44èmes journées de la Section Grand Ouest du Groupe Français des Polymères

8 et 9 juillet 2025
CERDATO

GFP ARKEMA

I. REMERCIEMENTS

Le comité d'organisation des 44èmes journées de la section grand ouest du GFP remercie l'ensemble des membres du bureau de la section grand ouest du Groupe Français des Polymères, pour leur soutien à la réalisation de ces journées :

- Loic LE PLUART (LCMT, Caen)
- Carole KARAKASYAN DIA (PBS, Rouen)
- Jean Luc AUDIC (ISCR, Rennes)
- Louise HESPEL (PBS, Rouen)
- Véronique MONTEMBAULT (IMMM, Le Mans)

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Merci également à Anne CHRISTMANN, Directrice du CERDATO, pour l'accueil réservé à la communauté de chercheurs en chimie et physique des polymères.

Nous vous souhaitons deux belles journées scientifiques remplies d'échanges et découvertes de la région et du centre de recherche !

Le comité d'organisation
Guillaume Lê
Clément Paul
Sylvie Duval
Catherine Savary
Laura Luiz

II. INFOS PRATIQUES

a. Echanger

Un serveur Discord « GFP 44 – Arkema CERDATO » a été créé pour faciliter les échanges pendant la conférence.

Plusieurs salons sont créés : #infos-pratiques, #transport, #prix-du-public, #diner-gala

Figure 1. QR Code d'accès au serveur Discord GFP44

b. Plan & Adresses

Figure 2. Plan du CERDATO

Hôtel Acropole **: 10 Rue de la Grande Malouve, 27300 Bernay**
Hôtel du Lion d'Or : **48 Rue du Général de Gaulle, 27300 Bernay**
Diner gala au Moulin Fouret : **2 Rte du Moulin Fouret, 27300 Treis-Sants-en-Ouche**

III. PROGRAMME

Mardi 8 Juillet		**Localisation**
9h00	Accueil	Salle C201
9h30	**"Innovative Materials, la stratégie R&D d'Arkema"** *Dr. Anne CHRISTMANN, Directrice du CERDATO*	
10h00	**"Liaisons réversibles dans les matériaux, une nécessité ?"'** *Pr. Fabrice BUREL, Laboratoire PBS Rouen (UMR6270)*	
	Session orale #1 : Biosourcé	
10h30	"Different approaches for the synthesis of hybrid silica-natural rubber films" *Pamela PASETTO*	
10h50	"Polysaccharide-based thermo-responsive hydrogels for bio-ink development" *Jordan MASURIER*	
11h10	"Study of an innovative mcl-PHA extraction and purification process" *Loic PLETACHER*	
11h30	Break	
11h45	"Use of Biobased Ionic Liquids for Paramylon Thermoplasticization" *Flavien MOUILLARD*	
12h05	"Synthesis of new biobased polyamides with intrinsic flame retardant properties" *Clément DESGOULIERES*	
12h25	"Formation of Bio-based Networks from Natural rubber via Successive Thiol-ene and Urethane Crosslinking" *Thawanrat CHAISIT*	
12h45	Dejeuner	ATRIUM & PARC
	Session poster #1	
14h00	**"Développement de revêtements pour le milieu marin avec un faible impact environnemental"'** *Dr. Fabrice AZEMAR, Laboratoire LBCM (EMR6076)*	Salle C201
	Session orale #2 : Revêtement, recyclage & dégradation	
14h30	Well-Defined Phosphorus-Containing Oligomers from Tire "Waste via Olefin Metathesis Depolymerization " *Alexis PERROT*	
14h50	"Design of modular ecological Poly(trimethyleneCarbonate) based coating " *Amina ADLAO ALI*	
15h10	"How do additives influence plastic degradation and the kinetics of microplastic formation?" *Amandine PASSIN*	
15h30	Gouter	ATRIUM & PARC
	Session poster #2	
16h10	"Impact of the mechanical properties of polymer films on their colonisation by microorganisms " *Cédric JAFFRY*	Salle C201
16h30	"Development of pH-sensitive smart antibacterial surfaces through grafting polysaccharide-based polyelectrolyte complexes. " *Gisele Patricia DEMGNE FOUBI*	
16h40	"Optimization of Mass Transfer Between a Viscous System and a CO2 Atmosphere: An Experimental Approach for Purification of Polymers by Supercritical CO2 Extraction " *Ambre PHISBIEN*	
17h10	Fin de la première journée	
19h00	**Diner Gala au Moulin Fouret**	

Mercredi 9 Juillet		Localisation
9h00	**"Les polymères au service des Sous-Marins de la Marine Nationale "** *Dr. Anne-Camille OZOUF, Naval Group*	Salle C201
	Session orale #3 : Membranes et Energie	
9h30	"Innovative approach to producing thick materials by frontal photopolymerization" *Ludivina CHALLY*	
9h50	"Polymer Electrolytes: Unlocking the Next Generation of Lithium Metal Batteries" *Rida FALLAHI*	
10h10	"From Hydrophobic to Hydrophilic: A New Copolymer for Polyvinyl chloride Membranes" *Mohammad Ebrahimi*	
10h30	Café	ATRIUM & PARC
	Session poster #3	
11h00	"Elaboration and Characterization of 3D-Printed PLA Membranes: Focus on Thermal and Barrier Properties and comparison with conventional Film-Extruded Membranes" *Lisa TAZROUT*	Salle C201
11h20	"Conception, Synthesis And Characterization of Hybrid Membranes For Proton Exchange Membrane Fuel Cells" *Anna PHAN*	
11h40	"Conception and Synthesis of New Organics porous functionals Materials for Energy Storage" *Djankiné COULIBALY*	
12h00	Dejeuner	ATRIUM & PARC
13h30	**Visite du CERDATO**	
16h00	Remise des prix	Salle C201
17h00	Fin de la conférence	

IV. ABSTRACT

Different approaches for the synthesis of hybrid silica-natural rubber films

Anutida Suwan,[1,2] Laksana Saengdee,[1] Christelle Pichon,[1] Nitinart Saetung,[2],Nathapong Sukhawipat,[3] Anuwat Saetung,[4] Pamela Pasetto[1]

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Keywords: natural rubber, functional oligomers, silica filler, hybrid polymeric films

Abstract: Thick or thin elastic films are used in many different applications, alone or in multilayer materials. Fillers are often added to reinforce the mechanical properties of polymers, however to have a real improvement, the particles should be homogeneously dispersed in the elastomeric matrix, and this is not the case when the charges are hydrophilic inorganic powders and the matrix is hydrophobic. The results of recent research projects that tackled the dispersion of silica particles in thick films obtained from natural rubber oligomers will be presented, highlighting the various strategies used to synthesize the films themselves, such as radical photopolymerisation and waterborn polyurethane[1], and to functionalize the silica surface.

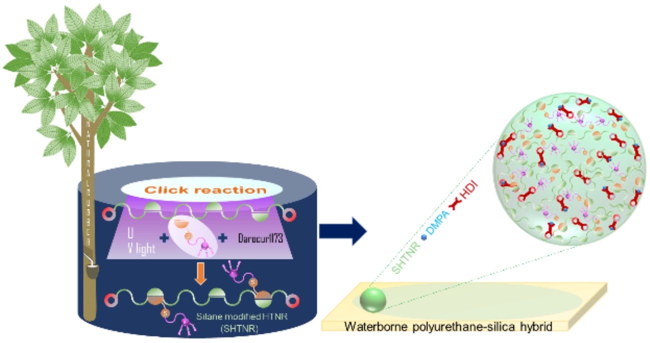

Figure 1 One of the strategies to prepare hybrid-silica-rubber films (Graphical abstract from ref. *Progress in Organic Coatings,* 184, **2023**,107835).

1) Suwan A., Sukhawipat N., Saetung A., Saetung N. , Pasetto P., *Progr in Org Coat*, **2025,** *201*, 109109. Saengdee L., Pasetto, P. Sukhawipat N., *Progr in Org Coat*, **2024**, *186*, 107988, 1-12.

Polysaccharide-based thermo-responsive hydrogels for bio-ink development

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Keywords: Hyaluronic acid; Hydrogels; Polyoxazolines; 3D printing; Bio-ink; Bio-printing

Abstract:

Hydrogels are soft materials made of crosslinked hydrophilic polymer chains, which can absorb a large amount of water. Their properties, akin to biological tissues, and their bio-compatibility[1] allow them to be used in a wide range of applications, including medical applications (wound healing, contact lenses and three-dimensional cell culture substrates)[2]. With the emergence and development of 3D printing, hydrogels are now being used as bioinks[3] for tissue engineering. The development of suitable bioinks requires materials with rheological properties that allow them to be extruded and to maintain a stable shape after printing. To this end, the use of a thermo-responsive hydrogel, whose gelation is induced by a change in temperature is a possible solution for the elaboration of bioinks.

Thermosensitive polysaccharide-based hydrogels have been developed by the PBS laboratory[4]. These hydrogels are made of hyaluronic acid chains grafted with LCST (Lower Critical Solution Temperature) polyoxazoline (POx) copolymers, which become associative when the temperature is raised above a given threshold. The aqueous sol/gel transition of hyaluronic acid functionalized in this way (HA-g-POx) can then be tuned by adjusting the monomer composition and the degree of polymerization of the POx grafts, but also according to their rate of grafting onto the HA chains (Figure1).

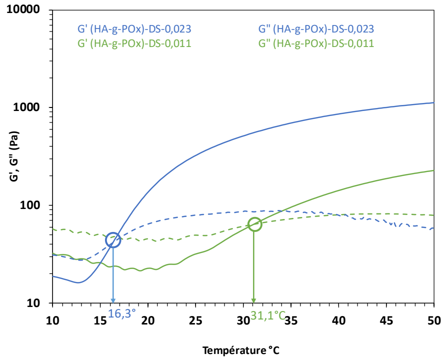

Figure 1. Temperature ramp of two HA-g-POx (30g.L-1 solutions in PBS buffer; DP_{POx}: 50; DS: 2,3% (blue) and 1,1% (green); Mn (HA): 990 000 g.mol^{-1}.

References :

1. Mitura, S and al. J Mater Sci. **2020**, 31-50
2. Sannino, A and al. Materials. **2009**, 2, 353-373
3. Kesti, M and al. **2015**, 11, 162-172
4. Madau, M and al. Polymer, **2022**, 244, 12

Study of an innovative mcl-PHA extraction and purification process

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Keywords: Polyhydroxyalkanoate, bioplastic, extraction, purification, bioprocess

Abstract: Public awareness on plastic pollution has raised in recent years with the discovery of microplastic particles not only in water, soil and food, but also inside the human body, with microplastics found in our airways, brain, intestines and liver [1]. This, along with the impact of fossil resources on the environment, has led to the search for alternatives like polyhydroxyalkanoates. As biosourced and biodegradable polymers, these bioplastics can be used both in packaging and in medical fields, as their structure makes them biocompatible [2]. In this study, the downstream step of medium-chain-length PHA (mcl-PHA) production based on solvents was studied. While PHA extraction is often performed from dried cell biomass produced through lyophilization, an energy-intensive process, an initial study of the interaction between water in biomass and solvent led to a new method for cell pretreatment. While extraction under conventional conditions from humid biomass led to a PHA yield of only 17 %, pretreatment to obtain an acetone volume fraction in the liquid phase around 0.5 was sufficient to achieve a yield around 100 %. The liquid phase was concentrated in impurities, which led to a purer PHA sample during the second extraction. This second solvent-based extraction relies on the solubility of the polymer in the studied solvents, and the resulting solvent/PHA ratio led to a residual biomass concentration of around 50 g L^{-1}. For solid separation, the solvent – PHA – Biomass blend was passed through a sieve with a pore size of 50 µm, and the resulting solution (with a solid concentration around 3 g L^{-1}) was filtered through a 1.4 µm ceramic membrane. An initial study of the filtration of this PHA solution proved that a 1.4 µm membrane was a better choice than a 0.14 µm one, as the permeate flux was greater (56.4 against 16,2 L m^{-2} s^{-1}), with total rejection of solid particles. However, soluble impurities (mainly lipids) are still present and need to be eliminated. As such, the solubilization – precipitation method is used, and while ethanol and methanol are often used for this purpose, water was found to be a good antisolvent with PHA. Thus, a low water volume fraction (0.1) was enough to ensure polymer precipitation. The result is a stable PHA suspension, and the bioplastic aggregation is achieved through agitation. A minimal shear rate of 250 s^{-1} was needed to start the process of mcl-PHA aggregation.

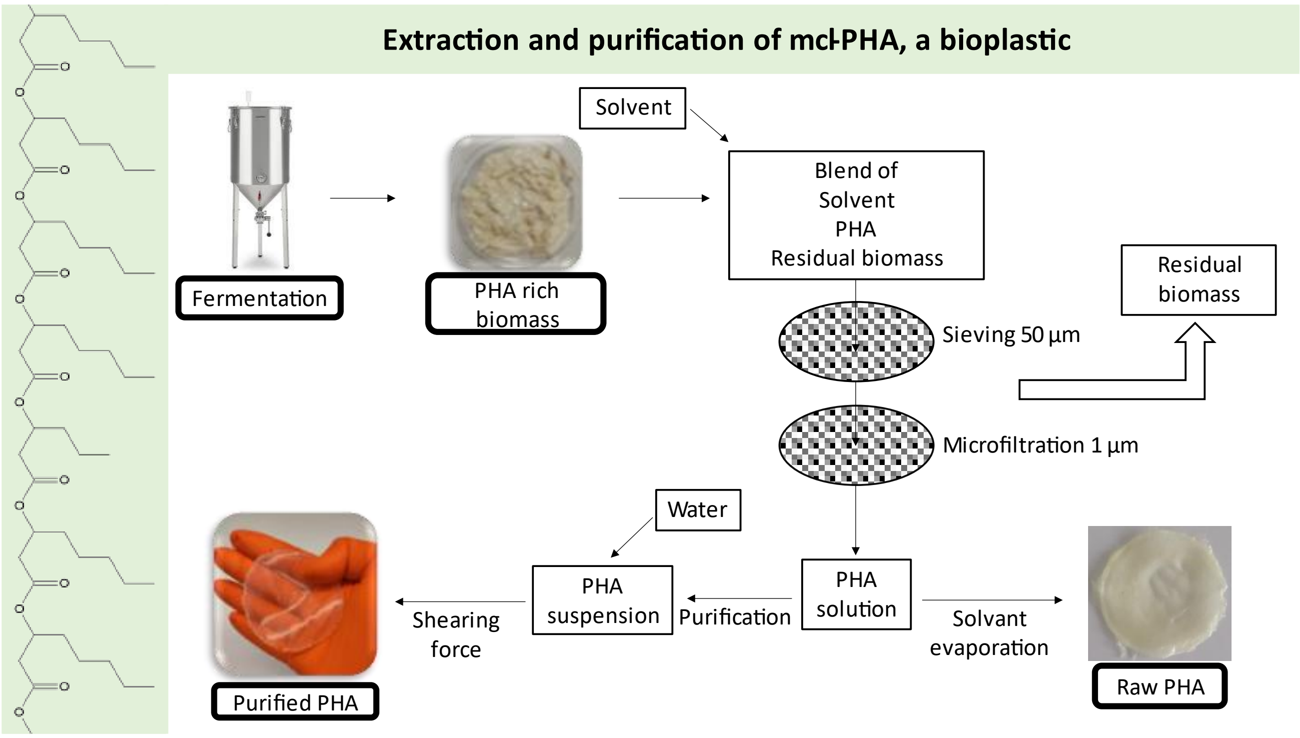

Figure 1 Extraction and purification of mcl-PHA, a bioplastic.

References:

1. Lee, Y. *et al.* (2023) 'Health Effects of Microplastic Exposures: Current Issues and Perspectives in South Korea', *Yonsei Medical Journal*, 64(5), pp. 301–308.
2. Koller, M. (2018) 'Biodegradable and Biocompatible Polyhydroxy-alkanoates (PHA): Auspicious Microbial Macromolecules for Pharmaceutical and Therapeutic Applications', *Molecules : A Journal of Synthetic Chemistry and Natural Product Chemistry*, 23(2), p. 362.

Use of Biobased Ionic Liquids for Paramylon Thermoplasticization

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Keywords: Paramylon, immunostimulant, ionic liquids, thermoplasticization.

Abstract: Paramylon is a rare glucan produced by *Euglena gracilis* microalgae as intracellular energy storage granules. Its linear macromolecular structure involves β(1-3) glycosidic linkages that induce a triple helix conformation. This structure gives unique bioactive immunomodulating properties with potential anti-inflammatory effects. However, it also results in a native hexagonal crystallinity stabilized by hydrogen bonds, water insoluble and that does not melt below the biopolymer's degradation temperature [1].

At ILMAT 6, we showed how biobased ionic liquids (ILs) could be designed as efficient solvents of paramylon [2]. Since then, we have been exploring the melt processing of paramylon using [Cholinium][Glycinate]/water mixtures as plasticizers [3]. We will show that this approach (Figure 1.a) can be extended to other ILs, in particular containing pharmaceutically active ions, in order to make paramylon-based bioactive thermoplastic materials, that can be shaped as films by hot compression moulding or as rods by extrusion. ILs-plasticized paramylon material's structure and their properties were investigated and will be discussed. Bioactivity was evaluated by using bone marrow derived dendritic cells (Figure 1.b) to assess immunostimulant properties.

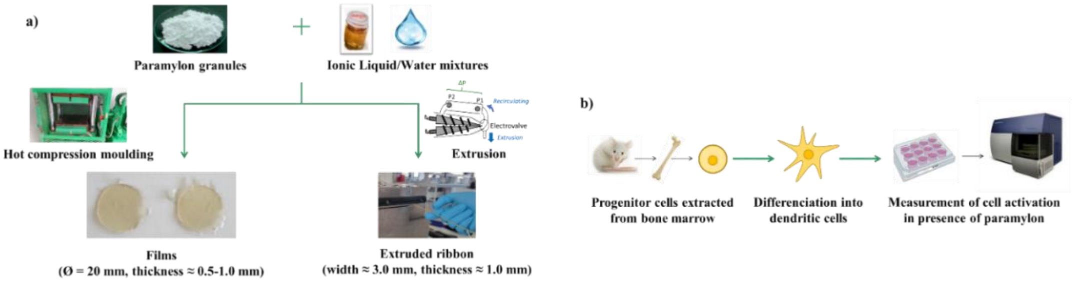

Figure 1.a) Design of paramylon-based thermoplastic materials by using thermomechanical processes; **b)** Evaluation of their biological activities by using bone marrow derived dendritic cells

References:
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2. Feuzing, F.; Mbakidi,J.-P.; Lazar,F.; Marchal, L.; Leroy, E.; Bouquillon, S. *J. Mol. Liq.* **2023**, *370*, 120983.
3. Feuzing, F.; Mbakidi, J.-P.; Pontoire, B.; Quéveau, D.; Roelens, G.; Lourdin, D.; Bouquillon, S.; Leroy, E. *Carbohydr. Polym.* **2023**, *306*, 120607.

Synthesis of new biobased polyamides with intrinsic flame retardant properties

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Keywords: polyamides, biobased, flame retardant, phosphorus

Abstract: Polyamide 11 (PA-11) is a biobased high performance polyamide synthesized from castor oil by Arkema, under the trade name Rilsan®. PA-11 is recognized for its high mechanical performances and good resistance to solvents. However, like most of organic polymers, it has a poor fire resistance.[1] In this context, our objective was to improve the fire resistance of PA-11 while maintaining its properties. In our strategy, some phosphorus-based flame retardant (FR) co-monomers were designed to be copolymerized with 11-aminoundecanoic acid, following a reactive fireproofing. The FR monomers were obtained by Pudovik reactions,[2] without catalyst, and in a good yield. The latter were characterized thanks to NMR analyses. These FR monomers showed good thermal stability up to 220°C without degradation, which allows them to be used in a polycondensation process. These comonomers were then copolymerised with 11-Aminoundecanoic acid to yield copolyamides with different phosphorus content and different features, that will be discussed in this presentation.

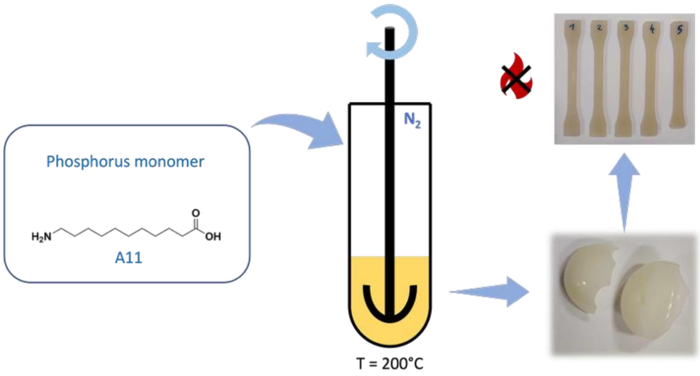

Figure 1: **Synthesis of biobased polyamides with intrinsic flame retardant properties**

References:

1. Negrell, C.; Fréméhard, O.; Sonnier, R.; Dumazert, L.; Briffaud, T.; Flat, J.-J. Self-Extinguishing Bio-Based Polyamides. *Polym. Degrad. Stab.* **2016**, *134*, 10–18. https://doi.org/10.1016/j.polymdegradstab.2016.09.022.
2. Hajibeygi, M.; Habibnejad, N.; Shabanian, M.; Khonakdar, H. A. Fabrication and Study of Thermal and Combustion Resistance of DOPO -functionalized Polyamide Reinforced with Organo-modified $Mg(OH)_2$ Nanoparticles. *Polym. Int.* **2021**, *70* (3), 317–330. https://doi.org/10.1002/pi.6137.

Formation of Bio-based Networks from Natural rubber *via* Successive Thiol-ene and Urethane Crosslinking

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Keywords: Thiol-ene click chemistry, hydroxyl telechelic natural rubber, 2-mercaptoethanol, UV photoinitiation, crosslinking, urethane

Abstract:

We reported a novel method of producing bio-based natural rubber (NR) networks *via* a two-step process involving thiol-ene functionalization and subsequent urethane crosslinking (Figure 1).

NR, a biopolymer rich in reactive carbon-carbon double bonds (C=C) in its backbone was first functionalized with 2-mercaptoethanol (2-ME) *through* UV-mediated thiol-ene click reaction at room temperature. The reaction was performed by varying initial molar ratios of thiol groups (SH) to double bonds (C=C). Characterizations by ^{1}H NMR, FTIR, SEC, and DSC show that the conversion of isoprene units increased from 3% to approximately 53% with increasing SH:C=C initial molar ratios, confirming efficient thiol-ene modification. The resulting NR polyols containing various hydroxyl functions at the chain-ends and along the backbone were successfully synthesized and characterized.

NR polyols were subsequently crosslinked with 4,4'-methylenebis(phenyl isocyanate) (MDI), an aromatic diisocyanate known for forming robust urethane linkages. Crosslinking was carried out at various initial molar ratios of isocyanate to hydroxyl groups (NCO:OH) to tune the network structure. FTIR, gel content, swelling experiments, and DSC were used to characterize the resulting NR networks. Increased NCO:OH initial molar ratios led to higher crosslink density, as evidenced by greater gel content, lower swelling degrees, and increased glass transition temperature (T_g) [1].

These results demonstrate that the physical and thermal properties of NR networks can be tuned by adjusting both the degree of thiol-ene functionalization and the extent of urethane crosslinking, paving the way for tailored, sustainable elastomeric materials.

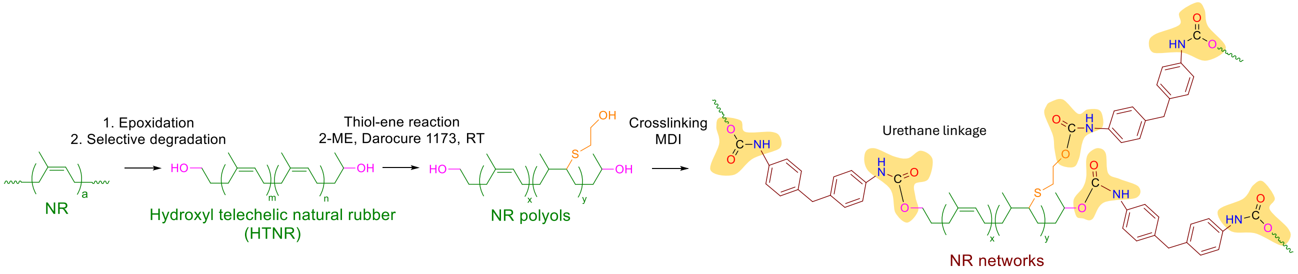

Figure 1. Synthesis schematic of bio-based natural rubber networks.

Reference:
1. Shin, J.; Matsushima, H.; Chan, J. W.; Hoyle, C. E. *Macromolecules*. **2009**, *42* (9), 3294-3301.

Well-Defined Phosphorus-Containing Oligomers from Tire Waste via Olefin Metathesis Depolymerization

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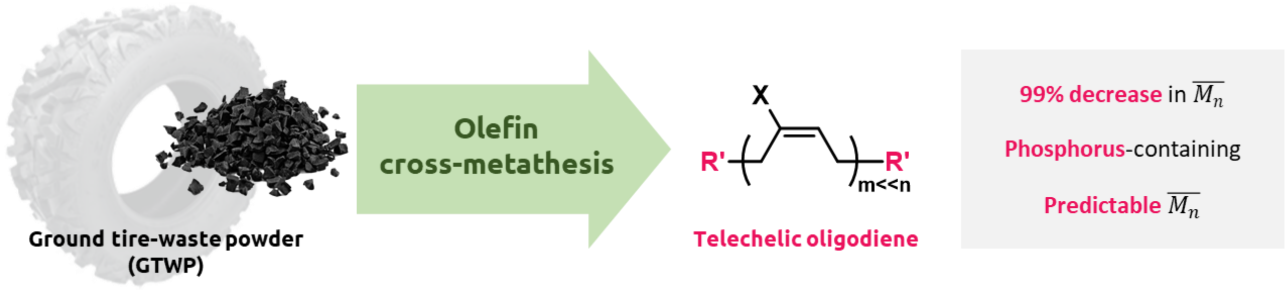
Keywords: chemical recycling; olefin metathesis; phosphorus; polyisoprene.

Abstract: Each year, hundreds of millions of tons of plastic waste are generated globally, including approximately one billion end-of-life tires.[1,2] To mitigate the environmental impact of this waste, the chemical valorization of polydienes found in tires offers a promising route to obtain reusable raw materials. In particular, olefin cross-metathesis using ruthenium-based catalysts represents a powerful method to simultaneously depolymerize and end-functionalize the polymers, yielding functional oligomers amenable to further processing.[3,4] Here, we report our efforts to synthesise phosphorus-containing oligomers from rubber waste through olefin cross-metathesis. Specifically, we demonstrate the efficient depolymerization of linear polyisoprene ($\overline{M_n}$ = 440 kg mol^{-1}) into phosphonate-terminated oligoisoprene ($\overline{M_n}$ = 5.4 kg mol^{-1}). Remarkably, the reaction also proceeds on vulcanized rubber networks, affording oligomers with $\overline{M_n}$ = 10 kg mol^{-1} despite the presence of additives and crosslinks. We developed a simple mathematical model correlating the molecular weight of the products with the extent of reaction, enabling fine control over the degree of polymerization. This framework paves the way towards the design of well-defined materials from phosphorus-containing oligomers derived from tire waste.

Figure 1. Overview of the depolymerization of tire waste by olefin cross-metathesis to obtain end-functional oligomers.



References:

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2. OECD. *Global Plastics Outlook: Economic Drivers, Environmental Impacts and Policy Options*. **2022**.
3. Sathe, D., Yoon, S., Wang, Z., Chen, H. & Wang, J. *Chem. Rev.* **2024**, *124*, 7007–7044.

4. Leimgruber, S. & Trimmel, G. *Monatsh. Chem.* **2015**, *146*, 1081–1097.

Design of modular ecological Poly(trimethyleneCarbonate) based coating

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Keywords: Polycarbonate, coating, synthesis, green chemistry

Abstract : There is growing interest in aliphatic polycarbonates, due to their biocompatibility, and biodegradable properties. Moreover, the monomers used to produce aliphatic polycarbonates can be biobased, and various functional groups can be incorporated to control the properties of the resulting polymers. For example, they can be incorporated to control the polymer structure or to regulate biodegradation. Currently, aliphatic polycarbonates are primarily being studied for biomedical applications[1].

The aim of this study is to develop poly(trimethylene carbonate) (PTMC) coatings and investigate their properties. PTMC exhibits limited mechanical properties and therefore requires a cross-linking step to form coatings. To achieve this, we propose the development of copolymers with trimethylene carbonate (TMC) and 5-methyl-5-allyloxycarbonyl-1,3-dioxan-2-one (MAC), using ring-opening polymerization (ROP) with organic catalysts[2]. MAC contains an allyl functional group that enables cross-linking of the copolymer chains via a thiol-ene reaction. However, to obtain a homogeneous coating, it is essential that the allyl group is randomly incorporated into the copolymer chain. Achieving the formation of random copolymers through controlled copolymerization, without the use of metal catalysts, is the main technical challenge of this study. In order to synthesize these random copolymers, we will perform kinetic monitoring of both monomers to identify the optimal polymerization conditions. The synthesized copolymers will enable the creation of networks with different cross-link densities, by adjusting molecular weights, monomer ratios, and cross-linking agents.

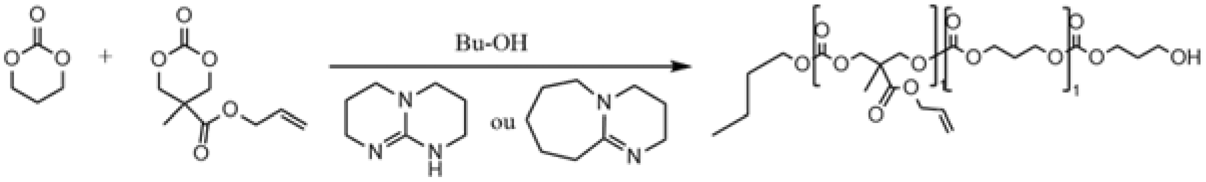

Figure 1 : Ring-opening polymerisation of MAC and TMC catalysed by organic catalyst

References:

(1) Fukushima, K. Poly(Trimethylene Carbonate)-Based Polymers Engineered for Biodegradable Functional Biomaterials. *Biomater. Sci.* **2016**, *4* (1), 9–24. https://doi.org/10.1039/C5BM00123D.

(2) Azemar, F.; Gimello, O.; Pinaud, J.; Robin, J.-J.; Monge, S. Insight into the Alcohol-Free Ring-Opening Polymerization of TMC Catalyzed by TBD. *Polymers* **2021**, *13* (10), 1589. https://doi.org/10.3390/polym13101589.

How do additives influence plastic degradation and the kinetics of microplastic formation?

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Keywords: plastic formulation, degradation, additives, microplastics

Abstract: In the environment, plastics are mainly exposed to various abiotic factors, such as UV radiation and mechanical abrasion. These factors accelerate the degradation of plastics and encourage the release of microplastics and nanoplastics. To slow down these degradation mechanisms and optimize processing and final properties, a range of additives are incorporated into plastic formulations. However, their presence raises questions about their fate and influence on the various degradation mechanisms. To better understand these processes and evaluate the role of additives, this study examines the accelerated UV ageing of polypropylene pellets containing controlled amounts of common industrial additives combined with the application of mild mechanical stress. Changes in surface oxidation levels, crystallinity rates and pellet weight were measured over the exposure period and compared to those of pellets without additives. Volatile compound emissions were determinated by weight loss measurements. Particulate and soluble degradation products were characterized using morphometric analysis and total organic carbon (TOC) quantification in the aqueous phase. These approaches provided insights into the degradation pathways and the nature of the by-products formed. The results revealed a correlation between the emission of volatile species and the formation of microplastics. It was also shown that the presence of additives has an impact on some polyolefin degradation mechanisms, influencing both the quantity and morphology of microplastics generated. Finally, these preliminary results suggest that additives are released into the aqueous phase in the early stages of aging when a mild stress is applied.

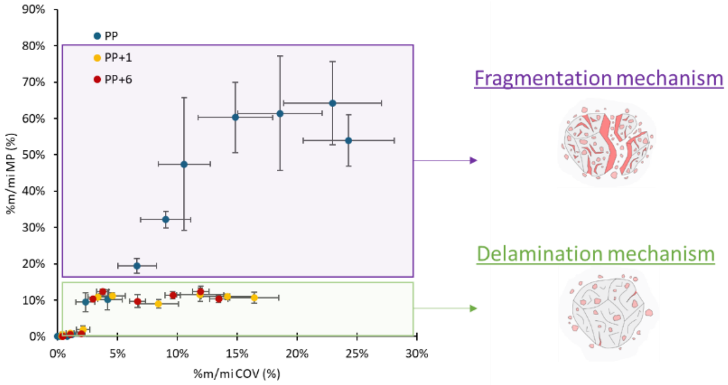

Figure 1: Generation of microplastics and volatile organic carbon for different plastics formulations under UV exposure and mild stress application

Impact of the mechanical properties of polymer films on their colonisation by microorganisms

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Colonisation of surfaces by living microorganisms is a major problem in many areas of activity, such as the medical and marine sectors. In the marine sector, there are solutions such as the use of anti-fouling paints to combat the fouling of immerged surfaces. In recent years, the research and development of these solutions has focused on so-called "fouling release coatings" (or FRC), whose principle is based on limiting the adhesion of microorganisms thanks to the physico-chemical properties of the surface.

In the early 1970s, Robert Edward Baier established a relationship between bioadhesion and the interfacial energy of materials. He showed that a minimum of bioadhesion is obtained at critical surface tensions between 20 and 30 mN/m1, typical of silicones. Many publications have shown that other parameters could also improve these anti-adhesive performances, such as mechanical properties2 or surface topography3. While many studies have investigated these parameters, few have succeeded in specifically isolating the role of each of them in relation to adhesion.

Based on these studies, a bilayer system was developed using PolyStyrene (PS) on PolyIsoButylene (PIB), allowing modulation of surface stiffness from MPa to GPa while maintaining constant surface chemistry and roughness. Adhesion and retention of Pseudomonas aeruginosa PAO1 were assessed under static and shear conditions. Adhesion was primarily governed by surface chemistry, with no significant influence from stiffness. Under shear flow, however, bacterial retention increased markedly on softer substrates, suggesting that compliance promotes stronger bacterial-surface interactions. Notably, the retraction work (i.e., the energy dissipation measured upon withdrawal of the indenter), showed a remarkable correlation with bacterial retention, highlighting the importance of interfacial energy loss in resisting detachment.

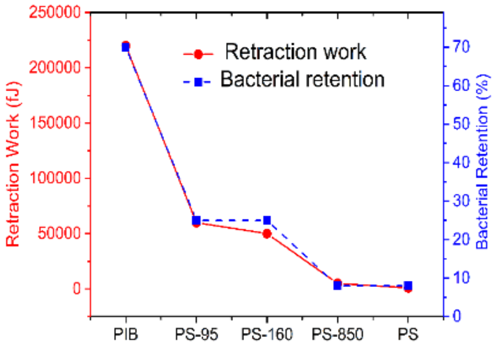

Fig. 1 : Comparison between the retraction work (mechanical energy measured during tip withdrawal) and bacterial retention percentages under shear flow for the same series of samples (PIB, PS monolayer, and PS–PIB bilayers).

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[2] Brady, « A Fracture Mechanical Analysis of Fouling Release from Nontoxic Antifouling Coatings ».
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Development of pH-sensitive smart antibacterial surfaces through grafting polysaccharide-based polyelectrolyte complexes.

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Keywords : Polyelectrolyte Complexes ; polysaccharides ; antibacterial surfaces ; PH-sensitive ; Staphylococcus aureus.

Global demand for medical devices is growing every year, from $425 billion in 2018 to $615 billion in 2025. The colonization of the surfaces of these medical devices by bacteria constitutes a real health and socio-economic deficit. The rate of infection in cases such as urinary catheters is 70-80%; this increases hospitalization time, increasing morbidity and mortality. One of the ways to control its infections is by preventing bacteria from sticking to surfaces [1]. Numerous studies focus on developing surfaces with physical and chemical properties that prevent bacteria from adhering to the substrate and/or releasing biocidal molecules capable of killing bacteria [2-3].

The goal of the project “PH-sensitive Intelligent Antibacterial Surfaces” (SAIS) is to develop a surface coated with Polyelectrolyte Complexes (PECs) that perform dual function: prevent bacterial adhesion and exhibit antibacterial activity by controlling the release of biocides (terpene compounds) trigged by pH changes in cases of bacterial contamination. PECs are formed through self-assembly of cationic and anionic polysaccharides via electrostatic interactions.

Anionic polysaccharides are modified by using laboratory methods to impart amphiphilic characteristics, allowing for increased sequestration of hydrophobic antibacterial molecules. PECs are characterized by different techniques (DLS, TEM). Then, polydimethylsiloxane (PDMS) surfaces, widely used for medical devices, are coated with PECs and characterized by IR, AFM, XPS for example. Finally, the antibacterial activity of these surface is tested against Staphylococcus aureus, the species most frequently encountered in nosocomial infections.

Table 1: Characterization of PECs

Samples	PECs DEAE-Dx_HA	PECs DEAE-Dx_HA-GA	PECs DEAE-Dx_HA-C8
Dh (nm)	180	317	400
PDI	0.1	0.3	0.6
Zeta potential (mV)	-37	-41	-31
TPC (particules/mL)	10^{10}	10^{10}	10^{10}

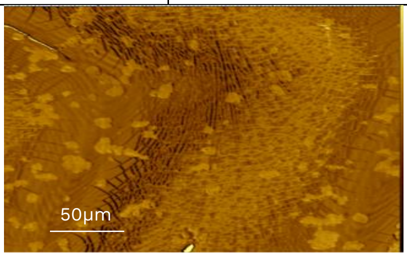

Figure : Atomic Force Microscopy (AFM), this adhesion image shows a PDMS surface coated with PECs

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Optimization of Mass Transfer Between a Viscous System and a CO_2 Atmosphere: An Experimental Approach for Purification of Polymers by Supercritical CO_2 Extraction

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Keywords: Extraction; Supercritical; Mass Transfer; Renewal; Exchange Surface

Recycling polymers after use is essential for sustainable production. It requires a purification step to remove additives from previous formulations, degradation products and various external pollutants. These compounds have various physicochemical properties (polarity, molar mass, boiling temperature, ...) making conventional solvent extraction or reduced pressure processes unsuitable. This work aims to set up an efficient continuous process for purifying polymer matrices by coupling twin-screw extrusion and supercritical CO_2 ($scCO_2$) extraction. This process enables high-temperature improving mass transfer phenomena and, above all, optimizes the renewal of the $scCO_2$/material exchange surface. However, a major challenge remains the residence time in the extruder, and therefore the extraction time, which is limited to a few minutes. Theoretically, this limitation can be overcome by reducing the thickness of the molten material in contact with the extracting fluid. Considering a semi-infinite geometry, a thinner film enhances the surface-to-volume ratio of the material and therefore minimizes the diffusion time of both CO_2 and solutes within the material. To study solute extraction, a mobile agitator (batch process) was designed to generate flows quite similar to those observed in twin-screw extrusion. Based on the principle of a scraper used in devolatilization process, this device shows the parallel between twin-screw extrusion and batch processes by forming a film continuously renewed by a bead of material, where extraction is almost instantaneous. Its geometry promotes perfectly exchanges between the material and CO_2 and has been used to investigate extraction kinetics visually tracked using a CO_2-sensitive pigment in a model viscous matrix. Finally, the same methodology was applied to twin-screw extrusion using a transparent barrel section to visualize the extraction process. Batch and continuous processes can be combined to determine the optimal extraction parameters. It turns out that maximizing CO_2/material exchange surface is more critical parameter than renewing it.

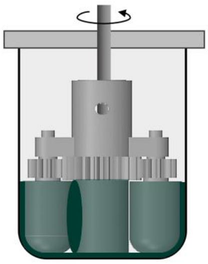

Figure 1 Schematic geometry of the new stirring mobile inspired from twin-screw extrusion

Innovative approach to producing thick materials by frontal photopolymerization

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Keywords: Frontal-photopolymerization; Self-sustained front; Energy efficiency; UV-curing

Frontal photopolymerization relies on the photolysis of an initiator by a UV source, generating radicals at the surface that initiate polymerization. The resulting exothermic reaction produces a self-sustained front that propagates in depth through thermal diffusion. This stable and localized polymerization front enables rapid and directional curing of the resin with low energy consumption.
Compared to conventional photopolymerization, which is limited by light penetration and requires irradiation of the entire volume, frontal photopolymerization allows the curing of thick materials from a single exposure point. It is particularly advantageous for energy-efficient processes and applications requiring precise spatial activation.

In response to the need for energy efficiency and regulatory constraints (REACH) aimed at protecting user health, this PhD project aims to develop a low-temperature process for producing materials via a photochemical route at ambient temperature.

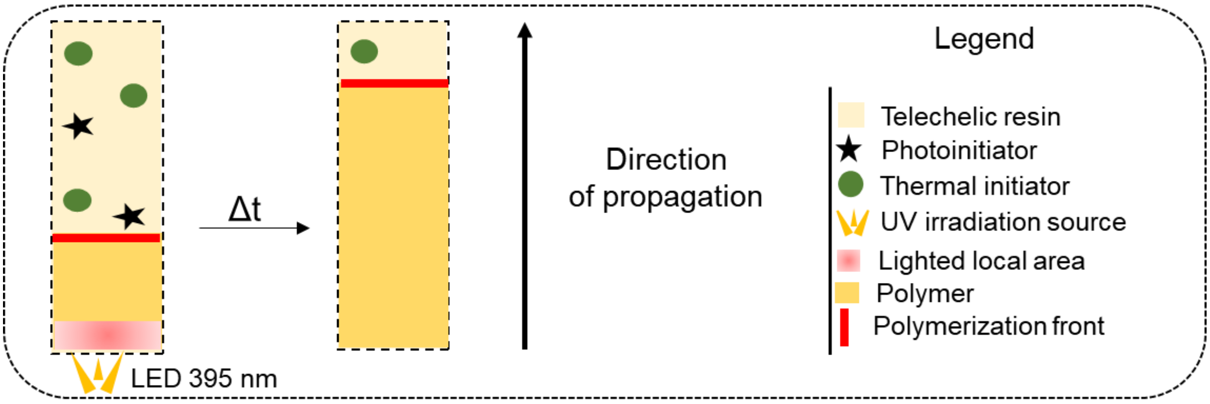

Figure. Frontal photopolymerization process.

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Polymer Electrolytes: Unlocking the Next Generation of Lithium Metal Batteries

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Keywords: Polyurethane, polymer electrolyte, lithium batteries, All-solid-state, ionic conductivity, polyurethane membrane

Solid or quasi-solid electrolytes are a way to use high-capacity anodes and high voltage cathodes in lithium metal batteries (LMB). The aim is to increase the energy density of LMB without the occurrence of lithium dendrites or uncontrolled reaction with liquid electrolytes [1]. Solid polymer electrolytes (SPE) are an option which has the advantages of low flammability, no leak, good flexibility, excellent thermal stability and high safety. Among others, polyurethane (PU) has attracted attention as a promising polymer electrolyte candidate for the future. The soft and hard segments of the polymer chain donated by polyols and isocyanates, respectively, give PU its characteristic multiphase structure [2,3]. The soft segment of PU can function as a polymer solvent to solvate cations, while the hard segment can be functionalized to retain a wider range of electrochemical stability, allowing the use of polymer electrolytes in electrochemical devices. In addition, PUs have a large thermal stability, easy membrane forming ability, mechanical strength and finally they are environment friendly. Nevertheless, in spite of all these advantages, little investigation has been so far.

In this work, a series of PU SPEs with various contents of hard segments and soft segments were synthesized and characterized. The best polymer sample, obtained as a flexible and transparent membrane, has been synthesized using 1,3-bis(isocyanatomethyl)-cyclohexane (1,3-IMC) and polyethylene glycol trimethylolpropane ether (TPEG, M_n=1,014 Da) in molar ratio 1.5:1. The corresponding SPE was obtained by adding 16 wt% LiTFSI which corresponds to a molar ratio [EO]: [Li] of 25:1. This SPE presents a good chemical and thermal behavior (decomposition temperature around 300°C) with a glass-transition temperature of -33°C). The ionic conductivity is 3.31×10^{-4} S cm^{-1} at 85°C and the electrochemical window reaches almost 4.8V (vs. Li$^+$/Li) which is enough for almost all common cathodes (LFP, NMC, NCA …). Notably, a $LiFePO_4$/SPE/Li cell employing a PU-based solid electrolyte delivers a discharge capacity of 119 mAh g^{-1} after 250 cycles at a current rate of 0.2C.

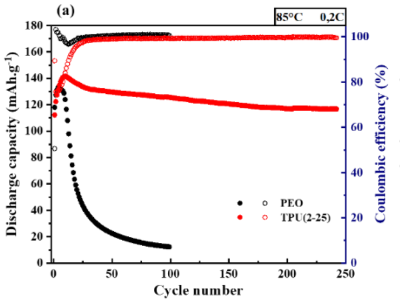

Figure (a) Galvanostatic cycling at 85°C and C/5

Table : Electrochemical and Thermal Properties of PU-Based Solid Electrolyte in $LiFePO_4$/SPE/Li Cells

Ionic conductivity (S cm^{-1})	Tg (°C)	Eox (V vs. Li$^+$/Li)	Capacity after 250 cycles (mAh.g^{-1})
3.3 10^{-4}	-27	4.8	119

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From Hydrophobic to Hydrophilic: A New Copolymer for Polyvinyl chloride Membranes

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Keywords: Polyvinyl chloride membranes; copolymer synthesis; hydrolysis reaction; hydrophilic modification

Abstract: Polyvinyl chloride (PVC) is a widely utilized polymer in membrane fabrication due to its excellent mechanical and chemical resistance, ease of processing, as well as cost-effectiveness [1]. However, the main drawback of PVC is its hydrophobic nature, which leads to concentration polarization and fouling phenomena, ultimately diminishing the transport properties of PVC-based membranes across various applications [1,2]. In this study, PVC-*co*-polyvinyl alcohol (PVOH) copolymer was incorporated into the membrane composition at varying concentrations–0 wt.% (M_0), 25 wt.% (M_1), 50 wt.% (M_2), 75 wt.% (M_3), and 100 wt.% (M_4)–to enhance the hydrophilic properties of the PVC membrane. The PVC-*co*-PVOH copolymer was synthesized through a hydrolysis reaction. Moreover, the chemical structure of the synthesized copolymer was validated using nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), and gel permeation chromatography (GPC) analyses. The membranes were prepared by solvent evaporation technique. The water contact angle and water uptake measurements (Fig. 1a,b) demonstrated an enhancement in the hydrophilic properties of the composite membranes compared to the pure PVC membrane.

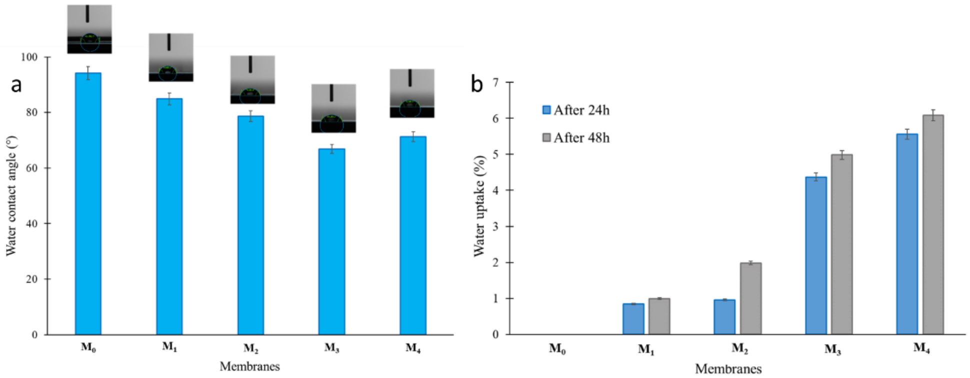

Figure Water contact angle (a) and water uptake (b) of PVC and PVC/PVC-*co*-PVOH membranes.

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Elaboration and Characterization of 3D-Printed PLA Membranes: Focus on Thermal and Barrier Properties and comparison with conventional Film-Extruded Membranes

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Keywords: Polylactide Acid; Membrane Process; 3D Printed Membranes

Polymer membranes are typically produced by film extrusion, a process that provides precise control over their properties. Additive manufacturing, particularly Fused Deposition Modeling (FDM), is emerging as a promising alternative due to its flexibility, low cost, and ease of use[4]. This process also allows for the design of complex membrane geometries.

Polylactic acid (PLA), a widely-used biobased polymer in 3D printing, offers good mechanical properties and low energy requirements[5]. Its relatively low melting temperature makes it thus advantageous for 3D printing. Furthermore, in the context of plastic pollution and environmental concerns, PLA is a promising polymer that can substitute usual non-degradable thermoplastic polymers.

The present study explores the feasibility of using FDM to produce PLA membranes. The resulting membranes was compared with conventionally extruded ones in terms of thickness, thermal properties, and barrier properties.

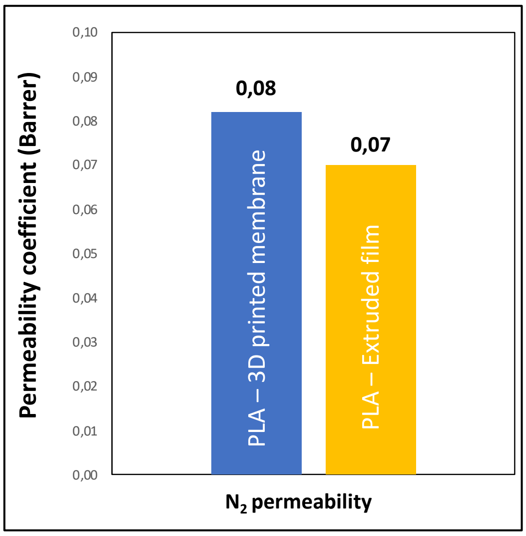

Figure: Effect of membrane process on N2 permeation performance.

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Conception, Synthesis And Characterization of Hybrid Membranes For Proton Exchange Membrane Fuel Cells

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Keywords: *PEMFC, membrane, hybrid, sol-gel, electrospinning*

To support the EU's carbon neutrality goals by 2050, this work focuses on developing organic-inorganic hybrid membranes for Proton Exchange Membrane Fuel Cells (PEMFCs) with high performances at high temperatures and low humidity. Commercial membranes often fail under these conditions due to poor mechanical stability and reduced poton conductivity.1

This PhD project explores hybrid membranes synthesized via sol-gel chemistry and electrospinning. PVDF-HFP was employed as the organic matrix for its relative low-cost, high performance and ease of processing. To enable proton conductivity through sulfonic acid groups, silica precursors were introduced to form the inorganic network. Electrospinning was used to create an interpenetrated organic-inorganic network, which is particularly interesting as it prevents phase separation between components.

By optimizing both the formulation and electrospinning parameters, well-defined fibers were obtained, leading to enhanced conductivity and mechanical properties. Densification of hybrid membranes by hot-pressing further improved mechanical strength and ionic transport. Some membranes achieved conductivities up to 10^{-2} S/cm at 80 °C and 80 % RH. These results demonstrate a scalable approach to fabricating membranes with enhanced performance for PEMFC applications.

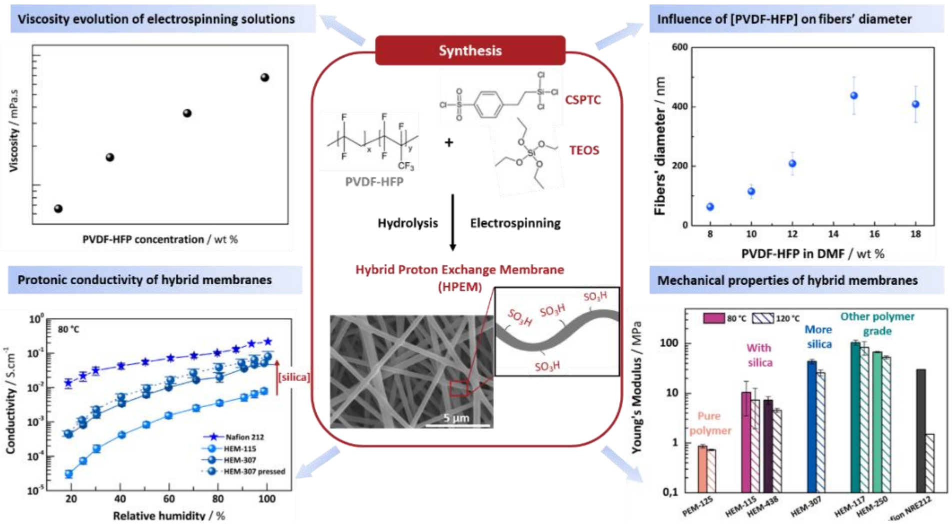

Figure: Influence of composition of electrospun fibrous membrane on morphology, conductivity and mechanical properties.

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Conception and Synthesis of New Organics porous functionals Materials for Energy Storage

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Keywords: Organic Electrode Materials; Lithium-ion batteries; p-type conjugated polymers

Abstract: Organic lithium-ion batteries, unlike commercial lithium-ion batteries, are made up of organic electrode materials. These Electrodes materials are known to be composed of very abundant elements such as carbon, hydrogen, oxygen, sulfur, nitrogen, etc. They are also recyclable, versatile, structurally tunable and relatively inexpensive to manufacture compared to their inorganic counterparts[1]. However, these organic materials are soluble in the electrolytes used in lithium-ion batteries, in addition to having relatively limited electronic conductivity and low redox potentials compared to inorganic materials[2].

In this work, we were interested in conjugated polymers based on p-type materials that are used as cathodes for organic batteries. Conjugated polymers are known to be poorly soluble in organic electrolytes and more conductive than small molecules. In addition, polythiophenes are known to be very stable in the p-doped (oxidized) state and to possess redox potential of about 4 V vs Li/Li^{+}[3]. Firstly, we are working in particular on linear poly(2,2-bithiophene) synthesized by oxidative polymerization using iron(III) chloride as an oxidizer and electrochemically characterized with four electrolytes composed of EDD (1M of $LiPF_6$ in EC/DEC/DMC (v/v/v)), one of which is additive-free and the others composed of 1% (EDD+1wt%ADN), 2.5% (EDD+2.5wt%ADN)and 5% (EDD+1wt%ADN) by mass of adiponitrile (ADN) used as an additive. This polymer shows a specific capacity of about 80 mAh/g for the electrolyte with 2.5wt% ADN and about 60 mAh/g at 100 mA/g for the others with good reversibility (Figure 1). In addition, poly(2,2-bithiophene)-based electrode is very stable even after 1000 cycles with less than 20% loss of capacity for each electrolyte at 900 mA/g (see Table 1). We plan to further increase the redox potential and capacity of this conjugated polymer by studying the structure-property relationship and the impact of electrolytes on the electrochemical performance of those polymers.

Table 1: Capacity retention after 1000 cycles at 900 mA/g.

	Capacity (mAh/g)/Capacity retention (%)	
	Cycle 1	**Cycle 1000**
EDD	**55.4/100**	**45.8/83**
EDD + 1wt%ADN	**51/100**	**44.8/88**
EDD + 2.5wt%ADN	**67/100**	**55/82**
EDD + 5wt%ADN	**52/100**	**43/82**

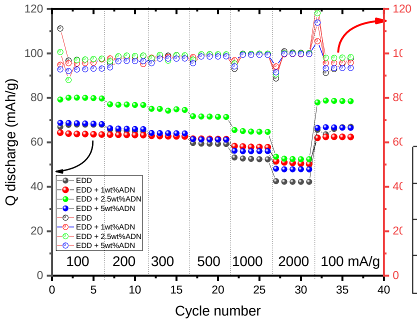

Figure : Rate capability of 2,2-bithiophene-based polymers with different electrolytes.

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