tensile tests demonstrated that improved flexibility and good adhesive properties can be obtained after swelling the films by 5-second immersion in water, resulting in a soft material suitable for contact and adhesion with the injured skin. The films showed excellent antioxidant capacity, which is essential in limiting the inflammation stage of the healing process to avoid wound complications.<sup>2</sup> In particular, 100% of radical scavenging activity was detected through the radical DPPH method test for CH-tan1, CH-tan5, and CH-tan10 in 6 hours, 30 minutes, and 10 minutes, respectively. Finally, the increasing tannin content did not affect the transparency of the films, thus allowing continuous monitoring of the wound state, while significantly improving the UV-blocking activity, going from 70% UV-absorbance for chitosan to 100% for chitosan containing 5 and 10 wt% of tannins. The obtained results demonstrated the potential applicability of the chitosan/tannin hydrogel films as a skin wound dressing.



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## POLYMER PHOTONICS FOR THERMAL MANAGEMENT

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### Abstract

Global warming, with its consequent increase of extreme natural phenomena has attracted the attention of the scientific community, now focused on central themes such as sustainability and energy efficiency and saving. In this regard, a non-negligible problem is represented by air conditioning, which in hot-climate developed countries accounts for high percentages of energy consumption of households, buildings and vehicles, henceforth emissions of CO<sub>2</sub>.<sup>1</sup> Air conditioning creates a vicious circle, heating the surroundings to cool down indoor, and its penetration in the markets of hot climate, highly populated developing countries such as India or Brazil is completely unsustainable.<sup>2</sup> Therefore, passive solutions able to replace or at least reduce the need for air conditioning are of extreme interest. In this regard, both i) reflecting sunlight and ii) emitting thermal radiation through the atmospheric transparency window (8-13 micrometers) achieve a passive cooling effect.<sup>3</sup> To reflect sunlight, we exploit dielectric mirrors made out of polymer materials. These are multilayer structures, made out by stacking thin polymer films (few 100s of nm) one on top of the other. Their periodic arrangement causes interference effects for visible - near infrared radiation, which make the structure a near perfect mirror for a narrow range of wavelengths.<sup>4</sup> Different materials can be combined to obtain more efficient mirrors, going from commodities such as polystyrene or cellulose acetate, to technical polymers such as poly(*N*-vinylcarbazole) and fluoropolymers like Aquivion. Such mirrors can achieve reductions in temperature increase of shielded samples higher than 25 %.<sup>5,6</sup> The materials making up the photonic crystals, adequately selected, can be combined with thick diffuse reflectors so that the same structures used as thermal shields can have a radiative cooling effect, joining reflection and emission for optimal passive reduction in temperature increase.<sup>3</sup> Given how plastic photonic crystals can be fabricated on large scale through co-extrusion, this is a promising result towards the use of aegises in thermal shielding applications.

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**ENHANCING THE PROPERTIES OF POLY(BUTYLENE SUCCINATE): THE GAME-CHANGING ROLE OF TECHNICAL LIGNINS**

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**Abstract**

The generation of sustainable, high-performance materials is of utmost importance to adhere to sustainable development goals and circular economy paradigms.<sup>1</sup> Utilizing technical lignins, a low-cost and widely available byproduct, could yield significant benefits. Due to its polyphenolic structure, lignin exhibits various characteristics of interest for the production of biobased active advanced materials, such as antioxidant, antimicrobial and UV-shielding ability. When incorporated into bioplastics, these properties enhance the polymer matrix, expanding its potential applications.<sup>2</sup>

In this framework, the work here presented focused on the development of bio(nano)composites by incorporating 15 wt% of industrially produced steam-exploded hardwood lignin into poly(butylene succinate) (PBS) through compounding and injection molding. Different particle sizes, including nanolignin (LNPs) obtained via a green and mild hydrotropic approach, were used.<sup>3</sup> The starting lignins were thoroughly characterized using GPC, <sup>31</sup>P NMR, and HSQC to elucidate their structure and functional properties. The results, benchmarked against wood fiber and softwood kraft lignin, demonstrated good antioxidant power (IC<sub>50</sub> 28 ± 1 µg) and structural similarity to milled wood lignin, which is considered representative of native lignin in plants.<sup>4</sup>

As to the biocomposites, the incorporation of lignin increased their crystallinity, in turn impacting the elastic modulus and tensile strength, and significantly enhanced antioxidant activity (IC<sub>50</sub> 14 ± 1 µg) and UV-blocking capability. These effects were particularly evident in the presence of LNPs. The produced materials were then subjected to accelerated aging tests (1000 hours, 50% RH, 50 °C, under constant simulated solar light, 1000 W/m<sup>2</sup>), showing that PBS undergoes hydrolysis of the polyester chains, leading to a reduction in molecular weight and the formation of aldehydic and carboxylic functionalities. These changes affected both tensile strength and crystallinity, which respectively decreased and increased.

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## SUSTAINABLE LUMINESCENT SOLAR CONCENTRATORS WITH SUPERIOR PHOTODEGRADATION RESISTANCE

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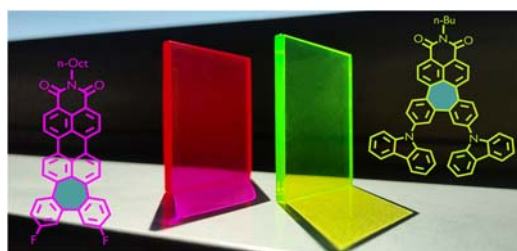
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## Abstract

Luminescent Solar Concentrators (LSCs) are light-concentrating devices with good efficiency under diffuse light and appealing aesthetics, making them an ideal technology for integrating building facades in cities. To achieve high-performance large-scale devices, solutions to lower the impact of their production and extend their lifetime would be highly beneficial. Photostability is vital for emitters in LSCs as they must withstand prolonged sunlight exposure over many years. UV radiation can degrade the structure of organic emitters, reducing LSC efficiency and necessitating panel replacements, which incur economic and environmental costs. This study examined two push-pull dyes with distorted heptagonal inclusions — Peri2F and Nap2Car<sup>1</sup> — as emitters for bulk LSCs at concentrations from 100 ppm to 250 ppm. Using chemically regenerated monomers for PMMA slab production, rather than synthetic monomers, lowers the global warming potential by approximately 4 times, enhancing the sustainability and circularity of LSC production. The most efficient Peri2F/recycled PMMA system achieved a device efficiency ( $\eta_{\text{dev}}$ ) of 0.7%, lower than that of devices using the state-of-the-art emitter LR305<sup>2</sup>. However, Peri2F demonstrated significantly better resistance to photodegradation. Forecast analysis predicts that an LSC with 100 ppm of Peri2F can match the performance of LR305 in recycled PMMA after about 1 year of use, with only a 2% decrease in emission intensity.



**Figure 1.** Peri2F (left) and Nap2Car (right) molecular structures and LSC appearances.

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**PHOTOCATALYTIC THERMOPLASTIC COATINGS LAYERED ONTO CEMENT SURFACES FOR GASEOUS POLLUTANTS ABATEMENT**

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**Abstract**

In contemporary times, photocatalytic remediation has emerged as a promising and sustainable strategy to mitigate xenobiotic volatile organic compounds (VOCs) pollutants in the atmosphere. This perspective has led to the integration of photocatalysis within the construction industry. Specifically, the incorporation of titanium dioxide nanoparticles (TiO<sub>2</sub> NPs) in cementitious matrices has been used in recent years, raising concerns regarding the environmental release of the photocatalyst through leaching and its notable wastage. Moreover, only nanoparticles exposed on the cement surface exhibit photocatalytic properties<sup>1</sup>. In the last years, our research group has developed a novel synthetic approach involving a bulk radical polymerization performed into the photocatalyst nanoparticles<sup>2</sup>, avoiding self-aggregation phenomena and enhancing light conveyance into the photocatalyst<sup>3</sup>.

This communication presents the photocatalytic performances and behaviours of PMMA-based<sup>4</sup> nanocomposites containing metal oxides, layered as thin films on cement surfaces, to simulate real-world applications. Photocatalytic experiments were carried out with a simulated solar light source, using toluene as a VOC model pollutant, and monitoring the oxidation products through an online GC apparatus. Experiments evidenced a significant performance of the PMMA-TiO<sub>2</sub>-SiC system over the other nanocomposites, with synergistic effects observed in multi-oxide systems, compared to individual oxide counterparts.

Finally, the photocatalytic activities of the nanocomposites were compared with existing TiO<sub>2</sub>-based photocatalytic systems used in the building industry, showing superior performance. The experimental results contribute to the research on efficient photocatalytic systems for air pollution abatement, emphasizing the importance of new polymeric-based materials in the building construction field.

**Acknowledgements.** This work was partially financed by “PON FSE REACT-EU 2014–2020 Azione IV-6”.

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**FRONTAL POLYMERIZATION OF SEMI-INTERPENETRATING POLYMERIC NETWORKS WITH TUNABLE MECHANICAL PROPERTIES FOR VERSATILE HYDROGEL APPLICATIONS**

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**Abstract**

Frontal polymerization (FP) is a self-perpetuating process where an initial trigger, either thermal- or photo-induced, creates a localized reaction region, called "polymerization front", which propagates along the reactor. Within this zone, the generated exothermic heat serves to increase the temperature, initiating further polymerization at the interface between the polymer and unreacted monomer phase. This leads to a propagation that occurs in a self-sustained and predictable manner, with fast reaction rates and short fabrication times, offering numerous advantages over other conventional polymerization methods in terms of time, energy and cost efficiencies. FP is particularly interesting toward the synthesis of hydrogels, which are materials characterized by crosslinked polymeric networks, with reversible swelling behaviour. Frontally prepared hydrogels have potential in different fields of application, including ion removal reagents, drug encapsulation and delivery, chemical sensors, and self-healing materials, where it is essential to control the pore-size and morphology while retaining flexibility and toughness.<sup>1</sup> In this work, FP was exploited to prepare a copolymer starting from Acrylamide (Aam) and GelMA (methacrylate gelatin) intercalated with gelatin, to form semi-interpenetrating polymeric network structures (semi IPN). Two series of samples were synthesized, differentiating for the degree of substitution of the pristine GelMA (30% and 75%) and the amount of gelatin. Thermal, morphological, and mechanical properties of the obtained hydrogels were assessed. First, reversible swelling behaviour confirmed the obtainment of a crosslinked network. Scanning electron microscopy (SEM) allowed to assess the variation of materials porosity according to the different hydrogels' composition. Rheological analyses revealed that the presence of gelatin within the semi-IPN network causes a decrease of rigidity of the plain copolymer and results in a wider linear viscoelastic range (LVER). Dynamic strain sweep tests established the high capacity of the different samples to recover their viscoelastic behaviour upon many cycles of high shear strain applied. Finally, semi IPNs were subjected to cyclic compression loading revealing optimal recovery properties. In conclusion, FP allowed to obtain highly and homogeneously crosslinked semi-IPN networks of Aam, GelMA and gelatin. The higher crosslinking degree of semi IPNs with respect to the starting components did not result in increased fragility, but in increased moduli without affecting the elasticity and the recovery properties. According to the different degree of substitution of GelMA and different amount of incorporated gelatin, it is possible to tune the resulting porosity, mechanical properties and swelling behaviour, making these systems suitable for a wide range of applications. All the starting materials are also biocompatible, encouraging their use in the field of drug delivery and tissue engineering.

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GLASS TRANSITION BEHAVIOUR IN POLYSULFONE NANOPARTICLES

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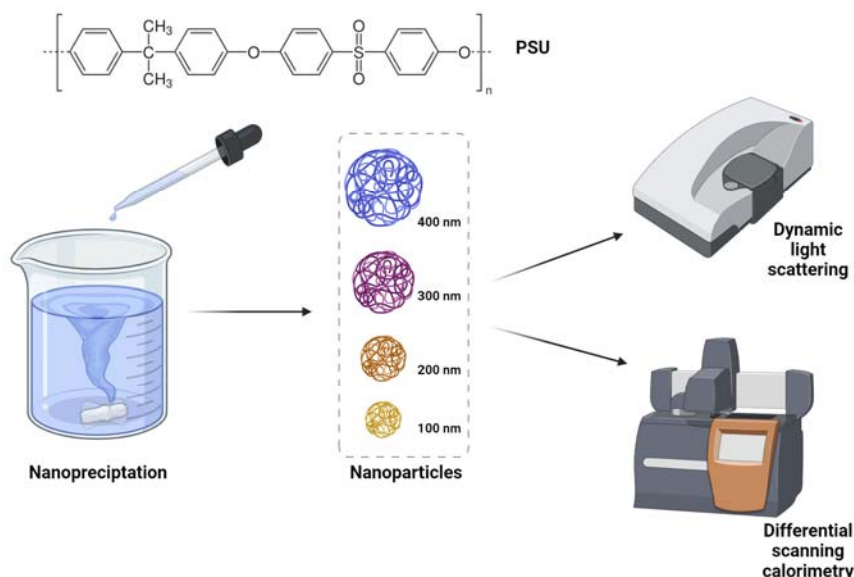
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Abstract

Technological developments in the contemporary era have generated a growing interest in the study of amorphous polymers with dimensions that are at the nanoscale. Beyond the practical applications, the miniaturization of polymers has ignited fundamental inquiries into the underlying physics governing property alterations at the nanoscale. Because of variations in polymer chain mobility brought about by confinement, polymers that are restricted at the nanoscale - due to size effects, interfacial effects, and spatial constraints - display considerably different thermodynamic properties from their bulk counterparts.<sup>1</sup> A topic of particular debate is the modification of glassy dynamics in nanostructured glasses. This interest was spurred by the discovery of a reduced glass transition temperature (T<sub>g</sub>) in thin polymer films in the early 1990s.<sup>2</sup> Since then, a substantial body of research has focused on investigating glassy dynamics in nanostructured polymers. This study focused on the thermal characterization of poly(sulphone) (PSU) nanoparticles. By changing the solvent and non solvent nature, nanoparticles with a range of size spanning from 400 to approximately 100 nm were prepared by nanoprecipitation method. These results were confirmed by dynamic light scattering. Differential scanning calorimetry was performed to analyse the thermal properties, providing information both on the devitrification kinetics and the segmental mobility.



**Figure 1.** Preparation and characterization of PSU nanoparticles.

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**3D PRINTING OF PHOTO AND THERMO RESPONSIVE LIQUID CRYSTALLINE ELASTOMERS FOR BIOMEDICAL APPLICATIONS**

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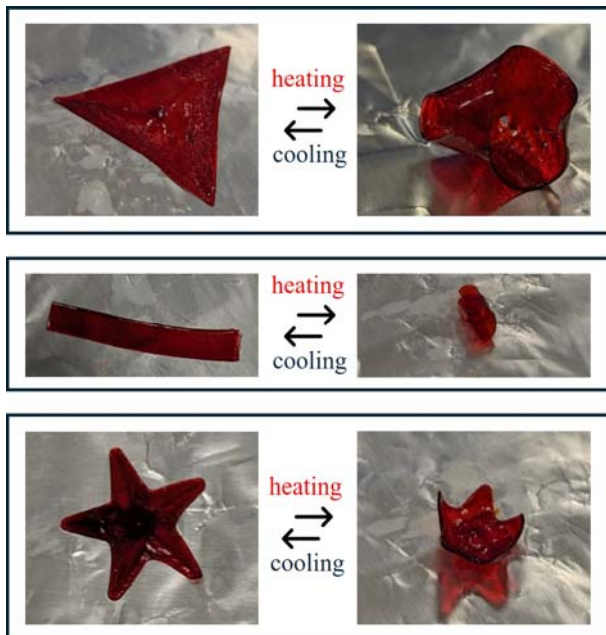
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Liquid Crystalline Elastomers (LCEs) stand out among the materials studied for the development of artificial muscles, given their capability of responding to external stimuli such as light irradiation or temperature changes. However, their application in biological settings, particularly within the human body, presents many challenges.

Here, we employ 3D printing to create LCE structures serving as artificial muscles, responsive to thermal activation or visible light. Additionally, we demonstrate their activation potential using LED arrays, enabling the possibility to develop of light-responsive biological interfaces for muscular support.



**Figure 1.** Different shapes and geometries obtained by DIW and their thermal actuation.

Through precise control of alignment and geometries, diverse actuators are attainable, allowing tuneable complex deformations (Fig. 1). Our study details the fabrication and characterization of LCE-based artificial muscles using cost-effective 3D printing, specifically employing Direct Ink Writing (DIW), a technique which can align the liquid crystals along the printing direction during the ink extrusion.<sup>1</sup>

Highly viscous oligomers based on diacrylate mesogens and dithiols, synthesized via a thiol-ene reaction, are used in DIW, with the inks containing an azobenzene dye for light actuation. Mechanical characterization and responsiveness to light and temperature are investigated post-printing, with structures adaptable for large-scale, custom-sized implantable patches.

**Acknowledgements.** The research leading to these results has received funding from Regione Toscana, Bando Ricerca Salute 2018, PERCARE project.

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## SELF-HEALING INTERPHASE IN POLYMER COMPOSITES

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### Abstract

In fibre-reinforced polymer composites, the interaction between the matrix and the fibres is crucial for the determination of the mechanical properties of the final product. A self-healing interphase could potentially re-establish the interaction between these two phases after damage if stimulated by heat. This process extends the service life of composites, reducing waste and repair costs and thus improving sustainability.

This work is focused on the application of a biodegradable poly( $\epsilon$ -caprolactone) (PCL) coating on the surface of glass fibres to allow interphase self-healing. Field emission scanning electron microscope (FESEM) analysis revealed a uniform deposition of the coating on the surface of the glass fibres. Self-healing was determined on epoxy-microcomposites through microdebonding tests, and it was calculated as the ratio of interfacial shear strength (IFSS) after and before the healing process. The healing process gave promising results, showing a complete restoration of interfacial shear strength compared to the initial fibre/matrix interphase.

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**INVESTIGATION OF THE EFFECTS OF CELLULOSE FILLERS ON THE PROPERTIES OF XANTHAN-BASED SOIL CONDITIONERS**

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**Abstract**

Soil conditioners (SC) are products that can be mixed into the soil in the planting hole to promote plant growth and improve the physical, chemical, mechanical and water regulation characteristics of the soil.<sup>1</sup> One of the main characteristics of these products is their ability to absorb large amounts of water to counteract the problems caused by drought and water scarcity. Several studies have shown that soil conditioners can effectively reduce water consumption during irrigation, lower the mortality rate of plants and, consequently, promote their growth.<sup>2,3</sup> However, traditional soil conditioners are based on synthetic polymers, mainly polyacrylamide, which have limited biodegradability and could release harmful by-products into the soil, posing risks to both the environment and human health.<sup>4</sup> On the basis of these considerations, the use of a bio-based polysaccharide such as xanthan gum (XG) may be very promising for this application due to its exceptional water absorption capacity and biodegradability.<sup>5</sup> To further enhance performance, wood-based fillers or cellulose fibres can be incorporated. These fillers offer the potential to optimise the characteristics of the SCs in terms of water absorption, water retention and mechanical stability. The aim of this study was to investigate the effect of different types of natural cellulose-based fillers on the properties of XG in order to develop new bio-based soil conditioners that could be used in forestry and agricultural applications. Rheological analysis showed that SCs with cellulose fillers characterized by a high aspect ratio and low oxide ash content exhibited an average increase of 21% in yield stress compared to neat xanthan gum. The presence of cellulose fillers in the composites resulted in a slower release of water than that of neat XG, limiting the volumetric shrinkage during the drying process. Furthermore, analysis of water absorption and water retention capacity of soils treated with the different SCs were carried out, demonstrating that the addition of 1.8 wt.% of SC with optimized composition to the soil led to an increase in water absorption capacity from 34% up to 69%. From the soil water retention curves, it was observed that the addition of SCs significantly increased the amount of water effectively available for plants in the area between field capacity and permanent wilting point (100–1000 kPa). From practical experiments on grass growth, it was observed that these SCs improved the water regulation of the soil, thus increasing the probability of plant survival under drought conditions.

**Acknowledgements.** This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101000406 – ONEforest.

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## EFFECT OF 3-HYDROXYVALERATE (3HV) CONTENT ON PROCESSABILITY AND PROPERTIES OF P(3HB-CO-HV)-BASED MATERIALS

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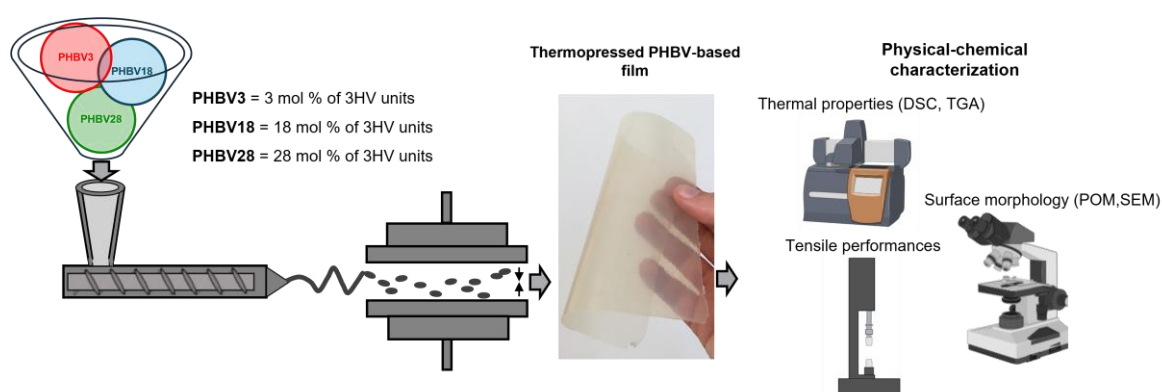
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### Abstract

Polyhydroxyalkanoates (PHAs) are a class of fully biodegradable polyesters produced by microbial cultures. Because of their similarity to PE and PP and their high barrier properties, *short-chain-length* PHA (*scl*-PHA) such as poly-3-hydroxybutyrate homopolymer (P3HB) and poly-3-hydroxybutyrate-*co*-3-valerate copolymers (P(3HB-*co*-3HV)) are the best candidates to replace fossil-based plastic in packaging systems. P(3HB-*co*-3HV)s are an attractive type of PHAs whose properties can be tailored by changing the 3-hydroxyvalerate monomer (3HV) concentration, offering the possibility of counteracting problems related to high crystallinity, brittleness and processability<sup>1</sup>. However, there are few studies about the effects of 3HV content on this last topic. The present study aims at providing new insights into the effect of 3HV concentration on the P(3HB-*co*-3HV) properties as a result of addition of nucleation agents and/or compounding with amorphous polymers as plasticizers. P(3HB-*co*-3HV)s containing 3, 18 and 28 mol% 3HV were processed into films by extrusion and subsequent moulding. The characterization results confirmed that increasing the 3HV content from 3 to 28 mol% resulted in a decrease in melting point (from 175 °C to 100 °C) and in an improvement in polymer toughness, as evidenced by an elongation at break increase from 7 % to 120 %. Then, the behavior of P(3HB-*co*-3HV)s filled with boron nitride, used as a nucleating agent, and/or compounded with low molecular weight amorphous PHA, employed as plasticizer, was evaluated. Water-vapor permeability measurements demonstrated the high barrier properties of produced P(3HB-*co*-3HV)-based materials.



**Figure 1.** Schematic representation of the production and characterization of P(3HB-*co*-3HV)-based materials

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## ADVANCED ISOCONVERSIONAL METHODS FOR SIMULATION OF REACTIVE THERMOSETTING MATERIALS

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### Abstract

Thermoset resins are extensively used for composite materials and adhesives due to their excellent high strength and stiffness.<sup>1</sup> However, several resins exhibit a brittle behavior and poor toughness and, therefore, several tougheners are introduced within the reactive system to tailor their morphological features, chemical composition, and mechanical properties.<sup>2</sup> Under this perspective, the challenge remains open to assess and control the reactivity of these systems to rationally develop products with desired features.

Computer simulation is a useful tool aimed at exploring the molecular mechanisms underlying physico-chemical phenomena that occur during the curing process. A multiscale approach has been followed to implement realistic models of such reactive polymeric materials. Several applications of the isoconversional method will be presented in the context of this work. First, experimental results and isothermal as well as non-isothermal modeling results, on a macroscopic scale, will be elucidated on bioderived furan-based epoxy resins.<sup>3</sup> The approach is further developed by using advanced isoconversional methods that allow to enclose the complexity of multi-step and simultaneous chemical processes on reprocessible epoxy vitrimers.<sup>4</sup> In the final part of this work, a preliminary approach, on a microscopic scale, is proposed to couple the morphology development and the reaction kinetics during the chemical process.

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## POLY-L-LACTIDE AND POLYGLYCEROL ADIPATE NANOCARRIERS FOR DRUG ENCAPSULATION

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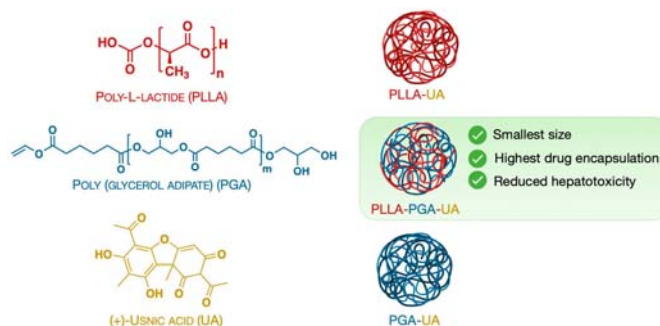
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### Abstract

Polymeric nanosystems offer immense potential for drug delivery by providing a versatile platform that can be finely tuned for various therapeutic applications, notably in drug delivery where they may allow for drug targeting and controlled release.<sup>1</sup> The present study investigates the use of nanoparticles (NPs) based on poly-L-lactide (PLLA) and polyglycerol adipate (PGA), alone and blended (50/50), for the encapsulation of usnic acid (UA), a natural compound with antimicrobial and anticancer activities, suffering from limited aqueous solubility and hepatotoxicity. Polymer NPs with sizes ranging from 100 to 150 nm were obtained by nanoprecipitation. PLLA-PGA (50/50) NPs were smaller in size and more susceptible to enzymatic degradation than pure polymers. FTIR-ATR and DSC analyses evidenced a partial miscibility of the PLLA-PGA (50/50) blend. All systems were able to encapsulate UA effectively, increasing drug apparent solubility. DSC measurements evidenced that UA was partially encapsulated in an amorphous state. That presumably contributed to the observed drug increased solubility. *In vitro* cytotoxicity tests performed on HepG2 cells showed a significant decrease in drug toxicity when encapsulated in polymers compared to free UA. The observation of cell cytoskeleton morphology evidenced that cells treated with UA-loaded nanoparticles were well arranged and formed a complex network, with several cell-cell interactions confirming the protective role of UA incorporation in nanoparticles. Overall, this research opens new avenues for the effective utilization of these highly degradable and biocompatible PLLA-PGA blends as nanocarriers for reducing UA cytotoxicity.<sup>2</sup>



**Figure 1.** Schematic representation of nanoparticles based on poly-L-lactide and poly (glycerol adipate), alone and blended.

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**DEVELOPMENT OF MAGNETIC MOLECULAR IMPRINTED POLYMER SYSTEMS FOR BIOMEDICAL APPLICATIONS**

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**Abstract**

In recent years, molecularly imprinted polymers (MIPs) have received increasing attention due to their unique characteristics such as high stability, simple preparation, robustness, specificity in molecule capture, and low cost of production. The molecular imprinting approach has allowed the development of promising systems to be used both in environmental applications for the capture of pollutants,<sup>1</sup> and in the biomedical field for drug administration, to remove undesirable substances from the body or as diagnostic sensors.<sup>2</sup> Moreover, the functionalization with small molecules can make MIPs a powerful tool for drug delivery. MIPs can also be combined with different nanomaterials such as silica (SiO<sub>2</sub>), iron oxide (Fe<sub>3</sub>O<sub>4</sub>), gold (Au) and silver (Ag) to produce multifunctional composite systems with improved properties.<sup>3</sup> In this work, innovative magnetic MIPs for ciprofloxacin (CPR) delivery were developed. CPR, a fluoroquinolone antibiotic of second-generation, possesses activity against Gram-positive and Gram-negative microorganisms and is frequently used for treating bacterial infections. We developed a nanostructured magnetic composite system consisting of an inorganic core (Fe<sub>3</sub>O<sub>4</sub> nanoparticles) and two polymeric shells, the first composed of chitosan (CS), to avoid nanoparticle aggregation phenomena, and the second one of a molecular imprinted acrylic polymer. CS was chosen for its biocompatibility, good antimicrobial activity, and absorbent capacity.<sup>4</sup>

To obtain the MIP system, an in-situ polymerization of methacrylic acid (MAA) with ethylene glycol dimethacrylate (EGDMA), as a crosslinking agent, and CPR, as a template, was used. Different concentrations of MAA, EGDMA and CPR were investigated. Finally, to evaluate the effectiveness of nanostructured magnetic MIPs, non-imprinted systems (NIPs) were also prepared. The successful coating of Fe<sub>3</sub>O<sub>4</sub> was confirmed by FTIR and elemental analysis. FESEM analysis showed the production of spherical nanoparticles with size of about 10 nm. Following the coating processes with CS, MMA and EGDMA the particle size increased up to 60 nm. The CPR absorption kinetics highlighted the greater effectiveness of MIP compared to NIP, due to the formation of specific cavities of the target molecule. Finally, antimicrobial tests showed a 100% reduction in bacterial growth in the case of MIPs, due to the higher release rate compared to NIPs.

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## LIQUID CRYSTALLINE NETWORK MICRO-TAGS FOR PHYSICAL ENCODING INFORMATION

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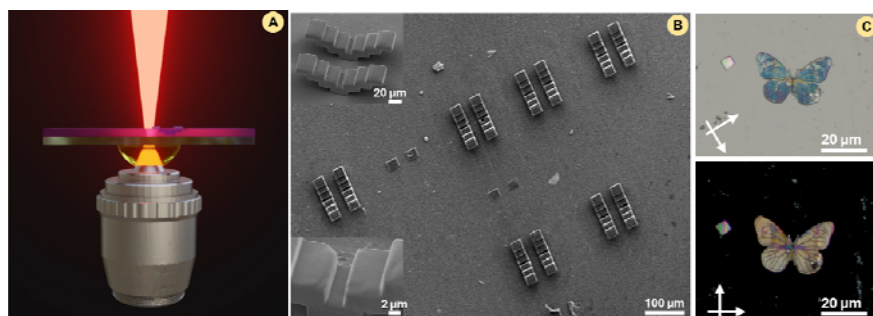
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### Abstract

The outstanding properties of Liquid Crystalline Elastomers Networks (LCNs) make them ideal candidates to address challenges in different fields of application, ranging from photonics to micro-robotics.<sup>1</sup> These materials offer a fully reversible shape change in presence of an external stimulation (temperature, light and so on) dependent from the LC alignment.<sup>2</sup> Moreover, manufacturing of acrylate-based formulations can be implemented by high-resolution lithographic techniques, such as Direct Laser Writing with Two Photon Polymerization, thanks to their easy processability and avoiding crystallisation processes (DLW-TPP) as shown in Figure 1.<sup>3</sup>

We demonstrated 3D printing micro-structures with a resolution up to 100 nm and with different structural complexity playing both on molecular and lithographic parameters. Combining this with the actuation under temperature and light, it was possible to create micro-labels with two different levels of encryption and decryption to hide simple information. This result paves the way for a future integration with other materials and can be used to create a physical encoding and decoding tag.<sup>4</sup>



**Figure 1.** LCN microstructures with DLW-TPP. **A)** Schematic view of two-photon polymerization process; **B)** Scanning electron microscopy images of LCN-micro stairs. **C)** Optical birefringence properties of microstructures, maximum of transmission at 45° minimum of transmission at 0°.

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**AMPHIPHILIC STAR-SHAPED COPOLYMERS AS VISCOSITY INDEX IMPROVERS FOR LUBRICANTS**EDOARDO PODDA<sup>1</sup>, KATIA SPARNACCI<sup>1</sup>, MICHELE LAUS<sup>1</sup><sup>1</sup>*Department of Science and Technological Innovation, Università del Piemonte Orientale, viale T. Michel 11, 15121, Alessandria, Italy.**Email: edoardo.podda@uniupo.it**Role: Research fellow - Postdoc***Abstract**

Viscosity index (VI) is an important parameter in lubricant applications which represents how a lubricant's viscosity changes as a function of temperature. In particular, the higher is the VI, the lower is the decrease of the viscosity as the temperature increases. This is very important in automotive applications because the lubricants must be efficient in a wide range of temperatures, exhibiting minimal changes in viscosity. During the preparation of lubricant formulations, polymeric additives are used as Viscosity Index Improvers (VIIs) to minimize the viscosity-temperature relationship.<sup>1</sup>

Due to the high shear stress present during the lubrication, these polymeric additives can be affected by chain breaking reactions, leading to a permanent viscosity loss (PVL). In fact, the higher is the PVL, the lower is the shear stability of the additive.<sup>2</sup>

Star-shaped polymers generally exhibit higher shear stability than linear polymers of similar molecular weight (Mw), because chain breaking reaction has less impact on their overall rheological properties.<sup>2</sup> Star polymers have a complex macromolecular architecture composed of linear polymeric chains, known as "arms," covalently linked to a central branching point named "core".<sup>3</sup> There are two main approaches to synthesizing these complex structures: core-first and arm-first. In the core-first strategy, polymeric arms grow directly from a multifunctional initiating core, and the number of arms correspond to the number of initiating sites on the core. In the arm-first strategy, well-defined pre-formed linear arms are linked together by reacting with a multifunctional crosslinking agent to form the star polymers.<sup>4</sup> In this study, star-shaped copolymers were prepared using reversible addition-fragmentation chain transfer (RAFT) polymerization following the arm-first technique. Specifically, RAFT polymerization was conducted via a one-pot, two-step synthetic procedure. In the first step, to create linear polymeric arms, a mixture of different hydrophobic and hydrophilic methacrylates were copolymerized in the presence of a non-ionic surfactant, using a base oil as solvent. In the second step, these arms were linked together by the addition of a crosslinking agent. Star formation was confirmed by GPC analysis, with yields consistently above 70% and increasing with higher crosslinker amounts. Monomer conversions were determined by NMR analysis, and were always above 85% for all monomers. Rheological measurements reveal that the complex viscosity increase both increasing the crosslinker amount employed, and increasing the hydrophilic units in the preformed arms. Tribological tests evaluated mechanical stability that is always better than commercial VII used as a benchmarks.

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**FISH COLLAGEN DERIVED BIOINK FOR EXTRUSION 3D PRINTING**

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**Abstract**

Three-dimensional (3D) bio-printing has revolutionized the creation of functional tissues and organ substitutes, surpassing conventional 3D scaffold fabrication.<sup>1</sup> This method uses computer-aided design to layer living and non-living materials precisely, making it ideal for tissue engineering, regenerative medicine, pharmacokinetics, and biological research.<sup>2</sup> Bioinks, essential for 3D bio-printing, embed cells within scaffolds and must protect them during printing while supporting their growth and differentiation.<sup>3</sup> Hydrogels, particularly natural polymers like collagen, gelatin, alginate, hyaluronic acid, chitosan, dextran, and fibrin, are commonly used for their biocompatibility and ability to support cell proliferation.<sup>4</sup> Collagen, the most abundant extracellular matrix protein, is crucial for tissue integrity and cell function.<sup>5</sup> Type-I collagen derived from land animals is the most commonly used but several drawbacks limited its use.<sup>6</sup> Fish collagen offers a safer alternative, mitigating concerns related to prion transmission, religious restrictions, and allergies associated with mammalian collagen sources.<sup>7</sup> However, its rapid degradation and poor mechanical strength are limitations to overcome. In this study, a fish collagen bioink developed by Typeone Biomaterials S.r.l. according to a proprietary process has been studied for evaluating its printability by extrusion for the development of micropatterned 3D scaffolds. In order to improve the bioink mechanical strength and stability during time, the UV crosslinking of the bioink has been investigated and optimised in terms of time and UV intensity. The thermal stability, rheological and viscoelastic properties and morphology of simple 3D printed constructs have been studied and correlated with printability properties. Finally, several scaffolds have been 3D printed and UV cross-linked.

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