

INSTITUTE OF MACROMOLECULAR  
CHEMISTRY CAS  
INTERNATIONAL UNION OF PURE  
AND APPLIED CHEMISTRY  
EUROPEAN POLYMER FEDERATION  
CZECH CHEMICAL SOCIETY



**24–28 JUNE 2024 PRAGUE**

# POLYMERS FOR SUSTAINABLE FUTURE 2024

**85<sup>th</sup> PRAGUE MEETING ON MACROMOLECULES**  
**11<sup>th</sup> CONFERENCE ON GREEN CHEMISTRY AND  
NANOTECHNOLOGIES IN POLYMERIC MATERIALS**



**BOOK OF ABSTRACTS AND PROGRAMME**

INSTITUTE OF MACROMOLECULAR CHEMISTRY  
CZECH ACADEMY OF SCIENCES

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

EUROPEAN POLYMER FEDERATION

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# **POLYMERS FOR SUSTAINABLE FUTURE 2024**

24–28 June 2024, Prague



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NANOTECHNOLOGIES IN POLYMER MATERIALS

Book of Abstracts and Programme



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**85<sup>th</sup> PRAGUE MEETING ON MACROMOLECULES  
11<sup>th</sup> CONFERENCE ON GREEN CHEMISTRY AND  
NANOTECHNOLOGIES IN POLYMER MATERIALS**

under the auspices of the  
International Union of Pure and Applied Chemistry,  
European Polymer Federation and  
Czech Chemical Society

**Organized by the Institute of Macromolecular Chemistry,  
Czech Academy of Sciences**

Hynek Beneš and Zdeněk Starý  
***Conference Chairmen***

Jiří Kotek  
***Director of the Institute***

Marcela Havelková, Marie Rodová  
***Local Organizing Team***

Josef Jůza, Jiří Kaprálek  
***Technical Support***

## **International Advisory Board**

Veronica Ambrogi (*Italy*)

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Alexander Bismarck (*Austria*)

Ugis Cabulis (*Latvia*)

Maria Valentina Dinu (*Romania*)

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Jean-François Gérard (*France*)

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JABLUM

Prague, June 2024

## **POLYMERS FOR SUSTAINABLE FUTURE 2024**



Dear Colleagues and Friends,

we are proud to welcome you to the "Polymers for Sustainable Future 2024" conference, which reflects the current global problems associated with the sustainability of polymers and plastic pollution. The conference combines two traditional scientific meetings, the 85th edition of Prague Meeting on Macromolecules (PMM) organized by the Institute of Macromolecular Chemistry Czech Academy of Sciences and the 11th edition of the Green Chemistry and Nanotechnologies in Polymeric Materials (GCNPM). Research in the field of sustainable polymers is highly important and topical as evidenced by a huge interest in participation on this meeting far exceeding the capacity of the venue. It is actually for the first time in the long history of PMM we had to reject participants.

Beyond its well-known historical beauty, Prague is a vibrant centre of modern science and technology. The city's commitment to sustainability and innovation mirrors our conference's theme, providing an inspiring environment for discussions on the future of polymers. We believe that besides the opportunity to engage with research and developments in the field of sustainable polymers, you will also enjoy the unique cultural and historical treasures that Prague offers.

We hope you will find the event intellectually stimulating and culturally enriching. Together, let's help to pave the way towards a sustainable future through the innovative world of polymers.

Warm regards,

Hynek Beneš & Zdeněk Starý  
*Conference Chairmen*



## **GENERAL INFORMATION**

### **Venue**

All sessions are held at the Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, Prague 6, Czech Republic.

### **Language**

The official language of the conference is English.

### **Registration**

On-site registration takes place on Monday, 24 June 2024, from 16:00 to 19:00 at the Institute of Macromolecular Chemistry and will continue the next day from 8:00 to 16:00.

Please be aware that only persons wearing name badges received upon registration are entitled to enter the lecture rooms at the Institute.

## **PRESENTATIONS**

The conference presentations consist of plenary lectures, invited lectures and oral communications. Two poster sessions are held on Tuesday, 25 June and Wednesday, 26 June 2024.

Time allocated for lectures including questions and discussion:

**Plenary lectures:** 45 minutes

**Invited lectures:** 30 minutes

**Oral communications:** 15 minutes

### **Presentation files upload**

We recommend that you upload your presentation at least one session ahead of your lecture.

IT administrator Mr Jiří Kaprálek will help you to upload and check your presentation. Please use your last name as the presentation file name.

### **Recordings**

Audio/video recording of the lectures or copying of lecture files is not allowed without the prior consent of the speaker. The organizers

reserve the right to take photographs for documentation during the meeting. In case you do not want to be photographed, please kindly inform the photographer or organizers.

### **Poster presentations**

Materials for fixing posters will be provided on-site. The posters can be mounted at the beginning of the poster session and should be removed thereafter. The area reserved for mounting a poster is 200 cm high and 100 cm wide.

### **POSTER SESSIONS**

**Poster session I:** Tuesday, 25 June 2024, 18:00 – 21:00

Posters P-01 – P-45

**Poster session II:** Wednesday, 26 June 2024, 18:00 – 21:00

Posters P-46 – P-90

### **SPECIAL AWARDS**

The scientific committee will evaluate student posters from poster sessions. Winners will be announced at the Conference dinner and awarded by the chairs of the conference. The best oral presentation given by young researchers and PhD students will be awarded at the end of the conference.

### **REFRESHMENTS AND LUNCHES**

Coffee and small refreshment will be served during breaks each day. Lunch buffets will be open from Tuesday till Friday in the dining hall of the Institute during the lunch breaks. The cost of refreshments and lunches is included in the conference fee as well as the welcome buffet and the conference dinner.

## **SOCIAL EVENTS**

*The costs of the following social events are included in the conference fee. Accompanying persons can pay for the conference dinner at the registration desk. Additionally, a special guided tour in the Prague city centre will be organized for them on Thursday afternoon.*

### **Monday, 24 June 2024**

#### **16:00 – 19:00 Registration and Welcome Buffet**

Participants of the conference will register and receive the conference materials.

### **Tuesday, 25 June 2024**

18:00 – 21:00 Poster session I. with barbeque in front of the Institute.

### **Wednesday, 26 June 2024**

18:00 – 21:00 Poster session II. with snack and Czech beers.

### **Thursday, 27 June 2024**

18:00 **Conference dinner** at the Klášterní Pivovar Strahov (Strahov Monastery Brewery)

*Strahovské nádvoří 301, Prague 1*

*(Pohořelec is the closest tram stop, tram 22, 23)*

Strahov Monastery (Strahovský klášter) is a Premonstratensian abbey founded in 1143. In the complex there is the church of the Assumption of the Blessed Virgin Mary, the rare Strahov Library with a number of medieval manuscripts, maps and globes, and the Strahov Gallery, one of the most significant Central European collections of Gothic painting, Rudolphian art, and Baroque and Rococo paintings.

Besides that, in the monastery brewery monks have been crafting amazing beer for more than 600 years. This tradition continues now in the brewery restaurant for beer lovers from around the world.

Join us there for a conference dinner!

## **PRAGUE TRANSPORT**

### **Public transport**

A ticket for a 30-min or 90-min journey costs 30 or 40 Czech Crowns (CZK) respectively and it is valid in all types of Prague public transport (trams, buses, metro and local trains - excluding the AE route and the Petřín funicular) for an unlimited number of transfers. The 24-hour ticket costs 120 CZK. Tickets are sold at the airport, at railway and metro stations, at newspaper stands, at hotel reception desks, etc. In trams and most of buses, tickets can be purchased using a contactless payment card. The Metro runs from 5:00 till midnight.

Ticket machines accepting contactless payment cards are at the tram stop and metro station near the conference venue. Persons over 65 years can travel for free; however, when checked by an inspector, they have to show passports.

### **Airport and railway stations**

The Václav Havel Airport Prague is situated 9 km from the Institute, with a comfortable connection by bus No. 191 to/from the “Sídliště Petřiny” stop next to the Institute (the stop is on request). International trains mainly arrive at and depart from the Praha Hlavní nádraží station (“Hlavní nádraží” metro station, red line C).

**The Institute is situated near the “Petřiny” metro station, green line A.**

## **EMERGENCY PHONE NUMBERS**

General emergency: 112  
Medical ambulance service: 155  
Police: 158

## **EXHIBITION - PET ART SCULPTURES**

*Discovering by chance that plastic bottles can be deformed by heat, I decided to create a sculpture from this material. The concept of PET art emerged almost instantly, yet initially, I regarded it merely as one of my visual experiments. Little did I foresee that plastic bottles would evolve into a consuming passion lasting for many years. Since 2004 I have used thousands of bottles crafting hundreds of objects. Through this endeavour, I have developed many specialised methods of technological processing.*

**Veronika Richterová**

### **About the author**

**Veronika Richterová** (\*1964 in Prague) studied monumental painting at the Academy of Arts, Architecture, and Design in Prague. Subsequently, she immersed herself in painting, creating enamelled metal sculptures, and crafting mosaics from shards. In 2004, she embarked on sculpting coloured PET bottles, gradually refining numerous original techniques thus creating large-scale works and functional PET lights. Initially crafting simple flowers, her repertoire expanded to encompass palms, cycads, cacti, Japanese ikebana, and tropical vegetation. Her next large theme is the underwater world with its fantastic landscapes full of corals, sponges and different animals. The artist cyclically revisits these themes, infusing them with her unique interpretation. While she occasionally draws inspiration directly from nature, her primary sources include books, magazines, internet photographs, and her extensive personal photo collection, often tied to vivid memories or profound experiences.

Her portfolio boasts over fifty solo exhibitions in the Czech Republic and abroad and participation in numerous international exhibitions, symposia, and group showcases. The last one so far, New PET Tropicana, has taken place this spring in Fata Morgana, the vast greenhouse of Prague Botanical Garden. Additionally, she has organised many workshops in diverse locations. Since 2007, she has amassed a collection exceeding 5,000 PET bottles, showcasing numerous designs from 128 countries worldwide. This remarkable collection serves as the foundation for the forthcoming PET-ART Museum. Beyond its role in documenting instances of DIY (“do-it-

yourself”) recycling, the museum aims to feature thematic photo collections and authored books. Currently, her huge Crystal chandeliers are displayed in Café Savoy in Prague.

More info about the author and her work can be found at [www.veronikarichterova.com](http://www.veronikarichterova.com).



## CONFERENCE PROGRAMME

**Monday, 24 June 2024**

16:00 – 19:00 **Registration and welcome buffet**

**Tuesday, 25 June 2024**

08:30 – 08:45 **OPENING**

Jiří Kotek (Director of the Institute)  
Hynek Beneš, Zdeněk Starý (Conference chairmen)  
Igor Lacík (Representative of IUPAC)

### LECTURE SESSION 1

*Chaired by: Igor Lacík (Slovakia)*

- 08:45 – 09:30 Plenary lecture PL-01  
**Anthony J Ryan** (*United Kingdom*)  
Neofossils: Carbon sequestration by plastics
- 09:30 – 10:00 Invited lecture IL-01  
**Maria Filomena Barreiro** (*Portugal*)  
Natural polymer-based pickering emulsions:  
From particle production to innovative applications
- 10:00 – 10:15 Oral communication O-01  
**Erika Ghiglietti** (*Italy*)  
Design of innovative strategies for the synthesis  
of bio-based nanocapsules: New perspectives
- 10:15 – 10:30 Oral communication O-02  
**Magdalena Hudek** (*United Kingdom*)  
Design of novel chitosan nanoparticles  
for antimicrobial applications

10:30 – 11:00

*Coffee break*

## LECTURE SESSION 2

*Chaired by: Anthony J. Ryan (United Kingdom)*

- 11:00 – 11:30 Invited lecture IL-02  
**Maria Kurańska** (*Poland*)  
Chemical recycling of biopolyurethane foams in line with the circular economy concept
- 11:30 – 11:45 Oral communication O-03  
**Krzysztof Polaczek** (*Italy*)  
Preparation of self-blowing non-isocyanate polyurethane foams starting from soybean oil cyclic carbonate
- 11:45 – 12:00 Oral communication O-04  
**Liudmyla Gryshchuk** (*Germany*)  
Bio-based hybrid polyurethane/indirect polyurea/epoxy foams for constructive applications
- 12:00 – 12:15 Oral communication O-05  
**Peter Krajnc** (*Slovenia*)  
Poly(HIPE)s from bio-based monomers
- 12:15 – 12:30 Oral communication O-06  
**Mikelis Kirpluks** (*Latvia*)  
Applying Michael 1.4-addition reaction to produce bio-based thermoset foams from rapeseed oil
- 12:30 – 12:45 Oral communication O-07  
**Federica Recupido** (*Italy*)  
Building the future: Innovations in sustainable porous materials for smart and energy-efficient construction

12:45 – 14:00

*Lunch*



## LECTURE SESSION 3

*Chaired by: Jannick Duchet-Rumeau (France)*

- 14:00 – 14:30 Invited lecture IL-03  
**Paola Fabbri** (*Italy*)  
The "full-bio" strategy: The relevance of functional bio-based additives for the formulation of innovative plastics
- 14:30 – 14:45 Oral communication O-08  
**Léa Simonnet** (*France*)  
Metal ionic liquids (MILs) as efficient catalytic curing agents of epoxy prepolymer
- 14:45 – 15:00 Oral communication O-09  
**Teresa Carranza** (*Spain*)  
Valorisation of collagen as bio-based ink for advanced 3D printing applications
- 15:00 – 15:15 Oral communication O-10  
**Elena Buratti** (*Italy*)  
Cutin-based coatings for enhanced hydrophobicity and anticorrosion properties
- 15:15 – 15:30 Oral communication O-11  
**Omar El Seoud** (*Brazil*)  
Cellulose dissolution and acetylation in mixtures of ionic liquids and molecular solvents. The fruitful synergism of experiment and theory
- 15:30 – 15:45 Oral communication O-12  
**Claire Morand** (*Spain*)  
Biosourced unsaturated polyesters for 3D-printing

15:45 – 16:15

*Coffee break*

## LECTURE SESSION 4

*Chaired by: Maria Filomena Barreiro (Portugal)*

- 16:15 – 16:45 Invited lecture IL-04  
**Jean-François Gérard** (*France*)  
Being repairable as one of the features  
of sustainable polymers for circular economy –  
Illustration for high performances thermoset  
matrices
- 16:45 – 17:00 Oral communication O-13  
**Alex Maokhamphiou** (*France*)  
Novel sustainable synthesis of formaldehyde-free  
phenolic resin by reactive extrusion
- 17:00 – 17:15 Oral communication O-14  
**Mohamed Yousfi** (*France*)  
Improving thermal resistance and impact toughness  
of PLA via melt blending with PEICT: Effect  
of isosorbide comonomer ratio
- 17:15 – 17:30 Oral communication O-15  
**Jan Thiel** (*Germany*)  
Melt spinning of bio-based thermoplastic  
polyurethanes in industrial environment
- 17:30 – 17:45 Oral communication O-16  
**Zeang Zhao** (*People's Republic of China*)  
Smart polymers and structures: From 3D to 4D  
printing
- 17:45 – 18:00 Oral communication O-17  
**Søren Hvilsted** (*Denmark*)  
HMF: The versatile key biobased building block
- 18:00 – 21:00 **Poster Session I. & Barbeque**

## Wednesday, 26 June 2024

### LECTURE SESSION 5

*Chaired by: Haritz Sardon (Spain)*

- 08:30 – 09:15 Plenary lecture PL-02  
**Katja Loos** (*Netherlands*)  
Unleashing the potential of enzymes for green furan-based polymer synthesis
- 09:15 – 09:45 Invited lecture IL-05  
**Robin Hutchinson** (*Canada*)  
Incorporation of biorenewable monomers to acrylic resins produced by radical copolymerization
- 09:45 – 10:00 Oral communication O-18  
**Seok Min Yoon** (*Republic of Korea*)  
Hierarchical metal-organic aerogel as a highly selective and sustainable CO<sub>2</sub> adsorbent
- 10:00 – 10:15 Oral communication O-19  
**Amit Kumar** (*Ireland*)  
Biomass-derived high-performance polyimide: Strategies of aromatic diamines syntheses
- 10:15 – 10:30 Oral communication O-20  
**Beatriz Agostinho** (*Portugal*)  
Sustainable approaches towards new furan-based polymers: New copolyesters based on 5,5'-oxybis(methylene)bis(furan-5,2-diyl)dimethanol (OBMF-H)

10:30 – 11:00

*Coffee break*

## LECTURE SESSION 6

*Chaired by: Robin Hutchinson (Canada)*

- 11:00 – 11:30 Invited lecture IL-06  
**Li Jia** (*United States of America*)  
Carbonylative polymerizations – A potential platform for sustainable commodity plastics
- 11:30 – 11:45 Oral communication O-21  
**Angela Giunta** (*France*)  
Itaconic acid: From oligomers to microgels
- 11:45 – 12:00 Oral communication O-22  
**Federico Mundo** (*France*)  
From urethane bis-carbonate monomers to polyurethane-hydroxyurethane polymers
- 12:00 – 12:15 Oral communication O-23  
**Jens Gaitzsch** (*Germany*)  
Responsive and green polyesters by radical ring-opening polymerisation
- 12:15 – 12:30 Oral communication O-24  
**Tatiana La Banca Schreiner** (*Portugal*)  
High bio-based content waterborne polyurethane-ureas for footwear applications
- 12:30 – 12:45 Oral communication O-25  
**Kacper Mielczarek** (*Poland*)  
Methods for syntesis high molecular weight poly(itaconic acid)

12:45 – 14:00

*Lunch*

## LECTURE SESSION 7

*Chaired by: Li Jia (United States of America)*

- 14:00 – 14:30 Invited lecture IL-07  
**Igor Lacík** (*Slovakia*)  
Radical polymerization in aqueous solutions
- 14:30 – 14:45 Oral communication O-26  
**Sara Mecca** (*Italy*)  
Unlocking vegetable waste potential: A novel circular biorefinery approach in sustainable biofilm formation
- 14:45 – 15:00 Oral communication O-27  
**Ana Carolina Lima** (*Portugal*)  
Optimisation of gelatine-alginate hydrogels synthesis for 3D printing
- 15:00 – 15:15 Oral communication O-28  
**Ringo Leung** (*New Zealand*)  
Microstructure and mechanical properties of copolymer synthesised from PET and PCL transesterification
- 15:15 – 15:30 Oral communication O-29  
**Cesare Gallizioli** (*Germany*)  
Ring-opening terpolymerisation of elemental sulfur waste with propylene oxide and carbon disulfide via lithium catalysis
- 15:30 – 15:45 Oral communication O-30  
**Hieu Do** (*France*)  
Multicomponent polycondensation: A novel sustainable approach to polythiourea using elemental sulfur

15:45 – 16:15

*Coffee break*

## LECTURE SESSION 8

*Chaired by: Paola Fabbri (Italy)*

- 16:15 – 16:45 Invited lecture IL-08  
**Jannick Duchet-Rumeau** (*France*)  
Polyvinyl chloride: A new material for tomorrow or how can it contribute to circular economy?
- 16:45 – 17:00 Oral communication O-31  
**Pedro Rodrigues Bizarro** (*France*)  
Physical recycling of PVC: Pressurized fluid extraction for plasticiser removal
- 17:00 – 17:15 Oral communication O-32  
**Magda Silva** (*Portugal*)  
Sustainable fibers based on recycled PET
- 17:15 – 17:30 Oral communication O-33  
**Marco Rollo** (*Italy*)  
Depolymerization of polyethylene terephthalate (PET) based-complex waste plastics with Lewis/Brønsted acidic deep eutectic solvents
- 17:30 – 17:45 Oral communication O-34  
**Jose A Pomposo** (*Spain*)  
Upcycling of PVC to efficient catalytic single-chain nanoparticles (SCNPs)
- 17:45 – 18:00 Oral communication O-35  
**Guido Grause** (*United Kingdom*)  
Separation of ethylene glycol and BHET from the catalyst solution as part of a continuous glycolysis process for PET

18:00 – 21:00 **Poster Session II. & Czech beer and snack**

**Thursday, 27 June 2024**

LECTURE SESSION 9

*Chaired by: Katja Loos (Netherlands)*

- 08:30 – 09:15 Plenary lecture PL-03  
**Haritz Sardon** (*Spain*)  
Chemical recycling of plastics where we are  
and how to improve the recycling rates
- 09:15 – 09:45 Invited lecture IL-09  
**Alberto Fina** (*Italy*)  
Melt processing of dynamic polymer networks
- 09:45 – 10:00 Oral communication O-36  
**Izaskun Larraza Arocena** (*Spain*)  
Partially and fully bio-based vitrimers:  
Characterization and recyclability analysis
- 10:00 – 10:15 Oral communication O-37  
**Gloria Huerta-Angeles** (*Czech Republic*)  
Structural characterization  
of nanocomposite hydrogels based on poly  
(itaconic-co-acrylamide)/laponite as absorbents
- 10:15 – 10:30 Oral communication O-38  
**Stéphanie Engelen** (*Belgium*)  
Biomass-rich epoxy-derived processablethermosets
- 10:30 – 11:00 *Coffee break*

## LECTURE SESSION 10

*Chaired by: Maria Kurańska (Poland)*

- 11:00 – 11:30 Invited lecture IL-10  
**Sébastien Livi** (*France*)  
Design of new degradable networks using cleavable ionic liquid monomers
- 11:30 – 11:45 Oral communication O-39  
**Danuta Matykiewicz** (*Poland*)  
The use of nettle fibers in the production of bioepoxy based composites
- 11:45 – 12:00 Oral communication O-40  
**Pauline Shamraienko (Voigt)** (*Germany*)  
Development of sustainable polymer materials from bio-based monomers
- 12:00 – 12:15 Oral communication O-41  
**Jocyla Rosalí Manhique** (*Portugal*)  
Thermoplastic polyurethanes formulated from biobased polyols for footwear applications
- 12:15 – 12:30 Oral communication O-42  
**Aleksander Prociak** (*Poland*)  
The effect of selected bio-components on the properties of rigid polyurethane foams
- 12:30 – 12:45 Oral communication O-43  
**Eva Laureys** (*France*)  
From single-use to multiple-use concept of epoxy-IL networks : Study of the physical properties and valorization approach

12:45 – 14:00

*Lunch*



## LECTURE SESSION 11

*Chaired by: Sébastien Livi (France)*

- 14:00 – 14:30 Invited lecture IL-11  
**Alexander S. Shaplov** (*Luxembourg*)  
High performance self-catalyzed epoxy-amine vitrimers for sustainable composites
- 14:30 – 14:45 Oral communication O-44  
**Adrian Wolf** (*Germany*)  
Benzoxazine/amine-based polymer networks:  
A new type of vitrimer
- 14:45 – 15:00 Oral communication O-45  
**Tim Maiheu** (*Belgium*)  
On-demand debonding of epoxy-based adhesives using  $\beta$ -amino ester chemistry
- 15:00 – 15:15 Oral communication O-46  
**Jian Liu** (*Netherlands*)  
Preparation of lignin-based imine vitrimers and their potential application as repairable, self-cleaning, removable and degradable coatings
- 15:15 – 15:30 Oral communication O-47  
**Oihane Echeverria-Altuna** (*Spain*)  
Advancing circularity: Exploring dynamic covalent bonds in bio-pur resin systems for structural composites
- 15:30 – 15:45 Oral communication O-48  
**Robin Tannert** (*Germany*)  
How sustainable are monomers synthesized via an enzymatic pathway?

15:45 – 16:15

*Coffee break*

## LECTURE SESSION 12

*Chaired by: Igor Krupa (Qatar)*

- 16:15 – 16:30 Oral communication O-49  
**Aileen Grace Mendoza Ongkiko** (*Philippines*)  
Design of a natural-based polymer carrier matrix used for the fabrication of a biofertilizer prototype via a sustainable and microorganism-friendly process
- 16:30 – 16:45 Oral communication O-50  
**Joel Fawaz** (*Austria*)  
Heterophasic polypropylene polymer design for packaging applications

18:00 – 22:00 **Conference dinner & Poster awards**

## Friday, 28 June 2024

### LECTURE SESSION 13

*Chaired by: Jean-François Gérard (France)*

- 08:30 – 09:15 Plenary lecture PL-04  
**Bernhard von Vacano** (*Germany*)  
Polymer recycling and sustainability at scale
- 09:15 – 09:45 Invited lecture IL-12  
**Maidor Iturrondobeitia** (*Spain*)  
End of life of polymer based products  
and environmental impact assessment
- 09:45 – 10:00 Oral communication O-51  
**Mateusz Dudziak** (*Germany*)  
Wastewater phosphorus enriched algae  
as sustainable flame retardant in poly(lactic acid)
- 10:00 – 10:15 Oral communication O-52  
**Julen Ibarretxe** (*Spain*)  
PHBH-alumina composites: Environmental impacts  
and toxicity
- 10:15 – 10:30 Oral communication O-53  
**Raquel Rodriguez** (*Spain*)  
New waterborne biobased acrylic binders with water  
repellency without the use of PFAS

10:30 – 11:00

*Coffee break*

## LECTURE SESSION 14

*Chaired by: Bernhard von Vacano (Germany)*

- 11:00 – 11:30 Invited lecture IL-13  
**Ian Teasdale** (*Austria*)  
Amino acid-phosphoramides: Biodegradable synthetic polymers from nature's building blocks
- 11:30 – 11:45 Oral communication O-54  
**Zhou Fang** (*Netherlands*)  
Accurate T<sub>g</sub> prediction by machine learning for accelerating the development of bio-based copolyester resins
- 11:45 – 12:00 Oral communication O-55  
**Sophia van Mourik** (*United Kingdom*)  
Utilizing MALDI ToF MS as a tool to investigate the potential of biodegradable polyurethanes
- 12:00 – 12:15 Oral communication O-56  
**Vincent Monteil** (*France*)  
Chemical recycling of silicones
- 12:15 – 12:30 Oral communication O-57  
**Valentine Delbruel** (*France*)  
Recycling of orthopedic production scraps for the additive manufacturing of orthoses
- 12:30 – 12:45 Oral communication O-58  
**Nirmala Devi** (*India*)  
Plant oil: A green platform for designed polymers and nanocomposites with versatile applications

12:45 – 14:00

*Lunch*

## LECTURE SESSION 15

*Chaired by: Ian Teasdale (Austria)*

- 14:00 – 14:30 Invited lecture IL-14  
**Igor Krupa** (*Qatar*)  
Utilization of recycled polyethylene waste for oil in water separation
- 14:30 – 14:45 Oral communication O-59  
**Tamara Calvo-Correas** (*Spain*)  
Valorization of TPU waste as filtering membranes for water pollutants
- 14:45 – 15:00 Oral communication O-60  
**Elżbieta Malewska** (*Poland*)  
Rebiopolyol-new component for synthesis of polyurethane foams
- 15:00 – 15:15 Oral communication O-61  
**Gabriel Perli** (*Spain*)  
Heterogeneous catalytic system for advancing plastic circular economy
- 15:15 – 15:30 Oral communication O-62  
**Nikolaos Giakoumakis** (*Belgium*)  
Enhancing styrene recovery and upcycling of the rubber phase of high impact polystyrene
- 15:30 – 15:45 Oral communication O-63  
**Dario Pindric** (*Austria*)  
Determination of the cleaning efficiency for contaminated HDPE using solvent-based recycling

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## **PLENARY LECTURES**





# PL-01

## NEOFOSSILS: CARBON SEQUESTRATION BY PLASTICS

A. J. Ryan<sup>a,c</sup>, F. Meng<sup>b,c</sup>, R. H. Rothman<sup>b,c</sup>, S. Walker<sup>b,c</sup>

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In the last 50 years more than 8 billion tons of the stuff vilified as “plastic” has been produced because their ubiquity and variety mean they are completely embedded in our lives. But the very properties of plastics that make them so useful, they are durable & cheap, also means that they are almost worthless post-use, expensive to recycle & easy to discard.

We are focused on delivering a circular economy for polymers, whether they are derived from fossil carbon or more recent biomass. But even a systems-based, multidisciplinary approach cannot solve the problem of plastics in the environment through a combination of reuse, repurposing & recycling: we must deal with the end-of-life.

So have come to us the conclusion we need to turn the problem on its head. Make more single-use plastic but using C that has been fixed by photosynthesis and taken from the atmosphere this year, not C fixed millennia ago. Neo-carbon not fossil-carbon to turn into neo-fossil plastic and put it back in the ground through curated burial.<sup>1</sup> The petrochemicals industry could continue to benefit from its capital assets and be persuaded to leave the oil & gas in the ground if it could see a profit from a "consume then conserve" plastic policy.

We could use durable (i.e. nondegradable) bioplastics plastics to sequester carbon. Making polymers from photosynthetic biomass takes CO<sub>2</sub> out of the atmosphere and we could bury that plastic. In fact, if we converted all the current 300 million tonnes of annual plastic production to non-degradable bioplastics, using 100% renewable energy and agricultural waste as the feedstock, we would be able to remove 1 billion tonnes of CO<sub>2</sub> from the atmosphere every year.

1. Ryan A.J., Rothman R.H., Nature Reviews Chemistry. 6: 1–3, 2022.

## PL-02

### UNLEASHING THE POTENTIAL OF ENZYMES FOR GREEN FURAN-BASED POLYMER SYNTHESIS

K. Loos

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The enzymatic synthesis of polymers via non-metabolic pathways has a long history but was overshadowed by petroleum-based methods. However, due to the depletion of petroleum resources and rising costs, enzymatic polymerizations are experiencing a resurgence. By combining biobased monomers and enzymatic polymerizations, both the field of enzymatic polymerization and the use of renewable resources can be accelerated, contributing to sustainability in the polymer and coatings industry.

Furan derivatives and furan chemistry offer a biobased alternative to phenyl-based polymers, with 2,5-Furandicarboxylic acid (FDCA) being a promising biobased furan monomer. However, its potential is limited by the occurrence of decarboxylation during polymerization. To overcome this challenge, alternative synthesis routes are needed. Enzymatic polycondensation of biobased furan monomers with aliphatic comonomers has successfully produced furan-based polyesters, polyamides, and polyesteramides, offering a green and robust solution for sustainable polymer production.

1. Silvianti, F.; Maniar, D.; Agostinho, B.; de Leeuw, T. C.; Woortman, A. J. J.; van Dijken, J.; Thiyagarajan, S.; Sousa, A. F.; Loos, K. *Biomacromolecules* 2024. DOI: 10.1021/acs.biomac.3c01433.
2. Post, C.; Maniar, D.; Voet, V. S. D.; Folkersma, R.; Loos, K. *ACS Omega* 2023, 8, 8991.
3. Silvianti, F.; Maniar, D.; Boetje, L.; Woortman, A. J. J.; van Dijken, J.; Loos, K. *ACS Polymers Au* 2023, 3, 1, 82.
4. Maniar, D.; Silvianti, F.; Ospina, V. M.; Woortman, A. J. J.; van Dijken, J.; Loos, K. *Polymer* 2020, 205.
5. Skoczinski, P.; Espinoza Cangahuala, M. K.; Maniar, D.; Albach, R. W.; Bittner, N.; Loos, K. *ACS Sustainable Chemistry and Engineering* 2020, 8, 1068.
6. Maniar, D.; Jiang, Y.; Woortman, A.; van Dijken, J.; Loos, K. *ChemSusChem* 2019, 12, 990.

## PL-03

### CHEMICAL RECYCLING OF PLASTICS WHERE WE ARE AND HOW TO IMPROVE THE RECYCLING RATES

H. Sardon

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Nowadays, less than 8% of the polymers produced each year are recycled and most of them are mechanically recycled: grinding and melt-processing, to obtain a low-quality material that will also rapidly end up as a waste.<sup>1</sup> Besides mechanical recycling and pyrolysis, chemical recycling of plastic has emerged as a method to retain the value of the plastics as it allows to obtain high purity monomers.<sup>2</sup> As plastics have been traditionally designed for durability and not for recyclability, their chemical conversion to new products is nowadays considered a grand challenge and difficult to achieve.<sup>3</sup> In this lecture we will summarize our main activities towards the selective chemical recycling of plastics and how we are trying to increase current recycling rates.

1. Sardon H.\* & Dove A.P., Plastic Recycling with a difference Science. 2018, 360, 380-381.
2. Jehanno C., Perez-Madrigo M., Demarteau J., Sardon H., Dove A.P., Organocatalysis for depolymerisation J Polym. Chem. 2019, 10, 172-18.
3. Jehanno C., Flores I., Dove A.P., Müller A.J., Ruipérez F., & Sardon H.\* Organocatalysed depolymerisation of PET in a fully sustainable cycle using thermally stable protic ionic salt Green Chem. 2018, 20, 1205-1212.

## POLYMER RECYCLING AND SUSTAINABILITY AT SCALE

B. von Vacano

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Sustainability for polymers involves optimizing their production, leveraging their unique benefits during the use phase, and utilizing their material value as resources at end-of-life.<sup>1</sup> In the production stage, energy efficient processes, sustainable design<sup>2</sup> and non-fossil feedstocks are the game to play. During the use phase, polymer sustainability benefits are directly linked to their functionality and benefits in application. Structural polymers in the form of prototypical thermoplasts are easily processed and shaped, at lower energy efforts for the creation of goods compared to alternative materials. Polymeric foams reduce greenhouse gas emissions as thermal insulating materials. Engineering plastics directly reduce energy consumption in mobility applications by lightweighting, and polymers are at the heart of any electric vehicle providing structural integrity in battery housings or flexibility in cable sheathing, and electric insulation at the same time. Sustainable use scenarios include repairability and reusability, which will likely gain importance in the future. For life cycle sustainability, the “end of life” of polymeric materials turns out to be a crucial stage. After reuse and repair options, recycling<sup>3</sup> closes the loops of material flow and decouples value from consumption. The prime goal must be to enable quantitative collection, both securing the inherent potential value of polymers for a next life cycle, but also preventing leakage of durable materials into the environment. To deliver on the promise of high value replacement of fossil-based linear plastics, recycling back into high-value applications is needed. To achieve this, any environmental burden, and efforts for e.g., greenhouse gas emissions due to the processing have to be mitigated. Mechanical recycling, depolymerization and technologies that lead to a conversion of mixed waste to feedstock need to be combined.

The future of sustainable polymers must be circular: Keeping the carbon-based building blocks in the loop avoids emissions from both fossil production and potential incineration at the end of life, while at the same time limiting the amount of non-fossil feedstock from renewable biomass or energy intensive CCU.<sup>4</sup> This transformation of the plastics value chain will require delivering both recycled content quantity and recycle quality at scale.

1. Meys *et al.*, *Science* 2021, 374,71.
2. von Vacano *et al.*, *Angew. Chem. Int. Ed.* 2023, 62, e202210823.
3. Mangold, von Vacano, *Macromol. Chem. Phys.*, 2022, 223, 2100488.
4. Bachmann, Zibunas, Hartmann, *et al.*, *Nat Sustain.*, 2023, 6, 599–610.

## **INVITED LECTURES**



## IL-01

### NATURAL POLYMER-BASED PICKERING EMULSIONS: FROM PARTICLE PRODUCTION TO INNOVATIVE APPLICATIONS

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Pickering emulsions, a type of emulsions stabilised by solid particles, were first introduced by Ramsden and Pickering in the early 20th century, primarily using inorganic particles, such as silica-based products. However, the emergence of natural-based Pickering stabilisers, with their distinct advantages such as biocompatibility, renewability, and potential for functionalisation, has sparked a new wave of interest in the field. This novel approach is now driving the development of a huge number of innovative products for different fields, such as cosmetics, food, and packaging. These systems can serve as a foundation for creating plant-based and low-fat food products, as well as for developing active packaging solutions. Their versatility extends to the co-encapsulation of functionalities with opposite hydrophilic/hydrophobic nature. Furthermore, their rheological properties can be tailored to be compatible with 3D printing processes, opening up a plethora of opportunities for customised nutrition. In this inspiring context, this research provides in-depth insights into various developed Pickering stabilisers derived from natural polymers. It will explore production methods, raw materials, characterisation techniques, and the development of applications within the topic of Pickering emulsions. This will be demonstrated by examining various case studies.

***Acknowledgements:** FCT/MCTES (PIDDAC) support to CIMO (UIDB/00690/2020 (DOI:10.54499/UIDB/00690/2020), UIDP/00690/2020 (DOI:10.54499/UIDP/00690/2020)) and SusTEC LA/P/0007/2020 (DOI:10.54499/LA/P/0007/2020).*



### CHEMICAL RECYCLING OF BIOPOLYURETHANE FOAMS IN LINE WITH THE CIRCULAR ECONOMY CONCEPT

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Currently, the development of polyurethanes focuses on the modification of such materials with biopolyols. In the longer term it is also important to take into account the recyclability of such biomaterials, which is the basis for the eco-design of products. The use of biopolyols instead of petrochemical polyols in the synthesis of biopolyurethanes significantly affects their chemical structures and related properties. Taking action in the area of recycling of materials synthesized with the use of bio-based polyols is an important milestone in the development of biopolyurethanes. The goal of the research was to assess the possibility of chemolysis of polyurethane biofoams synthesized from vegetable oil-based biopolyols with different chemical structures. The results of the chemolysis of different polyurethane biofoams were evaluated in terms of the hydroxyl and amine values, viscosity, molecular weight, MALDI-TOF and FTIR analysis of the new obtained rebiopolyols.

**Acknowledgements:** *This research was funded by the National Research Center in Poland (Narodowe Centrum Nauki, NCN) under contract number UMO-2021/43/D/ST5/01222.*

### THE "FULL-BIO" STRATEGY: THE RELEVANCE OF FUNCTIONAL BIO-BASED ADDITIVES FOR THE FORMULATION OF INNOVATIVE PLASTICS

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New sustainable solutions for the plastic sector, either bio-based/durable or bio-based/biodegradable, have been intensely investigated in recent years, with the focus almost exclusively kept on the polymer itself. For a long period, new compounds were formulated using standard additives in combination with bio-based polymers, but the new trend is definitely to pursue a „full-bio strategy“, in which bio-based additives are purposely developed to expand the potential and reach of biopolymers. We have demonstrated that novel bioplasticizers synthesised from levulinic acid does not significantly affect the typical biodegradability and biocompatibility of poly(hydroxyalkanoate)s, poly(lactic acid) and others, showing a remarkable plasticization effect, comparable to the best fossil-based commercially available solutions.<sup>1</sup> Glycerol trilevulinate plasticizer (GT) produces a significant plasticization effect on both amorphous and semicrystalline polymers and it undergoes enzyme-mediated hydrolysis to its initial constituents, envisioning a promising prospective for environmental safety and upcycling.<sup>2</sup> We also studied wood tannins as fully bio-based biodegradable multifunctional additives for bioplastics, demonstrating their antioxidant, UV protection, and gas barrier properties on PHB.<sup>3</sup> The presented outcomes show that fully bio-based additives offer new strategies to obtain attractive alternatives to petroleum-based plastic solutions.

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## IL-04

### BEING REPAIRABLE AS ONE OF THE FEATURES OF SUSTAINABLE POLYMERS FOR CIRCULAR ECONOMY – ILLUSTRATION FOR HIGH PERFORMANCES THERMOSET MATRICES

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Considering a circular economy for materials, and polymer materials in particular, means not only taking into account their end-of-life, *i.e.* their ability to be recycled and then reused, but also making them more durable and, in particular, capable of self-repair to extend the service life of the devices or products in which they are integrated.

Various strategies have been proposed, in particular to respond to mechanical degradation resulting from use, such as the propagation of (micro)cracks which ultimately lead to macroscopic material failure. One of the most relevant approaches currently being developed is the integration of nano/microcapsules that release reactive species to fill the cracks created by *in-situ* polymerization. This is the approach presented in this lecture, with the preparation of microcapsules from sol-gel synthesis, leading to silica-type or phenolic shells (fragile when a crack meets them). Epoxy networks with different crosslinking densities were considered as matrices. Microcapsules with different types of healing agents, preserved during the specific steps undergone by the reactive systems during their synthesis, are proposed. It will be shown that the introduction of such microcapsules, in particular containing ionic liquid reactive prepolymers, can enable the preparation of sustainable polymer materials likely to respond to increased durability of objects and products.

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### INCORPORATION OF BIORENEWABLE MONOMERS TO ACRYLIC RESINS PRODUCED BY RADICAL COPOLYMERIZATION

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Sustainability of commercial acrylic polymers can be greatly improved with the use of biobased monomers. Esters of itaconic acid provide a good alternative to oil-based monomers since they enable incorporation of different functionality and side chain length. The drawback of these monomers is their susceptibility to depropagation and overall lower rates of polymerization. In this work we propose to counter this disadvantage by using a highly reactive non-depropagating comonomer.

Firstly, dibutyl itaconate (DBI) batch homopolymerizations with varying monomer and initiator concentration, solvent type and reaction temperature were conducted to confirm reported propagation and termination kinetics and deepen the understanding of DBI depropagation. Conversion and molar mass distribution data were measured by <sup>1</sup>H NMR and size exclusion chromatography, respectively. The results were used to develop an improved representation of depropagation kinetics by fitting to a comprehensive kinetic model of DBI homopolymerization implemented in PREDICI, with the remaining kinetic coefficients taken from recent literature.

A series of batch copolymerizations of DBI with butyl acrylate were then conducted to investigate the influence of the comonomer on rate, copolymer composition and polymer molar masses. The results were used to develop a copolymerization kinetic model of the system to guide further development. Semi-batch experiments at commercially relevant process conditions demonstrated that up to 50% itaconate content can be feasibly incorporated in the copolymer resins.

## IL-06

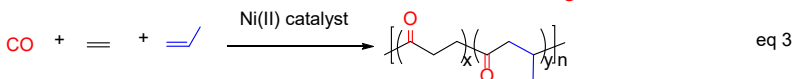
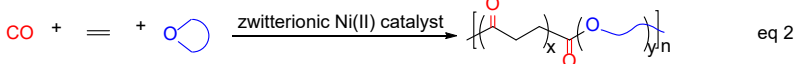
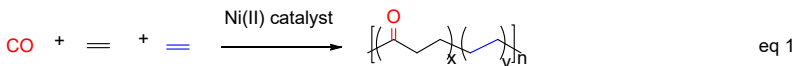
### CARBONYLATIVE POLYMERIZATIONS – A POTENTIAL PLATFORM FOR SUSTAINABLE COMMODITY PLASTICS

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Sustainable plastics aiming to replace the current commodity plastics should ideally have the following attributes. They are made from monomers that have low-carbon footprint and are readily available at scales and costs comparable to current commodity monomers such as ethylene and propylene. They are degradable on the surface of Earth as a fraction of them will inevitably leak into the environment. If they are made via transition metal-catalyzed polymerization, the catalyst is based on earth-abundant, inexpensive metals. And finally, they are ductile as polyethylene and polypropylene are, at least to some extent.

This presentation will focus on carbonylative polymerization as a platform for making sustainable plastics. Ni catalysts with various ligands will be discussed. Incorporation of comonomers, including ethylene itself (eq 1), cyclic ether (eq 2), and propylene (eq 3), into CO-ethylene alternating copolymer will be explored as ways to achieve the essential mechanical property of polyethylene and polypropylene replacements: ductility.



## IL-07

### RADICAL POLYMERIZATION IN AQUEOUS SOLUTIONS

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The understanding of radical polymerization is based on the knowledge of individual kinetic coefficients. There is no escape from this principal requirement. A great progress in understanding of the radical polymerization started in 1980s with the development of pulsed-laser initiated polymerizations providing the access rate coefficients.<sup>1,2</sup> The propagation rate coefficient,  $k_p$ , is of principal interest since it determines the rate of polymer chain growth and it is required to estimate accurate termination and a transfer rate coefficients.

This contribution will focus on radical polymerization in aqueous solutions. The presence of functional groups in the monomer chemical structure gives rise to intra and intermolecular interactions that are amplified by interactions with water used as a solvent. This greatly complicates understanding of the polymerization mechanism and kinetics compared to the polymerizations in non-aqueous solutions. The progress achieved in the last two decades on polymerization of water-soluble monomers in aqueous solutions has been recently summarized by Buback et al.<sup>3</sup> For different monomer categories, the dependence of  $k_p$  values on monomer concentration, monomer conversion, temperature, pressure, and for ionized and ionizable monomers, on degree of ionization and ionic strength became available along with understanding of fundamental mechanisms determining the magnitude of  $k_p$  values. Some of these aspects will be discussed during the presentation.

**Acknowledgement:** *This work was supported by the Slovak Scientific Grant Agency VEGA 2/0143/23 and by the Slovak Research and Development Agency under contract number APVV-22-0565.*

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## IL-08

### **POLYVINYL CHLORIDE : A NEW MATERIAL FOR TOMORROW OR HOW CAN IT CONTRIBUTE TO CIRCULAR ECONOMY ?**

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Poly(vinyl chloride) (PVC) is one of the most common thermoplastic materials employed today with many applications ranging from packaging, to healthcare devices, insulation, textile, building materials. PVC is a rigid polymer attested by its high glass transition temperature (80°C) but it is made softer by compounding with plasticizers. The most widely used plasticizers usually are esters derived from phthalic acid. These plasticizers with a low molecular weight can migrate from PVC causing environmental and health problems. PVC is also known to degrade at high temperature and gives off hydrochloric acid that in turn accelerates the thermal degradation process. Lead stabilizers were very used in the past to improve the decomposition temperature.

Today, we must face to two challenging issues : i) the recycling of PVC from manufactured products<sup>1</sup> and ii) the research of new more friendly environmentally alternatives to plasticizers and stabilizers<sup>2</sup> while respecting the new norms of legislation. In this lecture, a first part will deal with the recycling of PVC. The approach used to extract from PVC the phthalate based plasticizers will be described. The combination of supercritical carbon dioxide in presence of a co-solvent is suitable to extract the plasticizer from PVC. The second part will focus on the design of more friendly environmentally PVC. Ionic liquids have a double effect since they behave as relevant plasticizers and bring additional functions like fire retardancy and thermal stability. The impact of new additives on the thermomechanical properties will be discussed.

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### MELT PROCESSING OF DYNAMIC POLYMER NETWORKS

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Covalent Adaptable Networks based on vinylogous urethane exchangeable bonds were previously proposed as relatively fast dynamics networks, in principle allowing for the preparation by melt mixing. This was applied to linear phenoxy resins aiming to an alternative to conventional epoxy thermosets, proving thermomechanical and rheological properties are consistent with counterparts produced in solvent.<sup>1</sup> However, melt processing was possible only at relatively low crosslinking degree due to the extremely high viscosity of the system.

Thermoreversible dissociative networks are obviously easier to process in the melt, thanks to the shift of the dissociative equilibrium at sufficiently high temperature. A covalent adaptable network based on the thermo-reversible crosslinking of an ethylene-propylene rubber through Diels-Alder reaction was prepared by the functionalization of the rubber with furan groups was carried out in a melt blender and subsequently mixed with different amounts of bismaleimide in a microextruder.<sup>2</sup> The same matrix was later used to prepare nanocomposites based on reduced graphene oxide and silica.<sup>3</sup>

Preparation of H-bonded thermoreversible networks was also explored via melt blending on different polymers, including phenoxy resins, functional polyolefines and polyvinylbutyral. Recent results, limitations and challenges for melt blending of these different types of polymer dynamic polymer networks will be presented and discussed in this talk.

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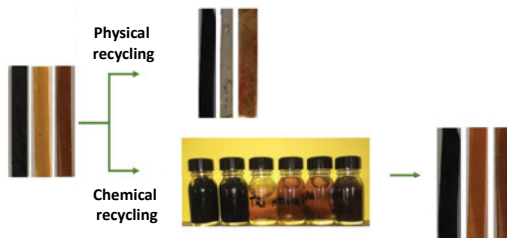
## IL-10

### DESIGN OF NEW DEGRADABLE NETWORKS USING CLEAVABLE IONIC LIQUID MONOMERS

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In the field of thermosetting polymers, ionic liquid monomers represent a real opportunity to design new sustainable and (multi)functional-dedicated polymer materials with enhanced properties such as thermal stabilities, mechanical performances, gas or water barrier properties, and self-healing properties. Recently, our laboratory has designed a new generation of more environmentally friendly, *i.e.* reusable and/or degradable epoxy-amine and epoxy-anhydride networks by using IL containing cleavable ester bonds. Thus, several architectures have been considered in order to highlight the impact of the architecture on the physical properties of the networks.<sup>1-3</sup>



Here, epoxy networks with glass transition temperatures including between 60 °C to 200 °C combining with good thermomechanical and mechanical properties, as well as hydrophobic behavior have been developed.

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## HIGH PERFORMANCE SELF-CATALYZED EPOXY-AMINE VITRIMERS FOR SUSTAINABLE COMPOSITES

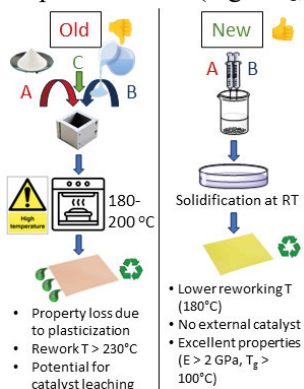
C. Ziane<sup>a,b</sup>, S. V. Zubkevich<sup>a</sup>, D. F. Schmidt<sup>a</sup>, A. S. Shaplov<sup>a</sup>

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Vitrimer networks combine the benefits of thermosets (high mechanical performance and dimensional stability) and thermoplastics (repairability, reprocessability, and recyclability) thanks to associative bond-exchange. Their capacity for reuse and recycling promises increased sustainability through reduced energy and resource consumption and waste minimization. Many transesterification (TER) based vitrimers have been reported, but few satisfy industrial needs for ease of processing (through the rapid, low-T curing of easy to handle liquid formulations), reuse / repair / recycling (at temperatures not far above  $T_g$ ), and structural performance (high  $T_g$ , modulus and strength).

Here we suggest novel high performance vitrimers based on epoxy-amine chemistry.<sup>1</sup> By varying the diamine and bis(epoxide), outstanding properties are realized ( $T_{onset}$  to 260°C,  $T_g$  to 145°C,  $\tau^* \sim 15-20$  min at 180°C,  $E'$  to 3 GPa). Tertiary amines generated during crosslinking serve as internal TER catalysts, avoiding the need for external catalysts that plasticize the network and may leach over time. These simple two-component liquid formulations cure readily at low T, making them particularly attractive for the composite and automotive industries.



**Figure 1.** Comparison of existing (left) and new (right) TER vitrimers

**Acknowledgements:** This work was supported by Luxembourg National Research Fund (FNR) via SusPoCo (PRIDE21/16748260) project.

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## IL-12

### END OF LIFE OF POLYMER BASED PRODUCTS AND ENVIRONMENTAL IMPACT ASSESSMENT

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Plastic pollution is considered one of the greatest dangers of the 21<sup>st</sup> century; it arises from the accumulation of plastic waste in various ecosystems, particularly oceans and waterways. Plastic pollution poses threats to wildlife, ecosystems, and human health.<sup>1</sup> The end-of-life problem of plastic products refers to the challenge of managing plastic waste once it has served its intended purpose. Historically, much of the plastic waste has been disposed of in landfills or incinerated. However, these disposal methods are unsustainable due to their environmental impacts and limited capacity. As a result, there is growing interest in finding more sustainable solutions for managing plastic waste: reusing, recycling and specially designing novel upcycling systems.

In the context of plastic products, Life Cycle Assessment (LCA) can be used to assess the environmental impacts of different types of plastics, design strategies as well as alternative end of life scenarios. In this research, LCA is used to evaluate different end of life scenarios of commonly used Polyamide (PA) based products<sup>2</sup> (nets, automotive sector) and alternative bio based and biodegradable polymers such as poly hydroxy butyrate (PHB)<sup>3</sup>: mechanical recycling and reusing, upcycling and biodegradation. By comparing the life cycle impacts, focusing in the Global Warming Potential, Terrestrial Eco toxicity, Marine Eutrophication, etc., opportunities to improve the sustainability of plastic products are identified.

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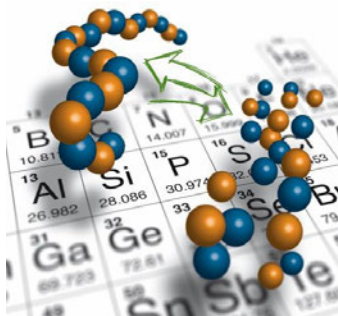
## IL-13

### AMINO ACID-PHOSPHORAMIDES: BIODEGRADABLE SYNTHETIC POLYMERS FROM NATURE'S BUILDING BLOCKS

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Traditional polymer chemistry has historically focused on producing exceptionally thermodynamically stable carbon-based macromolecules. In stark contrast, nature employs heterogeneous building blocks, such as phosphates, to create molecules in a state of constant flux. In this work, we harness the potential of phosphorus and amino acid-based molecules to design and synthesize biodegradable materials, aligning with nature's dynamic hydrolytically reversible bonds. Much like, for example, the reversible phosphocreatine pathway, we introduce phosphorus-nitrogen bonds to incorporate cleavage points in polymers, whereby the hydrolysis, and thus degradation rate, is finely tuned by the nature of the substituents on the P-N centre. We are building upon this P-N foundation, preparing phosphoramides and their chemically related phosphoramidates and phosphazenes and incorporating them into macromolecules. In stark contrast to many previously reported "degradable" materials, our creations degrade promptly under pH-neutral, biologically relevant conditions. We describe the design and synthesis of various materials, including photopolymers for 3D printing,<sup>1</sup> as well as super-soft elastomers. Moreover, we extend this to developing water-soluble drug carriers, bottlebrush polymers as potential polymer therapeutics<sup>2</sup> and MRI contrast agents



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## IL-14

### UTILIZATION OF RECYCLED POLYETHYLENE WASTE FOR OIL IN WATER SEPARATION

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This presentation reports our recent results in developing new polymeric media based on recycled polyethylene waste, which can be incorporated into current treatment technologies for the sorptive removal of oil from polluted waters. The first focuses on industrial wastewater – so-called produced water, and adsorbents are applicable for removing emulsified oil droplets. The target influent oil-in-water is 30 to 100 mg/L, and the target effluent is <10 mg/L. This request is dictated by governmental regulations for discharging industrial wastewater into land or sea. The second focuses on removing free oil spills from the water surface. Polymer structures include i.) grafted LLDPE-based adsorbents, ii.) foams produced from paraffin wax waste formed during LDPE synthesis, and iii.) foams from LDPE packaging waste. Removal of negatively charged crude oil droplets was ensured by grafting and direct polymerization of vinyl monomers containing N-based cations (e.g. [3-(methacryloylamino)propyl]dimethylamino-N-oxide) on polyethylene particles.<sup>1</sup> Free oil spills were efficiently absorbed by PE-based foams prepared by parallel foaming and crosslinking of waste paraffin wax<sup>2</sup> and LLDPE waste.

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## **ORAL COMMUNICATIONS**



### DESIGN OF INNOVATIVE STRATEGIES FOR THE SYNTHESIS OF BIO-BASED NANOCAPSULES: NEW PERSPECTIVES

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Encapsulation, a widely-used technology having diverse applications, involves the incorporation of active ingredients within an outer coating layer.<sup>1</sup> General aims include the controlled/selective release of the cargo and the ease of dosing of liquid/volatile materials as solid powders. While various synthetic approaches exist in the dedicated literature, sustainability remains a concern. Within this context, we focused on the development and optimization of an efficient protocol for producing bio-based and crosslinked micro- and nanocapsules by originally modifying the Mini Emulsion Solvent Evaporation (MESE) method, with a main emphasis on ensuring the sustainability of the entire process. Ethylcellulose (EC) is selected as bio-polymer for the external shell of our capsules. Additionally, we pushed forward the technology of crosslinking particles by developing a versatile and novel approach whose first step is conducted directly in the aqueous dispersing phase. This innovation led to the generation of EC core-shell capsules with a hard external coating layer capable of retaining the loaded active ingredient within the polymer shell.

The robustness of the methodology is extensively explored and various hydrophobic payloads are successfully incorporated. Specifically, we successfully encapsulated several hydrophobic palladium (II) catalysts, assembling innovative EC-based “nanoreactors” for catalysis applications, where the catalytic species should be ideally localized into the cavity or at least in the matrix network of the EC polymer shell.<sup>2</sup> These nanoreactors operate efficiently in cross-coupling reactions with minimal metal loadings and without the need for additional organic solvent, addressing the industrial demand for more environmentally-friendly and sustainable chemical process with the benefit of less metal contamination of the product.

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### DESIGN OF NOVEL CHITOSAN NANOPARTICLES FOR ANTIMICROBIAL APPLICATIONS

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Chitin and chitosan (de-acetylated chitin) are biopolymers derived mainly from langoustine shell waste and are great candidates for novel antimicrobial applications. Chitosan is soluble in weakly acidic aqueous solutions and is polycationic, which gives rise to its antimicrobial properties. We have employed computational simulations to study the binding of chitosan to two different substrates to design new composite nanoparticles with antimicrobial properties. The model substrates studied are chitin nanocrystals and silica nanoparticles. Chitin nanocrystals are stable, biocompatible and biodegradable, and silica nanoparticles have been used for medical applications for a long time and are readily available. Using fully atomistic molecular dynamics and enhanced sampling methods, we evaluated the binding energies of chitosan to the substrates and studied the dynamics of the adsorption process.<sup>1</sup> We show that the adsorption of chitosan to the chitin nanocrystal surface is driven by dispersion forces and hydrogen bonding, while the adsorption to the silica surface is driven by electrostatics. Furthermore, we have simulated the development of a biopolymer film at the substrates, providing insight into the loading capacity of the nanoparticles and the availability of the chitosan to interact with its environment. Our work therefore shows how computational simulations can be used to guide the design of novel composite materials for antimicrobial applications.

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### PREPARATION OF SELF-BLOWING NON-ISOCYANATE POLYURETHANE FOAMS STARTING FROM SOYBEAN OIL CYCLIC CARBONATE

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Polyurethanes (PU) foams represent a wide class of polymeric materials, with tunable features, having applicability in various sectors. Their synthesis involves the use of isocyanates, which are classified as carcinogenic, mutagenic, and toxic to reproduction (CMR). Greener and alternative routes have been widely proposed in the literature, meant to synthesize non-isocyanate PU (NIPU) foams. Bio-based NIPU foams are herein prepared through self-blowing route, involving the decarboxylation of cyclic carbonates assisted by thiolization. Bio-based precursors based on sustainable sources are selected: i.e. a synthesized 5-membered rings cyclic carbonate from epoxidized soybean oil and commercial bio-based diamine. Diatomite a natural and nanoporous material, was used as a cell nucleating agent. Different foams are prepared by varying precursor concentrations, curing temperatures, mixing time and characterized from morphological, thermal and mechanical point of view. NIPUs differ in terms of apparent density, morphological and mechanical properties. The selected process represents an alternative route to produce PU foams by utilizing sustainable components achieving a foam sustainable index  $\geq 70$  %.

**Acknowledgments:** *This study was carried out within the MICS (Made in Italy–Circular and Sustainable) Extended Partnership and received funding from the European Union Next Generation EU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) –MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3 –D.D. 1551.11-10-2022, PE00000004) and the Horizon EU project: GREen ENdeavor in Art ResToration (Green Art), Grant Agreement no. 101060941.*

### BIO-BASED HYBRID POLYURETHANE/INDIRECT POLYUREA/EPOXY FOAMS FOR CONSTRUCTIVE APPLICATIONS

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Constructive sector has high potential for effective implementation of more efficient use of biomass and industrial by-products for development of bio-based value added products. Among others, special attention should be paid for cellular materials – foams, being widely used for insulation, manufacturing of sandwich panels and other structural elements.

Novel organic-inorganic polyurethane/indirect polyurea/epoxy hybrid bio-based foams were prepared from bio-polyether/polyester polyols and bio-epoxy resins; polymeric methylene diphenyl diisocyanate (PMDI) and water glass (WG). Due to silicification reaction of WG, in-situ formation of inorganic fillers (polysilicate and sodium carbonate) with regularly/homogeneous distribution in the polymers matrix results in composite materials with enhanced thermal stability, flame retardancy and mechanical properties (compressive strength as well as E-moduli).

Formation of PUR-chains is carried out due to classical polyaddition reaction “polyol-PMDI”. Formation of polyurea is carried out in indirect two-steps way: i) reaction of PMDI with water from WG and formation of polyamines and CO<sub>2</sub> (which is responsible for foaming); ii) further reaction of newly formed amines with PMDI and formation of polyurea. At the same time, newly created NH<sub>2</sub>-groups work as hardener for epoxy resin. Different ratios of polyols, epoxy resins, PMDIs and WG allow moderating the foams density and (impact) mechanical properties.

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## POLY(HIPE)S FROM BIO-BASED MONOMERS

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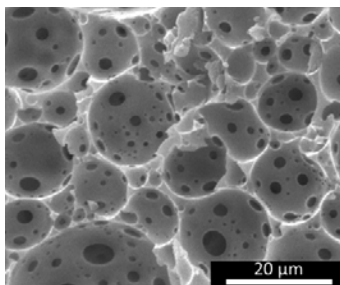
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Poly(HIPE)s are hierarchically porous monolithic polymer materials with an interconnected cellular morphology and a high degree of porosity, typically over 75%.<sup>1</sup> Due to their open porosity, low density and the possibility of porosity and morphology tuning, numerous applications have so far been demonstrated.<sup>2,3</sup> While most polyHIPEs are prepared from fossil sourced monomers, only a few examples of bio-based monomers being used are reported. We have included natural terpenes, terpenoids and modified terpenoids into high internal phase emulsions and resulting polymer monoliths exhibited high porosity and interconnected cellular morphology (Figure 1). Myrcene, limonene, carvone, among others and modified plant sourced monomers were successfully included in the prepolymerisation emulsion resulting in bio-based polyHIPEs.



**Figure 1:** Scanning electron micrograph of carvone based polyHIPE.

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### APPLYING MICHAEL 1,4-ADDITION REACTION TO PRODUCE BIO-BASED THERMOSET FOAMS FROM RAPESEED OIL

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The development of advanced new materials and technologies for bio-based products is immensely needed as the world is facing an ever-increasing variety of challenges due to increasing public concern about global sustainability. Thus, it is essential to develop materials that utilize renewable feedstock. In this study, a bio-based rigid thermoset foam material was developed from rapeseed oil. The principal curing reaction of the thermoset foams was Michael 1,4-addition. Several Michael donors were synthesized from rapeseed oil<sup>1</sup> and the acetoacetate group functionality on the foaming process and material properties was investigated. The foaming process was ensured by a physical blowing agent, expanding within the reacting foam mass due to the heat generated by the curing reaction. Moreover, the impact of a 1,1,3,3-tetramethylguanidine catalyst on foaming kinetics was analyzed using FOAMAT equipment, while the curing process of the bio-based thermoset was assessed with a dielectric polarization sensor. Additionally, the morphology of the developed foam was examined using scanning electron microscopy, and a thorough characterization was conducted using techniques such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and mechanical testing. The study uncovered a direct relationship between the crosslinking density of the foamed thermoset and its foaming behaviour, mechanical properties, and glass transition temperature. Remarkably, the rapeseed oil-based thermoset foams demonstrated relatively low thermal conductivity ranging from 33.9 to 35.4 mW/(m·K), making them promising materials for thermal insulation in civil engineering applications.<sup>2</sup>

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### **BUILDING THE FUTURE: INNOVATIONS IN SUSTAINABLE POROUS MATERIALS FOR SMART AND ENERGY-EFFICIENT CONSTRUCTION**

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To date “Energy efficiency” still turns out to play an important and valuable role in achieving the resolution of emergency related to the impact of energy consumption on global warming and the circular bio-economy in the construction sector. In this regard, the civil construction sector and beyond, new global technological standards, requiring increasingly “smart” infrastructure, are driving the development of building materials with multifunctional characteristics.<sup>1</sup> However, it is of paramount importance to pay attention to the sustainability of materials and technologies, with the possibility to valorize biomass products and making innovative functional bio-composites for the building sector. In this scenario, two different categories of sustainable porous materials have been developed:

- PUR cross-linked silica “aerogel-like”, hybrid PURs in which two porous morphologies co-exist simultaneously and a reduction of  $\lambda^1$  and increasing in mechanical properties are obtained.
- Bio-based composite polyurethane foams produced through the total replacement of petrochemical polyol with renewable polyols (Cardanol or biosuccinic-based polyol),<sup>2</sup> and the addition of functional nanofillers (silica and diatomite). permit to realize a bio-inspired Multifunctional Porous Materials (MPM), whereas, the different functionalities of each components make them suitable for several applications by satisfying, at the same time, different purposes (low thermal conductivity, good acoustic performances, fire resistance, etc).<sup>3</sup>

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## METAL IONIC LIQUIDS (MILS) AS EFFICIENT CATALYTIC CURING AGENTS OF EPOXY PREPOLYMER

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The 4,4'-methylenebis(N,N-diglycidylaniline) (TGDDM) is a tetrafunctional epoxy prepolymer, commonly used for high-performance carbon fiber-reinforced composites. The high functionality of TGDDM is useful for applications such as aerospace, automotive and aircraft. In fact, high cross-link densities and high glass transition temperature ( $T_g > 180^\circ\text{C}$ ) are required.<sup>1</sup> According to the literature, TGDDM is conventionally cured with aromatic diamines.<sup>2</sup> Ionic liquids have been recently reported in literature as efficient hardeners of epoxy prepolymers, mainly DGEBA,<sup>3,4</sup> improving their physical properties. However, the anionic polymerization of epoxy compounds, initiated and catalyzed by “catalytic curing agents” such as imidazole or ionic liquids, has been poorly investigated for TGDDM. This work proposes to study the polymerization of TGDDM induced by MILs<sup>5</sup>: (Bmim)2MCl4, where Bmim is 1-butyl-3-methylimidazolium and the metal M is cobalt, manganese or zinc. Here, high epoxy group conversion ( $> 98\%$ ) was obtained using only 5 phr of MILs. Moreover, these epoxy networks exhibit good thermal properties ( $> 350^\circ\text{C}$ ) and glass transition temperatures ranging from  $180^\circ\text{C}$  to  $200^\circ\text{C}$ . The kinetics curing was supervised by near infrared spectroscopy and differential scanning calorimetry.

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## VALORISATION OF COLLAGEN AS BIO-BASED INK FOR ADVANCED 3D PRINTING APPLICATIONS

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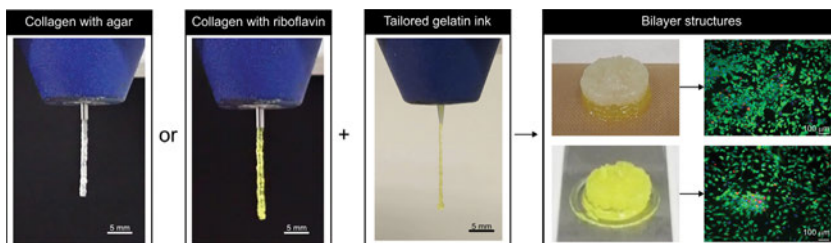
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Residues from slaughterhouses, such as hooves, bones, and skins, offer a significant opportunity for the extraction of proteins like collagen. This structural protein is not soluble in water, posing challenges for sustainable processing. In this study, collagen was valorised by mixing it with two different stabilizers: agar from *Gelidium sesquipedale* or riboflavin from *Eremothecium ashbyii*. Rheological characterization of both mixtures was carried out. First, temperature sweeps were performed to determine the most adequate printing temperature. The flow test showed the shear thinning behaviour of the samples, with a decrease in viscosity with a shear rate increase. Solid-like behaviour, storage modulus over the loss modulus, was confirmed by the frequency sweep. Bilayer structures were 3D printed, using tailored gelatin ink with the abovementioned collagen inks, to mimic the complexity of the skin. The 3D printed bilayer structures achieve more than 90% live cells in the indirect cytotoxicity test, suggesting the potential of these scaffolds for dermal tissue.



**Figure 1.** Ink formation using collagen inks and tailored gelatin ink. Bilayer scaffolds 3D printed with collagen-based ink and tailored gelatin ink and cytotoxicity results.



### CUTIN-BASED COATINGS FOR ENHANCED HYDROPHOBICITY AND ANTICORROSION PROPERTIES

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In the quest for sustainable solutions to environmental challenges, the use of agro-food byproducts as raw materials to produce eco-friendly coatings has gained considerable popularity. One of the most prevalent agricultural wastes are tomato peels, that are typically discarded during food processing. However, recent researches have highlighted their potential as a valuable resource, since they are very rich in natural biopolymers, such as polyesters.<sup>1</sup> The main component is cutin, an amorphous polymeric network of polyhydroxylated C16 and C18 fatty acids monomers.<sup>2</sup> The main characteristic of this biopolyester is its high hydrophobicity, that thus make cutin particularly suitable for applications as coating. Our research uses hydrolyzed cutin monomers, extracted through alkaline hydrolysis from tomato agro-wastes on an industrial scale,<sup>3</sup> to create hydrophobic poly(ester-urethane) resins by copolymerization with 1,4-butanediol and isophorone diisocyanate. This approach combines the biodegradability of the polyester component with the versatility and adhesivity of the polyurethane component. The coatings were characterized by spectroscopic (FT-IR, <sup>1</sup>H and <sup>13</sup>C-NMR) and thermal (TGA, DSC) analysis and subsequently applied on paper and on copper substrates. The barrier and anticorrosion properties were tested, showing excellent impermeability and high protective efficiency against corrosion of tested substrates (aluminum and copper alloys).

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## O-11

### CELLULOSE DISSOLUTION AND ACETYLATION IN MIXTURES OF IONIC LIQUIDS AND MOLECULAR SOLVENTS. THE FRUITFUL SYNERGISM OF EXPERIMENT AND THEORY

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We studied the dependence of dissolution of microcrystalline cellulose (MCC) in binary solvent mixtures of ionic liquids (ILs) and molecular solvents (MSs), DMAc and DMSO. The ILs were based on 1-(n-butyl)-3-methylimidazolium cation, BuMeIm<sup>+</sup>, with acetate (AcO<sup>-</sup>) and chloride (Cl<sup>-</sup>) anions. We changed the mole fraction of the MS ( $\chi_{\text{DMAc}}$  or  $\chi_{\text{DMSO}}$ ) and the temperature (T). The order of maximum m% (mass fraction of dissolved MCC) was BuMeImAcO-DMSO > BuMeImAcO-DMAc >> BuMeImCl-DMSO. We employed molecular dynamics (MD) simulations to rationalize this order, by calculating the root-mean-square-deviation (RMSD) and the radial distribution function, g(r). Values of RMSD showed that chain separation of the biopolymer model follows the same order as maximum m%; more chain separation indicates larger m%. Additionally, the maximum values and the sharpness of the g(r) peaks followed the same order of m%, due to hydrogen bonding between the hydroxyl groups of the biopolymer and ions of the IL. Conclusions from MD simulations were corroborated by turbidity and conductance measurements of cellobiose-IL-MS solutions. More chain separation is also expected to influence biopolymer reactivity. This was confirmed by the degree of substitution (DS) of cellulose acetate, synthesized in these media. Under comparable experimental conditions, the observed order of DS was the same as m%: 1.92, 0.98 and 0.1 for acetylation by acetic anhydride in BuMeImAcO-DMSO, BuMeImAcO-DMAc, and BuMeImCl-DMSO, respectively. Thus, theoretical calculations can be fruitfully employed to predict the best solvents for biopolymer dissolution/derivatization, saving labor and material.

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## BIO-SOURCED UNSATURATED POLYESTERS FOR 3D-PRINTING

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The replacement of petro-sourced chemicals for molecules from renewable sources is an important topic for the chemical industry. Polyesters are the family of polymers the most studied from bio-sourced monomers. They are vastly employed in a broad range of applications.<sup>1</sup> A few processes have been developed for the synthesis of conventional polyesters, such as PET, PBT or PLA.<sup>2</sup> Synthesised from the transformation of cellulose, maleic acid is one of the most promising bio-sourced monomers for the preparation of unsaturated polyesters.<sup>3</sup> Indeed, the available double bond allows to use them as photocurable resins. The diols used in this study are also bio-based, obtained from cellulose or plant oils. They are linear, branched diols or glycols. Low molecular weight polyesters are targeted, around 1000 – 2000 g.mol<sup>-1</sup>, as resins of low viscosity are required for 3D-printing. To synthesise these polyesters, 5 fully bio-based organo-catalysts are screened. Depending on the catalyst used or the diol used, the *cis*-/*trans*- content of the resulting polyester is changed. With the different catalysts, polyesters containing from 10 to 90% of *trans*- conformation can be obtained. With linear diols, polyesters with low *trans*- content are obtained, while with ramified diols and glycols, high *trans*- content are obtained. More polyesters have *trans*-content, more they are visually viscous. To decrease the viscosity and improve the reactivity to UV light, the resins can be combined with several reactive diluents. They can be acrylates, terpenes, thiols.

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## NOVEL SUSTAINABLE SYNTHESIS OF FORMALDEHYDE-FREE PHENOLIC RESINS BY REACTIVE EXTRUSION

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Over the past century, phenolic resins have known a continuous development for broad range of applications (wood adhesive, electronics, transportation, buildings).<sup>1</sup> Phenolic thermosets exhibit strong mechanical properties with high thermal and chemical resistance due to a highly crosslinked network.<sup>2</sup> However, these resins are synthesized from phenol and formaldehyde which are both toxic fossil-based monomers.

This research introduces a novel method for synthesizing thermosetting phenolic oligomers through a green solvent-free and flexible reactive extrusion route. In that frame, terephthalaldehyde, a non-toxic aromatic dialdehyde, has been selected to substitute formaldehyde while resorcinol has been chosen as a replacement of phenol. The structure of both monomers leads to an enhanced reactivity allowing the bulk synthesis in a short residence time (few minutes) inside the extruder at temperatures over 150°C. First, the mechanism of the chemical reactions occurring in these processing conditions were determined (NMR and mass spectrometry). In addition, differential scanning calorimetry analyses were carried out to investigate the kinetics of the reactions and to evaluate the activation energies (37 to 67 kJ.mol<sup>-1</sup>). It was demonstrated that multiple and consecutive reactions (electrophilic aromatic substitution and condensation) occur during the synthesis by reactive extrusion and that a post-reactivity may benefit specific applications.

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## **IMPROVING THERMAL RESISTANCE AND IMPACT TOUGHNESS OF PLA VIA MELT BLENDING WITH PEICT: EFFECT OF ISOSORBIDE COMONOMER RATIO**

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Nowadays, the growth of PLA market into high-value engineering sectors is mainly hindered by its intrinsic brittleness and low heat resistance. Several methods have been used to overcome PLA weaknesses. Among them melt blending with engineering thermoplastics could represent a cost-effective processing route. PEICT (Poly (ethylene glycol 1,4-cyclohexane dimethylene isosorbide terephthalate) which incorporate the 100% biobased isosorbide comonomer is widely deployed in hot-fill packaging industry. It combines a low stress-cracking, high impact-resistance with an eco-design flexibility and transparency. PEICT could be thus a potential candidate to improve the final properties of PLA. In this context, PLA/PEICT blends (50 wt-% PEICT) were processed by twin screw extrusion followed by injection molding without compatibilizers. First, melt surface tension of coexisting components, morphology, mechanical, impact strength and related HDT and Vicat softening temperatures were investigated. Different PEICT grades were selected involving various  $T_{\alpha}$  relaxation temperatures ranging from 90 °C to 120 °C. The effect of ISB comonomer ratio (up to 29.3mol-%) on final properties was highlighted. A good compromise between all physical performances was noticed with 9.4mol% of ISB comonomer. The Young modulus for PLA/PEICT blends were found to follow the rule of mixture without compromising the tensile strength. Compared to the neat PLA, the elongation at break of the blends was improved by five times. More interestingly, an increase of 193% in impact strength was observed reflecting a transition from fragile to ductile behavior. Finally, HDT and VST data showed that the addition of PEICT increased significantly the thermal resistance of blends. In conclusion, PLA/PEICT associations developed in the present work represent an interesting polymer combination with good cost-renewability-properties balance suitable for high-temperature applications such as cosmetics and beverage industries.

### **MELT SPINNING OF BIO-BASED THERMOPLASTIC POLYURETHANES IN INDUSTRIAL ENVIRONMENT**

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Elasticity is the provision of elongation and recoverability, affecting a textile's functionality. In many textiles, elasticity is provided by "elastanes", yarns that consist of elastomeric polyurethane (PU). The polymer chains of an elastomeric PU are morphologically structured in soft (more amorphous) and hard (more crystalline) segments to allow high elongation and recovery.<sup>1</sup> This morphological and chemical constitution results in the elastomeric character of elastane, requiring the application of solution spinning technologies for filament yarn production as these PU are not meltable. Solution spinning of PU causes challenges: Production speed is slow and conversion costs are high, thus the obtained filament yarns are expensive. Additionally, for dissolving the PU potentially hazardous solvents such as dimethylformamide (DMF) must be used and need to be recovered. These challenges may be overcome by switching from solution to melt spinning technologies. Specially designed thermoplastic polyurethanes (TPU) fulfil property and processing needs of high elasticity and melt spinnability. They are linear but still basically structured in hard and soft segments. Soft segments of TPU are typically composed of polyols while hard segments are composed of isocyanates and a chain extender.<sup>2,3</sup>

Polyols can be obtained from bio-based sources. In this presentation, key challenges and techniques for the melt spinning in industrial environment (TRL 6 to 7) of TPU made from polyols of bio-based sources are presented.

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## O-16

### SMART POLYMERS AND STRUCTURES: FROM 3D TO 4D PRINTING

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With progressive advancements in various cutting-edge technologies, smart structures with both robust stability and manipulatable functions are highly pursued to meet the critical requirements in the various complicated environments. On the other hand, development of additive manufacturing technology has fundamentally exhibited great advantages, which provides an exclusive platform for manufacturing smart structures. Based on 3D printing added with additional dimension, either time or space, for manipulating shape, property or functions, in the present talk, I would initially analyze the key scientific issues in 4D printing technology, including design, materials, apparatus, software, manipulation and applications. Based on an advanced structure strategy for achieving smartness, I would give several examples based on our current studies for better understanding how 4D printing play a significant role in designing and manufacturing smart structures and smart devices based on the uniqueness of various materials. The 4D printing technology is expected to open up a novel strategy for substantially endowing the advanced structures with smartness and exceptionality.

## O-17

### HMF: THE VERSATILE KEY BIOBASED BUILDING BLOCK

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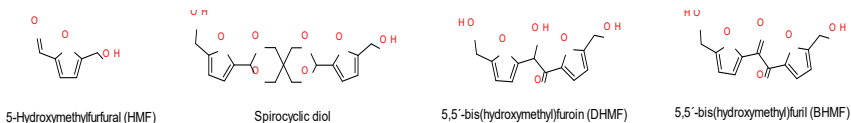
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5-Hydroxymethylfurfural, HMF, has long been known as the imperative biobased starting material for a significant number of sustainable key green chemicals like essential diols and dibasic acids amongst others. Various routes for HMF have been developed but still, the availability of HMF is low, and thus the price is prohibitively high. Within the STEPS program we have recently elaborated a simple and efficient process for HMF in high yield in only one step starting from fructose. Although the societal demand for biobased materials is constantly increasing the price of such materials is always challenged by the normally much lower price of the existing fossil-based analogues.

In this contribution, we want to emphasize several functional molecules that have been produced from HMF. One example is a rigid spirocyclic diol based on HMF and pentaerythritol that can be polymerized to renewable polyesters and poly(urethane-urea)s. This diol enables the production of sustainable rigid polyurethane materials like coatings and foams. The second example is 5,5'-bis(hydroxymethyl)furoin (DHMF) which is prepared by carboligation of two HMF molecules using chemical catalysts or enzymes. A third example is 5,5'-bis(hydroxymethyl)fural (BHMF) obtained by oxidation of DHMF. DHMF and BHMF are currently being investigated as cross-linkers for polyurethane binders with applications in floor coatings. Both DHMF and BHMF are also expected to have great potential as building blocks for polyesters and polyurethanes.





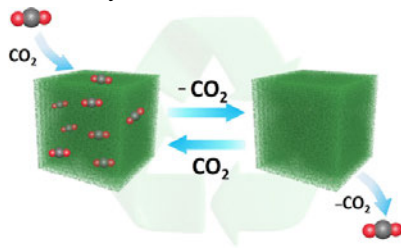
## HIERARCHICAL METAL-ORGANIC AEROGEL AS A HIGHLY SELECTIVE AND SUSTAINABLE CO<sub>2</sub> ADSORBENT

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Amorphous aerogels, while showcasing significant potential as CO<sub>2</sub> adsorbents due to their high surface areas and ease of diffusion, often fall short in applications due to their lack of well-defined porosity and selective adsorption capabilities. This study introduces a novel hierarchical metal-organic aerogel (HMOA) engineered to overcome these limitations. The aerogel features meticulously structured micropores (diameter ~1 nm) achieved through the coordinative integration of chromium(III) ions and organic ligands. This design not only provides the HMOA with a high surface area but also ensures a reusable surface characterized by optimal binding energies for CO<sub>2</sub> adsorption. Impressively, the aerogel demonstrates a high CO<sub>2</sub> adsorption capacity, exceptional CO<sub>2</sub>/N<sub>2</sub> selectivity as per the ideal adsorbed solution theory (IAST), and maintains 100% regenerability over 20 vacuum-induced cycles. Additionally, the HMOA can be synthesized via straightforward ambient drying techniques, preserving its microporous network. The robustness of this micropore formation, combined with the aerogel's flexible coordination framework, positions the HMOA as a viable and scalable solution for industrial CO<sub>2</sub> capture.



**Figure:** Hierarchical metal-organic aerogel as sustainable CO<sub>2</sub> adsorbent.

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## O-19

### BIOMASS-DERIVED HIGH-PERFORMANCE POLYIMIDE: STRATEGIES OF AROMATIC DIAMINES SYNTHESSES

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Polyimides (PIs) are renowned for their exceptional performance characteristics and are widely utilized across diverse industries, including automotive, aerospace, and electronics. However, the aromatic diamine monomers are predominantly sourced from petrochemicals. To address this challenge, we have devised various strategies for synthesizing alternative aromatic diamines utilizing biomass-derived materials, particularly 4-aminocinnamic acid<sup>1</sup> and 4-aminophenylalanine<sup>2-4</sup>. Subsequently, these diamines were condensed with available dianhydrides to prepare different series of PIs. The structural elucidation of these aromatic diamines and their corresponding PIs was comprehensively conducted using techniques such as FTIR, NMR, and Mass spectroscopy. Thermomechanical properties of these PIs were determined through TGA, DSC, and tensiometer analysis. The resulting PIs exhibited a diverse range of properties, including ultra-high thermomechanical stability, solubility, and the potential for self-assembly.

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### SUSTAINABLE APPROACHES TOWARDS NEW FURAN-BASED POLYMERS: NEW COPOLYESTERS BASED ON 5,5'-OXYBIS(METHYLENE)BIS(FURAN-5,2-DIYL)DIMETHANOL (OBMF-H)

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Due to their unique set of properties, polymers have quickly become an irreplaceable material to our society, with world polymer production reaching over 400 Mt in 2022.<sup>1</sup> The vast majority of these polymers (over 90%) are based on fossil resources, therefore, in a quest to develop more sustainable options, redesigning plastics is a priority already in place. Among the countless polymers that fit this category, furan-based polyesters, such as poly(ethylene 2,5-furandicarboxylate) (PEF) are some of the most investigated.<sup>2</sup> However, despite their greener origin, the conventional synthesis of these polymers still involves harsh conditions such as high temperatures (180 - 220 °C), with the majority making use of metal-based catalysts. So, another aspect of moving towards greener materials is to rethink their synthesis and develop more sustainable approaches. In this work, we studied the enzymatic synthesis of furan-based polyesters and copolyesters using 5,5'-oxybis(methylene)bis(furan-5,2-diyl)dimethanol (OBMF-H),<sup>3</sup> an HMF more stable derivative. The obtained copolymers were characterized by FTIR, <sup>1</sup>H and <sup>13</sup>C NMR, GPC, XRD, DSC, and TGA.

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## O-21

### ITACONIC ACID POLYMERIZATION: FROM OLIGOMERS TO MICROGELS

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Itaconic acid (ITA) has been identified as one of the most promising bio-based chemical building blocks and a potential sustainable substitute for the widely used thickener agent based on poly(acrylic acid).<sup>1</sup> Previous researches have investigated the radical homo-polymerization of ITA in aqueous media, showing slow kinetics, small conversion and low molecular weight.<sup>2,3</sup> In this study, we deeply investigate the radical polymerization of ITA to overtake the current limit, reaching the optimal condition in term of monomer solubility and polymerization rate. Then, we propose a straightforward approach to fabricate bio-based soft colloids composed entirely of ITA, for applications in cosmetic formulations. Microgel-like particles were obtained through mechanical fragmentation of pITA hydrogels. Their properties in aqueous suspension were investigated utilizing steady, oscillatory rheology, and confocal microscopy. The effects of polymer concentration and degree of ionization on microstructural properties and rheological behavior were investigated. The resulting soft colloids exhibit different architectures, ranging from slightly branched polymers to compact microgels with heterogenous shape.

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**FROM URETHANE BIS-CARBONATES MONOMERS  
TO POLYURETHANE-HYDROXYURETHANE POLYMERS**

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Polyurethanes (PUs) are versatile polymers with a wide spectrum of applications. PUs are commonly produced in the industry via the polyaddition of isocyanates with polyols. However, isocyanates are harmful to the environment and human health.<sup>1,2</sup> As a *greener* route, non-isocyanate polyurethanes (NIPUs) are an interesting alternative to replace conventional PUs.<sup>1,2</sup> Among the different routes towards NIPU thermoplastic and thermosets, one of the most promising is the polyaddition of pluriamines reacting (poly-) cyclic carbonates.<sup>1</sup> leading to polyhydroxyurethanes (PHUs). This class of polymers differentiates from conventional PU due to the presence of primary and secondary hydroxyl groups on the polymeric backbone. Urethane bis-carbonate monomers were very scarcely reported in the literature,<sup>3</sup> nonetheless, they were not valorized. In this work, urethane-activated bis-cyclic carbonate was synthesized in a two-step isocyanate-free route reacting glycerol carbonate, difunctional amine, and dimethyl carbonate.<sup>3</sup> Subsequently, the conversion rate of the substrate was compared with other cyclic carbonates to evaluate the activating effect of the urethane group in beta-position. Finally, thermoplastics and thermosets were synthesized, and their thermal and adhesive properties were tested on different substrates.

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**RESPONSIVE AND GREEN POLYESTERS BY RADICAL RING-OPENING POLYMERISATION**Y. Deng<sup>a,b</sup>, F. Mehner<sup>a,b</sup>, T. Meißner<sup>a,b</sup>, J. Gaitzsch<sup>a</sup>*<sup>a</sup>Leibniz-Institut fuer Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden, Germany**<sup>b</sup>Technische Universität Dresden, Fakultät Chemie und Lebensmittelchemie, Bergstraße 64, 01069 Dresden, Germany (gaitzsch@ipfdd.de; <https://www.ipfdd.de/gaitzsch>)*

Polyesters as biodegradable polymers play a key role in solving increasingly pressing environmental challenges. Radical ring-opening polymerisation (RROP) of cyclic ketene acetals (CKAs) presents a synthetic strategy to synthesise functional polyesters with a broad scope of accessible properties like semi-crystallinity, hydrophilicity and pH sensitivity.<sup>1</sup>

RROP bares a plenitude of possible features that can be included into the final fully biodegradable polymers. In polymerising the 2-methylene-1,3-dioxepane (MDO) towards poly-MDO, increasing the branching density systematically decreased the melting temperature. It allowed to fine-tune macroscopic properties of the material.<sup>2</sup> Polymerising the hydrophilic CKA 2-methylene-1,3,6-trioxacane (MTC) to poly-PMTC now opened up a new array of options as potent non-toxic and equally degradable nanoparticles.<sup>3</sup> It was also the ideal candidate to be copolymerised with amine-bearing CKAs (Alk-MACs), which then produce a broad range of pH responsive polyesters.<sup>4</sup> Hence, the polymer composition and polymer architecture can be varied well within RROP to yield a range of functional and fully biodegradable materials that are fit to meet the challenges of the modern society.

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## HIGH BIO-BASED CONTENT WATERBORNE POLYURETHANE-UREAS FOR FOOTWEAR APPLICATIONS

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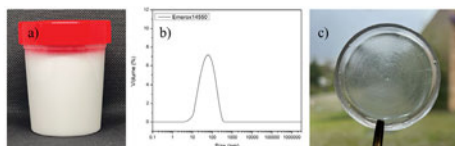
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The versatility of waterborne polyurethane-urea (WBPUU) dispersions makes them promising materials according to specific demands, including as adhesives in footwear applications. Adopting sustainable synthesis routes and using bio-based resources is gaining attention within the circular bioeconomy. In this work, WBPUU dispersions were formulated with different commercial polyester polyols with a biobased content varying from 80-100% through a two-step polymerisation process, following a base process developed in the group complying with EU regulations. A reference synthetic polyol-based formulation was also prepared for comparison purposes. The particle size, solids content, viscosity, and pH of the dispersions were determined, and films were produced and analysed regarding morphology, physicochemical and thermal properties (Figure 1). Overall, the bio-based WBPUU dispersions and films showed promising properties to replace the synthetic counterparts.



**Figure 1.** a) Dispersion, b) particle size distribution, and c) film.

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## METHODS FOR SYNTHESIS HIGH MOLECULAR WEIGHT POLY(ITACONIC ACID)

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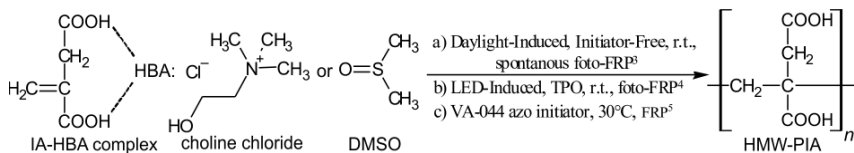
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Itaconic acid (IA) is a vinyl monomer of renewable origin, industrially produced by biotechnological methods from biomass feedstock. The free-radical polymerization (FRP) of itaconic acid gives the polyelectrolyte - poly(itaconic acid) (PIA). However, so far typical methods of IA polymerization in aqueous or organic solutions only allow to obtain PIA with low to moderate molecular weight ( $M_w = 1\ 000 - 100\ 000\ \text{g/mol}$ ).<sup>1,2</sup>

We have recently succeeded in developing methods (Fig. 1) to synthesize high molecular weight PIA (HMW-PIA) which molecular weight is an order of magnitude higher ( $M_w = 100\ 000 - 500\ 000\ \text{g/mol}$ ).<sup>3,4,5</sup>

To obtain HMW-PIA, the key factor is to carry out FRP at mild temperatures (20 – 30°C), but due to IA low solubility in water, the process must be carried out in systems where IA forms hydrogen bond complexes with the strong hydrogen bond acceptor (HBA) such as quaternary ammonium salts (e.g. choline chloride) or dipolar aprotic solvents (e.g. DMSO).



**Fig. 1:** Scheme for preparation HMW-PIA by mild temperature FRP.

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### **UNLOCKING VEGETABLE WASTE POTENTIAL: A NOVEL CIRCULAR BIOREFINERY APPROACH IN SUSTAINABLE BIOFILM FORMATION**

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Bio-waste produced in the EU ranges between 118 to 138 million tonnes yearly.<sup>1</sup> The 60 % is composed by food waste, mainly consisting of natural macromolecules such as cellulose, lignin, hemicellulose and pectine. Actual management methods, such as landfilling and incineration, break these structures down, underutilizing their potential and posing environmental concerns. This work builds upon a different concept of recycling, where the processing steps aim to be minimal and to preserve the natural species and their value, transferring the structural properties from the plant to the resulting material.<sup>2</sup> In particular, we propose a general protocol for integrating mechanically pre-treated waste, in the reported example green kiwi peel (GKP), into biofilms simply blended with biocompatible and sustainable film-former polymers. The process consists in drying, powdering and partially hydrolyzing the vegetable powder: this step can be performed either with mild acid or different enzymatic cocktails. The biological treatment allows for the fine tuning of the treated powder composition, affecting in the desired direction the output material features, with a special focus on the mechanical properties. Finally, we have preliminary evidence that the discarded liquid from both processes can be valorized as growth media for yeast growth that are able to produce species that can be inserted in the process again, as a circular biorefinery protocol.

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### OPTIMISATION OF GELATINE-ALGINATE HYDROGELS SYNTHESIS FOR 3D PRINTING

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Recent advances in 3D printing and hydrogel-based materials have created new opportunities for transformative applications in several fields, including biomedicine, pharmaceuticals, and customized nutritional products. This study investigates the development of printable inks for 3D-printed structured materials using gelatin-alginate hydrogels. By incorporating an enzymatic crosslinking mediated by transglutaminase (TGase) and reinforced with cellulose nanocrystals (CNC), hydrogels can be tailored to have specific rheological properties. This fact enables the customization of products to meet individual patient requirements, namely the incorporation and delivery of bioactives. The composite hydrogel developed in this study, which varied in TGase concentration (0-30 U/g gelatin) and CNC content (0-0.25%, total-basis), exhibited elastic behaviour and improved rheological properties after TGase treatment and the CNC incorporation. Increasing enzyme concentration led to increases in viscosity (0 U/g: 259.70 Pa.s; 30 U/g: 1,197.11 Pa.s) and storage modulus (10 U/g: 196.61 Pa; 30 U/g: 448.99 Pa). Moreover, incorporating 0.20% CNC showed favourable effects for the optimised system (20 U/g TGase concentration).

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## MICROSTRUCTURE AND MECHANICAL PROPERTIES OF COPOLYMER SYNTHESISED FROM PET AND PCL TRANSESTERIFICATION

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Only 17% of recycled polyethylene terephthalate (PET), a popular plastic used in beverage and food packaging, is estimated to be reapplied to its original applications.<sup>1</sup> The property's degradation associated with mechanical recycling processes limits the application of recycled PET. Therefore, improving the sustainability of PET requires uncovering new recycling methods to diversify and enhance recyclability. Copolymerizing PET and polycaprolactone (PCL) through catalytic transesterification offers a rapid modification to convert PET into a new copolymer with the potential to offer a more sustainable alternative to polybutylene terephthalate (PBAT).<sup>2</sup> One of the essential aspects is understanding the effectiveness and limitations of variables in controlling the microstructure through catalytic transesterification and the mechanical properties/microstructure relationships. The homopolymer reagent ratio was the most significant factor in determining their respective block lengths in the copolymer. Moreover, other experimented factors, such as catalyst loading, shear rate, and reaction time, effectively reduce homopolymer block length until a statistical copolymer is reached. Due to its highly amorphous nature, the copolymer's mechanical property heavily depends on its microstructure and molecular mass. The findings will help future studies design a copolyester's microstructure and properties from copolymerizing with polyesters through catalytic transesterification.

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## RING-OPENING TERPOLYMERISATION OF ELEMENTAL SULFUR WASTE WITH PROPYLENE OXIDE AND CARBON DISULFIDE VIA LITHIUM CATALYSIS

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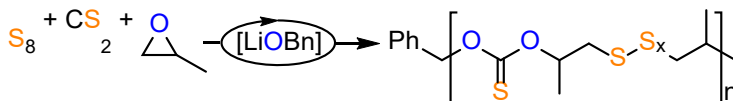
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Elemental sulfur, a waste product of the oil refinement process, represents a promising raw material for the synthesis of degradable polymers. We show that simple lithium alkoxides facilitate the polymerisation of elemental sulfur S<sub>8</sub> with industrially relevant propylene oxide (PO) and CS<sub>2</sub> (a base chemical sourced from waste S<sub>8</sub> itself) to give poly(monothiocarbonate-alt-S<sub>x</sub>) in which x can be controlled by the amount of supplied sulfur. The in-situ generation of thiolate intermediates obtained by a rearrangement, which follows CS<sub>2</sub> and PO incorporation, allows to combine S<sub>8</sub> and epoxides into one polymer sequence that would otherwise not be possible. Mechanistic investigations reveal that alkyl oligosulfide intermediates from S<sub>8</sub> ring opening and sulfur chain length equilibration represent the better nucleophiles for inserting the next PO if compared to the trithiocarbonates obtained from the competing CS<sub>2</sub> addition, which causes the sequence selectivity. The polymers can be crosslinked in-situ with multifunctional thiols to yield reprocessable and degradable networks. Our report demonstrates how mechanistic understanding allows to combine intrinsically incompatible building blocks for sulfur waste utilisation.



**Figure 1.** Controlled synthesis of poly(ester-alt-polysulphide) from an epoxide, anhydride, and elemental sulphur.

**MULTICOMPONENT POLYCONDENSATION: A NOVEL  
SUSTAINABLE APPROACH TO POLYTHIOUREA USING  
ELEMENTAL SULFUR**

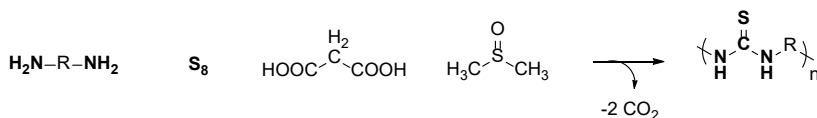
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Malonic acid and its derivatives have long been recognized for their propensity to undergo mono-decarboxylation under relatively mild conditions, primarily serving as a C<sub>2</sub> synthon. However, in this communication, we introduce a novel application wherein they act as a C<sub>1</sub> synthon through a double-decarboxylation process facilitated by sulfur and dimethyl sulfoxide (DMSO). In the presence of amines as nucleophiles, this method enables the synthesis of a diverse array of thioureas,<sup>1</sup> thioamides,<sup>2</sup> and *N*-heterocycles<sup>3</sup> in good to excellent yields under mild heating conditions<sup>[4]</sup>. Interestingly, this multicomponent strategy can be extended to polycondensation, thus affording high molar mass polythioureas.



**Figure 1.** Synthesis procedure of polythioureas used in this work.

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### PHYSICAL RECYCLING OF PVC: PRESSURIZED FLUID EXTRACTION FOR PLASTICISER REMOVAL

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'Legacy' plastics can pose significant problems for recycling. This is the case of materials that were formulated long ago, using substances which are now currently regulated. Widely used in construction and building, PVC materials frequently present this issue, due to large lifespans and significant presence of 'legacy' additives such as phthalates plasticisers and lead stabilisers in their composition. Deformation through solvent-based techniques, such as dissolution-precipitation and solid-liquid extraction, seeks the separation of these additives to obtain a purified polymer that can better be re-incorporated in the value-chain.<sup>1</sup>

This work focuses on Pressurized Fluid Extraction (PFE), which uses organic solvents at temperatures and pressures above their normal boiling point to obtain faster mass-transfer kinetics and higher separation efficiencies. Despite being widely used in solid sample analysis and having several mentions of being a promising technique on the scope of recycling, there is a limited number of works using PFE for PVC feedstocks. Furthermore, there is also a lack of knowledge regarding the mass-transfer kinetics behind plastic PFE.<sup>2,3</sup>

Using several PVC feedstocks with known compositions, we were able to follow the PFE of phthalate plasticisers and we studied several factors that impact the separation efficiency, such as extraction parameters, the nature of the plasticiser, presence of other additives and the molecular weight distribution of the PVC resin. Optimized extraction parameters lead to phthalate free, REACH compatible material. Overall, our results highlight the importance of considering the solubility of the additive in the solvent and help gather missing data on additive diffusivity inside the polymer matrix, opening the way for a scale up of the technique.

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### SUSTAINABLE FIBERS BASED ON RECYCLED PET

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An increasing awareness on the environmental impact of fossil-based plastics has motivated industries and society to transition to a circular economy. In the last years, the recycling of PET has grown significantly due to advances in collection and recycling technology.<sup>1</sup> This has offered the possibility to use recycled PET (rPET) in the textile industry with a significant decrease in carbon emissions and raw material consumption.<sup>2</sup>

The aim of this work was the production of sustainable microfibers made of rPET and bio-PET, with improved overall performance and durability for non-woven applications, particularly in personal protective equipment. The focus was to use rPET flakes as simple as possible in terms of plastic sorting, and optimize their properties during twin-screw extrusion. Primary and secondary antioxidant additives were incorporated into the blend to prevent polymer degradation caused by heat, light and oxygen exposure. An epoxy-based chain extender was also introduced to ensure the recovery of the mechanical properties of the rPET. The effect of the additives on the thermal/mechanical/rheological properties of rPET were analyzed. The addition of the chain extender caused an increase in the molecular weight. The rheological tests of rPET formulations revealed differences in intrinsic viscosity values, that ranged from 0.4 to 0.8 dl/g, being highly associated to differences in fiber formability. By incorporating essential additives, it was possible to obtain mechanically robust and thermally stable microfibers, with great potential to be used in novel sustainable non-woven products.

**Acknowledgements:** *This abstract was developed within the scope of the Innovation Pact “Sustainable Plastics”, co-financed by NextGenerationEU, through the Business Innovation Agendas’ investment from the Recovery and Resilience Plan (RRP) - Project no.7.*

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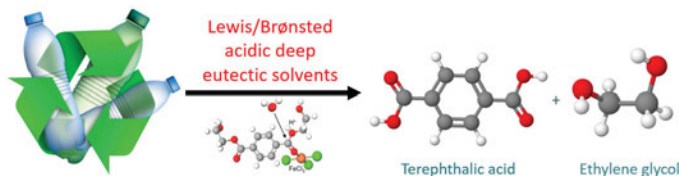
## DEPOLYMERIZATION OF POLYETHYLENE TEREPHTHALATE (PET) BASED-COMPLEX WASTE PLASTICS WITH LEWIS/BRØNSTED ACIDIC DEEP EUTECTIC SOLVENTS

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The relentless rise in the demand for PET manufacturing poses a significant environmental issue.<sup>1</sup> The chemical recycling of polyethylene terephthalate (PET) holds potential as an effective method for generating recycled monomers. Recently, deep eutectic solvents (DESs) have shown interesting proprieties in the glycolysis and hydrolysis of PET, occasionally even under mild operating conditions.<sup>2,3</sup> This research introduces bifunctional Lewis/Brønsted acidic deep eutectic solvents (LBDESs) containing  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  combined with various acids for PET depolymerization (Figure 1). LBDESs formed with methanesulfonic acid and *p*-toluenesulfonic acid are capable of quantitatively depolymerizing PET under mild conditions (100 °C, 1h), producing high purity terephthalic acid (TA) in high yield (>96 %).<sup>4</sup> For weaker, more cost-effective and sustainable Brønsted acids, like acetic acid, a straightforward post-reaction procedure significantly enhances the yield of TA.<sup>5</sup> Additionally, employing the aforementioned LBDES, we illustrate the effect of depolymerization with different sources of post-consumer PET that frequently are challenging to mechanically recycle due to the presence of various additives.



**Figure 1.** Depolymerization of PET-based complex waste plastics with LBDESs.

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## UPCYCLING OF PVC TO EFFICIENT CATALYTIC SINGLE-CHAIN NANOPARTICLES

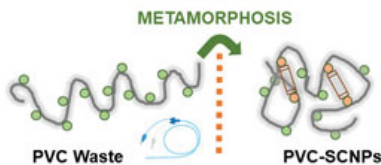
J. A. Pomposo<sup>a,b,c</sup>

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This talk reports on a complementary concept of polymeric waste valorization (upcycling) by metamorphosis of a commodity plastic of common use in daily life like polyvinyl chloride (PVC) to “valorized” PVC single-chain nanoparticles (vPVC-SCNPs).<sup>1</sup>



The full valorization process can be run in a green, dipolar aprotic solvent like *N*-butylpyrrolidone (NBP) and involving, when required, a simple mixture of ethanol and water (1/1 vol.) as non-solvent, leading to well-defined, uniform vPVC-SCNPs that are stable during storage in the solid state for months. These nanoparticles when loaded with 7.3 mol % of Cu(II) ions become an efficient and recyclable catalyst in the solvent-free homocoupling reaction of polar alkynes, showing enzyme-mimetic behavior in the oxidation of 3,5-di-*tert*-butylcatechol to 3,5-di-*tert*-butyl-*o*-quinone, as well as very high turnover frequency (TOF) in the peroxidative oxidation of styrene to benzaldehyde.

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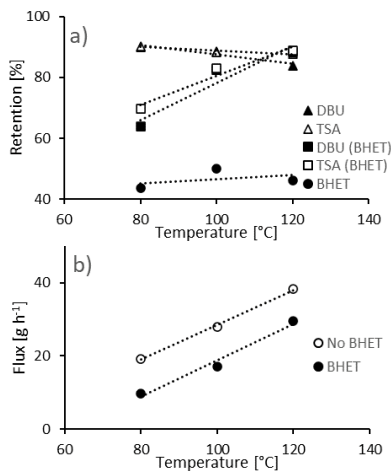
## SEPARATION OF ETHYLENE GLYCOL AND BHET FROM THE CATALYST SOLUTION AS PART OF A CONTINUOUS GLYCOLYSIS PROCESS FOR PET

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The glycolysis of poly(ethylene terephthalate) (PET) is one of the most promising plastic recycling processes. For the development of a continuous process, the separation of a novel organocatalyst<sup>1</sup> from the product by nanofiltration between 80 and 120 °C was investigated. The catalyst, consisting of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) and TSA (p-toluenesulfonic acid) was dissolved in ethylene glycol and filtered through a TS40 nanomembrane (molecular weight cut-off < 200 Da). The membrane was stable at moderate pH and temperatures up to 140 °C. The experiments were carried out in the presence and absence of BHET (bis(2-hydroxyethyl) terephthalate).

In the absence of BHET, the retention of DBU and TSA reached about 90%, being slightly lower at high temperatures (Figure 1). The flux increased linearly with temperature. The presence of BHET affected the flux and the retention of the catalyst at low temperatures. At the maximum temperature the retention was the same as without BHET. The membrane retained less than 50% of the BHET. The results suggest that a 2-step filtration process could be used to separate the BHET-containing solution from the catalyst.



**Figure 1:** Nanofiltration of ethylene glycol at 2.76 MPa: a) retention of DBU, TSA and BHET and b) flux of solution with and without BHET.

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### **PARTIALLY AND FULLY BIO-BASED VITRIMERS: CHARACTERIZATION AND RECYCLABILITY ANALYSIS**

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The development of vitrimers has been gaining great interest lately, since the presence of dynamic covalent bonds in their structure allows the rearrangement of their topology, which leads them to combine the great properties characteristic of thermoset materials with the recyclability proper of thermoplastics.<sup>1</sup>

Willing to benefit from this behavior and to contribute to the state environmental awareness, in this work the preparation of partially and fully bio-based vitrimers was studied, parting from a bio-based acid and two different types of epoxy resins, one fossil-based and one bio-based. Systems prepared with the fossil-based resin showed good thermal and mechanical behavior, whereas fully bio-based systems showed low glass transition temperatures and poor mechanical properties, thus, a mix of epoxy resins was employed in order to increase the bio-based content while maintaining good properties. Mechanical and chemical recycling of the materials was also successfully analyzed, though the conditions needed and the success degree was dependent on the formulation of the materials.

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**STRUCTURAL CHARACTERIZATION  
OF NANOCOMPOSITE HYDROGELS BASED  
ON POLY (ITACONIC-CO-ACRYLAMIDE)/LAPONITE  
AS ABSORBENTS**

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Water pollution is a major issue around the world. Development of more effective absorbents is an ongoing research. However, the use of sustainable materials has to be prioritized as we are facing a decrease in fossil resources. In this work, the structural characterization of two copolymers based on biomass derived-itaconic acid will be presented. Particularly, the synthesis of poly (acrylic acid-co-itaconic acid) and poly (itaconic acid-co-methacrylamide) will be discussed. The structural analysis of these copolymers was performed by <sup>1</sup>H, <sup>13</sup>C NMR, HSQC, HMBC and infrared spectroscopy. The molecular weight was characterized by FFF and compared by GPC. Physical hydrogels were prepared by crosslinking with laponite RD, whose structure was characterized by SAXS and rheology. The properties of the materials will be discussed in terms of composition and compared with the corresponding homopolymers poly (acrylic acid), and poly (itaconic acid) based hydrogels.<sup>1</sup> Interestingly, the nanocomposite copolymeric-hydrogels showed higher mechanical properties than the homopolymer ones. The applicability of the nanocomposite hydrogels for adsorption of Methylene Blue (MB) and Congo red (CR) will be discussed.

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## BIOMASS-RICH EPOXY-DERIVED PROCESSABLE THERMOSETS

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The sustainable development of polymeric materials has become increasingly important due to the depletion of fossil-based resources, as well as an ever-increasing public awareness of problems associated with a petrochemical-based economy. Undeniably many commercial thermosets that are used in coatings, adhesives, and high demanding applications are making use of epoxies, epoxy acrylates or acrylic resins due to their high chemical resistance and dimensional stability.<sup>1</sup> Covalent adaptable networks are networks with the dimensional stability of thermosets but with the intrinsic recyclability of thermoplastics. As a result they offer a solution to the inherent recyclability issues of thermosets.<sup>2</sup> Herein, three different dynamic networks based on different dynamic chemistries will be presented. In vinylogous urethane vitrimers a vanillin derivative is introduced to obtain fast reprocessing and high  $T_g$ s.<sup>3</sup> Fast siloxane vitrimers containing lignocellulosic biomass allow for the formation of flax fiber composites.<sup>4</sup> Dynamic  $\beta$ -amino esters with a tuneable drop in viscosity will be presented.<sup>5</sup> This research aims to contribute to a circular economy for reversibly cross-linked materials.

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### THE USE OF NETTLE FIBERS IN THE PRODUCTION OF BIOEPOXY BASED COMPOSITES

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Due to the increasing use of polymer construction materials obtained from fossil sources, it is becoming justified to design new composite materials based on more sustainable raw materials.<sup>1</sup>

The subject of the work was to assess the possibility of using Himalayan nettle fibres to produce layered composites based on epoxy bio based resin. Two types of silanes were used to modify the fibres: 3-chloropropylmethyldimethoxysilane and N-(2-aminoethyl)-3-aminopropyl trimethoxysilane at concentrations of 1 and 2%. The properties of nettle fibres were determined using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). Six-layer laminates reinforced with nettle fabric were produced.<sup>2</sup> Thermal stability, Charpy impact strength, flexural strength, impact resistance, density and water absorption of the composites were evaluated. Silanization of fibres had a positive effect on the mechanical properties of the tested composites.

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## DEVELOPMENT OF SUSTAINABLE POLYMER MATERIALS FROM BIO-BASED MONOMERS

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Ensuring sustainability as part of the material performance and development is a pressing issue of our time, requiring fundamental changes in the materials and their production. The selection of sustainable raw materials is crucial for the development of a product or process, due to the new structures having serious implications on the product performance, process efficiency and costs, newly require system-design to begin at the molecular level.

The study started with the development of new sustainable methacrylate monomers from bio-based structures like betulinol (derived from birch bark) and 2,3:4,5-Di-O-isopropylidene-glactaric acid diethyl ester GalX (by-product of the sugar production from sugar beets). Those structures were functionalized into dimethacrylate monomers and tested for the substitution in polymer materials like resins and elastomers.<sup>1</sup>

Extensive investigations of the bio-based monomers were conducted in two-component resins, showing comparable results to the oil-based reference resin in curing behavior and material properties.<sup>2</sup> Additionally, for the betulinol monomer the homo polymerization was realized by reversible addition-fragmentation chain-transfer (RAFT) polymerization for the first time. Combined with other bio-based monomers the synthesis and investigation fully bio-based thermoplastic elastomers (TPE) material was realized, showing interesting different material characteristics depending on the block lengths.

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## THERMOPLASTIC POLYURETHANES FORMULATED FROM BIOBASED POLYOLS FOR FOOTWEAR APPLICATIONS

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Thermoplastic polyurethanes (TPUs) are used in several industrial sectors, with high relevance for footwear, which is an industrial sector of great importance in Portugal, especially in the North region. Making the transition from petroleum-based to high-biobased content formulations is highly demanded in a bioeconomy context. The aim of this study was to investigate bio-based TPU formulations (BIOTPUs) through the evaluation of novel raw materials, particularly polyols featuring a high biobased content. To achieve this goal, a thorough market analysis was conducted to identify suppliers of biobased polyols holding technical properties compatible with the ones of synthetic counterparts. Thus, polyols exhibiting a linear structure, matching the hydroxyl number and molecular weight of a synthetic benchmark (polycaprolactone 2000, PCL2000), were targeted, and polyols with a biobased content from 80-100% were selected. The obtained BIOTPUs were characterised in terms of density, abrasion resistance, hardness, mechanical properties, and tear strength, then compared with the reference TPU synthesised with PCL2000. Even though the produced BIOTPU samples did not always fully comply with the properties of the synthesized reference TPU, they were quite promising, corroborating the interest in the followed synthetic path. Moreover, there is a need for higher industrial investment to diversify the market offer of biobased raw materials.

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### THE EFFECT OF SELECTED BIO-COMPONENTS ON THE PROPERTIES OF RIGID POLYURETHANE FOAMS

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An important group of porous materials used in industry as thermal insulation materials in various conditions are polyurethane foams (PURF). Among polyurethanes produced for thermal insulation applications, the largest share are rigid closed-cell foams. Biopolyols from renewable raw materials can be used to produce sustainable PURFs. Modification of the polyurethane matrix with natural fillers allows to improve selected properties and increase the content of biocomponents in the foam.<sup>1</sup> The properties of rigid PURF are influenced by many factors, including: type and quantity of ingredients used, technical method of foaming and application conditions.<sup>2</sup>

The study analyzed the influence of the characteristic of selected biopolyols (functionality, hydroxyl number, viscosity) and the type of cellulose as a biofiller on the useful physical and mechanical properties of the modified foams. In addition, some tests were carried out at different temperatures.

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## FROM SINGLE-USE TO MULTIPLE-USE CONCEPT OF EPOXY-IL NETWORKS : STUDY OF THE PHYSICAL PROPERTIES AND VALORIZATION APPROACH

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Today, advanced polymer materials represent an area of interest both for the research into high-performance materials and for the research into the reduction of plastic waste. To achieve this goal, we must re-think our approach to the “end-of-life management” of these advanced materials so that they can be reused or recycled. Herein, an epoxy system named tetraglycidyl methylene dianiline (TGMDA) cured with phosphonium ionic liquid was investigated. Compared to conventional epoxy-amine or epoxy-IL networks, we have highlighted a significant increase of the relaxation temperature ( $T_{\alpha}$ ) related to the glass transition temperature (166°C for 7phr of IL and 162°C for 10phr of IL) combined with a good thermal stability (>330°C) and intumescence property of the systems. Then, mechanical recycling of micro-sized reinforced epoxy-IL networks was evaluated with a special focus on the impact of these particles’ functionality having the same chemical nature. Thus, by using 20 wt% of these particles, the storage modulus was doubled combined with an increase of the glass transition temperature from 162 °C to 175°C showing the importance of the ionic interactions.

In summary, this work illustrates for the first time a value-added approach for epoxy-IL networks with zero-waste and low-cost.

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## BENZOXAZINE/AMINE-BASED POLYMER NETWORKS: A NEW TYPE OF VITRIMER

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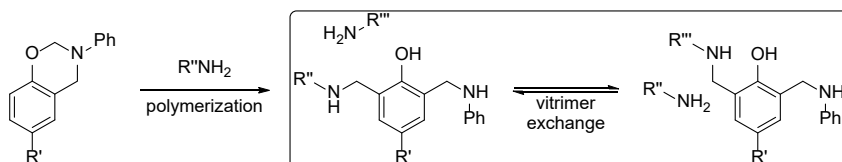
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It is known that benzoxazines can react with additional amines yielding copolymers with high mechanical strength and toughness. Recently, we have discovered for the first time that these benzoxazine/amine-based networks (Scheme 1) also feature vitrimeric properties like Arrhenius-like stress-relaxation and reprocessability, in the absence of any functional groups commonly used in vitrimers, like esters/alcohols or disulfide bridges.<sup>1</sup>

Benzoxazines react with primary aliphatic or polyether amines, resulting polymer networks with varying properties and structures depending on stoichiometry and polymerization conditions. The structures comprise a combination of different aminoalkylated phenols, expressing primary, secondary, or tertiary amino groups (in free chain ends, linear, or crosslinked structures, respectively), as well as electrophilic methylene bridges.

At elevated temperatures, the electrophilic methylene bridges interact with nucleophilic primary or secondary amines in an  $S_N$ -like reaction that involves a proton transfer (Scheme 1), initiating dynamic covalent exchange of amines, thus creating a complex reaction equilibrium that can explain the vitrimer behavior of benzoxazine/amine-based polymers.



**Scheme 1:** Simplified benzoxazine/amine reaction and assumed vitrimer mechanism.

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**ON-DEMAND DEBONDING OF EPOXY-BASED ADHESIVES  
USING BETA-AMINO ESTER CHEMISTRY**

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Adhesives are omnipresent in a myriad of materials used in our daily lives, as recognised by the continuous global growth of the adhesive market. Yet, challenging times lie ahead when considering the disassembly of those materials to allow their structural repair or their recycling. Therefore, the design of adhesives with switchable properties that allow for the formation of reversibly bonded joints is highly desired.<sup>1-4</sup>

The goal of the work presented here is to develop on-demand debondable epoxy adhesives by introducing dynamic crosslinks into the matrix. This is done using a one-pot approach in which commercially available acrylates, amines and epoxies are combined. First, an aza-Michael addition of the amine to the acrylate occurs whereby secondary amines are formed which ring open the epoxies. Dynamicity in this system originates from the retro aza-Michael reaction, also known as  $\beta$ -amino ester chemistry, which takes place at higher temperatures.<sup>5</sup> This dynamic behaviour is studied *via* rheological measurements. The adhesive performance of the most promising materials are then tested together with their potential for on-demand debonding.

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### **PREPARATION OF LIGNIN BASED IMINE VITRIMERS AND THEIR POTENTIAL APPLICATION AS REPAIRABLE, SELF-CLEANING, REMOVABLE AND DEGRADABLE COATINGS**

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Biobased materials are developed and utilized to reduce dependence on petroleum-based resources, protect the environment and reduce carbon emissions. Meanwhile, chemical recycling of thermosetting materials is an emerging strategy to increase the added value of post-consumer waste. Nevertheless, most thermosets have proved difficult to recycle due to the high stability of their crosslinked structure. Vitrimers, crosslinked by dynamic chemical bonds, are the perfect solution to recycling problems. Here, we report lignin-based vitrimers prepared by imine chemistry. First, aldehyde-modified lignin was successfully prepared by treating OH functionalized lignin with a dialdehyde via an acetalization reaction. The modified lignin acts as both a hard segment and crosslinker and the soft segment is a fatty acid diamine (Priamine™ 1075), which is chemically crosslinked via imine chemistry. The mechanical properties of lignin-based vitrimers (LPs) with more than 81.4% biobased content can be adjusted by blending the ratio of hard to soft segments. The resulting imine bond in LPs is highly dynamic at elevated temperatures allowing the material to be thermally recycled three cycles via imine metathesis and transimination without any catalyst. Unique hydrolytic properties of the imine bond endow the material with chemical recycling properties under acidic conditions. A potential application for this work is a coating, which can be prepared by hot pressing. In addition to the excellent coating properties, the LP coatings also possess thermal repairable, self-cleaning, removable, and degradable properties, which are not available with conventional coatings.

**ADVANCING CIRCULARITY: EXPLORING DYNAMIC  
COVALENT BONDS IN BIO-PUR RESIN SYSTEMS  
FOR STRUCTURAL COMPOSITES**

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The sustainability of thermoset PUs can be enhanced by replacing the petrochemical-based polyol by a combination of a high hydroxyl index castor-oil-based polyol and bio-based glycerol (BIO-Gly), resulting in a high-performance thermoset BIO-PUR that exhibits the reactivity and final properties required for structural applications.<sup>1</sup> However, these networks cannot be depolymerized, reformed, reused, or recycled, constituting one of the main drawbacks of BIO-PUR in terms of environmental impact.

In this study, we explored a viable end-of-life option for high-performance BIO-PUR formulations through the incorporation of dynamic covalent bonds. This technology hinges on the development of specially engineered polyols containing reversible Diels-Alder (DA) cleavage points (BIO-PUR-DA).<sup>2,3</sup> The thermo-reversibility of the DA/r-DA reaction was assessed using differential scanning calorimetry (DSC) and Fourier-transform infrared spectroscopy (FTIR). Additionally, the processability of the novel BIO-PUR-DA formulation was investigated and preliminary studies of reprocessability were performed.

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## HOW SUSTAINABLE ARE MONOMERS SYNTHESIZED VIA AN ENZYMATIC PATHWAY?

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The future of plastics production is expected to at least partially shift towards a biological feedstock, necessitating the development of monomers derived from biological sources.

In this study, we aimed at synthesizing biobased thermosets/vitrimers starting from eugenol. The synthesis process involved a dimerization of eugenol followed by an epoxidation with 3-chloroperbenzoic acid (mCPBA) to yield the resulting diepoxy derivative, which served as a monomer.<sup>1,2</sup> While the initial molecule originates from a biological source, the functionalization step relies on mCPBA, an halogenated petrochemical reagent that is also needed in an overstoichiometric amount, posing a clear discrepancy with the intended goal of enhancing sustainability.

To address this challenge, we developed a reaction procedure using an enzymatic pathway employing *Candida antarctica* lipase B. We anticipated this to be a more sustainable reaction pathway, also in terms of “green chemistry”.<sup>3</sup> However, despite the environmental benefits, the enzymatic reaction exhibited drawbacks in terms of reaction time and heat requirements compared to the petrochemical counterpart. Evaluation of the reactions based on simpler concepts such as atom economy and E-factor favored the enzymatic approach. For a deeper dive, we conducted a comprehensive life cycle assessment (LCA) to assess the CO<sub>2</sub> footprint of each reaction. This analysis incorporated environmental impacts of starting chemicals and energy consumption. Our results provide a direct comparison and identifies optimization parameters for further improvement of the monomer synthesis.

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**DESIGN OF A NATURAL-BASED POLYMER CARRIER MATRIX  
USED FOR THE FABRICATION OF A BIOFERTILIZER  
PROTOTYPE VIA A SUSTAINABLE AND MICROORGANISM-  
FRIENDLY PROCESS**

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Due to the lack of feasible polymer-based biofertilizers as alternative to synthetic fertilizers, this study aimed to utilize chitosan and carrageenan as main components of the natural-based polymer carrier matrix (PCM) used for the immobilization of plant-growth promoting bacteria (PGPB). The polyelectrolyte complexation of these macromolecules was used as the main mechanism in the design of the PCM. The physico-chemical properties of these polymers were extensively characterized, namely, the degree of sulfation and degree of acetylation by nuclear magnetic resonance and UV-Vis spectrometry, and the molar mass distributions by size exclusion chromatography. The screening of numerous process parameters resulted in the successful formation of spherical core-shell beads. The mechanical properties of these beads were further examined by plane/plane squeezing (compression) tests. The simultaneous process of matrix formation and immobilization of the PGPB *Azospirillum baldaniorum* Sp245, leading to the production of a biofertilizer prototype, was also established. The immobilization, survival and the release of these bacteria were evaluated *via* imaging by confocal microscopy and quantification of cell number. Accordingly, *in vitro* and *in vivo* greenhouse experiments investigated the plant growth of wheat and evidenced an enhanced plant growth and development. Moreover, the immobilization, survival and the release of these bacteria were shown to result from their entrapment in the successfully developed chitosan-carrageenan based PCM.



## HETEROPHASIC POLYPROPYLENE POLYMER DESIGN FOR PACKAGING APPLICATIONS

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Packaging applications, in general, demand an optimum combination of optics, sealing, and stiffness. Additionally, for food-packaging applications, low extractables and retained performance after sterilization are required. These desired properties can be achieved *via* plastics, as reflected by their market use of 44% worldwide.<sup>1</sup> However, with the current legislation and market focus on design for recycling (DfR), the use of multi-material blends to improve packaging properties is thus under pressure. Polypropylene (PP), a versatile polymer, can be as-such tailored according to the application demands by optimizing the catalyst system, production process and polymer design.<sup>2</sup> Therefore, PP heterophasic copolymers get more importance due to their mechanical strength than PP mono-phasic systems.<sup>3</sup> The current work discusses the benefit of using an in-reactor heterophasic PP with 1-butene rubber fraction (PP/BPC) over the more commonly used ethylene (PP/EPC). The former demonstrated higher stiffness, lower extractables, better optics, and better sealing properties than the latter, fulfilling the requirements for sustainable packaging.<sup>4</sup> This type of polymer design can be produced by the Borstar™ Nextension Technology.

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### WASTEWATER PHOSPHORUS ENRICHED ALGAE AS SUSTAINABLE FLAME RETARDANT IN POLY(LACTIC ACID)

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We propose environmentally friendly flame retarded composites based on biodegradable poly(lactic acid) matrix (PLA) and variable concentrations of phosphorus-enriched microalgae biomass (*Desmodesmus sp.*). The results were assessed by comparing them with meaningful benchmark systems. Biocomposites based on PLA as matrix and phosphor-enriched microalgae, phosphorylated lignin, thermally treated sewage sludge, biochar, and zinc phytate as flame retardants were prepared using a microcompounder and analysed for molar mass, thermal decomposition coupled with evolved gases analysis, flammability, and fire behaviour. The addition of almost all fillers resulted in an acceptable slight decrease in molecular weight, whereas biochar was found to be too degrading and was discarded. The distinct biofillers show different flame retardancy effects; the kind of filler not the phosphorus content controls the efficiency. Phosphor-enriched microalgae show the best flame retardancy effect, thus different concentrations were checked. A reduction in maximum heat release rate, effective heat of combustion and fire load was observed for the composites compared with PLA. Materials containing algae and zinc phytate obtained satisfactory limiting oxygen index and reduced flame spread in horizontal UL 94 tests. A combination of phosphorus-enriched algae and flame retardants is suggested as a promising route for future development.

**Acknowledgement:** C. Thomsen (iSeaMC GmbH), L. Thomsen (University of Gothenburg), G. Mourgas (Tecnaro GmbH), and M. Schweizer (Tecnaro GmbH). Financial support: Bundesministerium für Bildung und Forschung, BMBF KMU Innovativ 031B1289B FirePhyte.

### PHBH-ALUMINA COMPOSITES: ENVIRONMENTAL IMPACTS AND TOXICITY

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Poly-hydroxy-alkanoates (PHAs) are biobased polyesters with properties similar to common petroleum-based polymers, making them viable, more environmentally friendly alternatives. However, their market adoption is limited by a higher price, low thermal stability during processing, and significant brittleness. These limiting properties can be improved by combining different monomers (to form copolymers, such as Poly-Hydroxy-Butyrate-co-Hexanoate, PHBH) and by using additives (such as alumina). In this work, the environmental impacts, the toxicity to marine organisms (brine shrimp larvae and rotifers) and the biodegradability by immersion in natural seawater with added biota (rotifers and microalgae) of PHBH and PHBH-alumina nanowire composites were studied. Life Cycle Assessment was used for the environmental impact analysis, by which the impacts of preparing the PHBH-alumina composites using solvent casting and melt-blending techniques were studied. Additionally, the environmental impacts of PHBH composites were compared with those of common polymers, including PA, PE, PP, and PET. In most of the assessed impact categories (land use being the main exception), PHBH composites showed a moderated to significant reduction of the impacts. The studied PHBH and PHBH-alumina composite films did not provoke acute toxicity (no signs of immobilization) on brine shrimp larvae after 24 and 48 h of exposure. In addition, biodegradability of the PHBH films was observed within one month of films immersion with biota. Rotifers exposed to the degrading films showed lower ingestion capability compared to the control culture. The results show that, overall, PHBH composites present an environmentally sound alternative to some of the most used commercial polymers, but the impact of degradation products on aquatic biota needs further investigation.

### **NEW WATERBORNE BIOBASED ACRYLIC BINDERS WITH WATER REPELLENCY WITHOUT THE USE OF PFAS**

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The increasing environmental regulations and public concern have driven the polymer industry to move towards more environmentally friendly processes and sustainable polymers based on renewable resources to produce novel polymers able to substitute their petroleum-based counterparts and avoiding the use of toxic materials. Among possible alternatives vegetable oils appears as a strategic option. However, this vegetable oils require a structural modification since triglycerides present unsaturation which are not sufficiently reactive for free radical polymerization processes. Moreover, their use can not only be connected to environmental issues, also to the functionalities that can be provided during their modifications.

The objective of this work has been to synthesize new biobased waterborne binders based on the copolymerization of fossil-based monomers and biomonomers obtained from vegetable oils which have been designed to provide water repellency without using PFAS. In this study batch miniemulsion polymerizations were carried out and the influence of parameters such as biomonomers type, concentration and ratio have been analyzed on copolymers polymerization process and on copolymers final properties.

**ACCURATE  $T_g$  PREDICTION BY MACHINE LEARNING  
FOR ACCELERATING THE DEVELOPMENT OF BIO-BASED  
COPOLYESTER RESINS**

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For many industrial applications, the glass transition temperature ( $T_g$ ) of polyester resins is limited in a narrow range. For instance, the  $T_g$  of printing toners varies from 60 to 70 °C. Any value outside this range could lead to insufficient melting for processing or agglomeration under storage conditions. Similar principle also applies to powder coatings and heat seal adhesives. Considering  $T_g$  is correlated to many factors in the polymer composition, developing a new (co)polyester with a  $T_g$  falling in such a small range is time and labor-consuming via the conventional trial-and-error approach. Therefore, we report on a machine learning method to predict the  $T_g$  specifically for novel (co)polyesters derived from 2,5-furandicarboxylic acid (FDCA), a promising bio-based substitute for fossil-based phthalic acids as a rigid building block for producing polyesters. For training the model, a dataset encompassing 124 FDCA-based homo- and co-polyester data was collected from literature in which 36 different diols were involved. Subsequently, 32 structural, topological and electrical descriptors were calculated as features of each polyester at both monomer and polymer level. Based on this dataset, three machine learning regression models including LASSO, random forest and neural network-based multi-layer perceptron were trained. After regularization and optimization, the performance of each model was evaluated by an external validation dataset that contains 11 polyesters that we synthesized with monomers at both inside and outside the training set. Among these three models, random forest turns out to be the best performer with a  $R^2$ -value of 0.91 and root mean squared error (RMSE) of 3.86 °C on the validation set. It is believed that the accuracy this model reached could facilitate the development of furan-based renewable (co)polyester resins with specific  $T_g$  requirements.

### UTILIZING MALDI TOF MS AS A TOOL TO INVESTIGATE THE POTENTIAL OF BIODEGRADABLE POLYURETHANES

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Flexible polyurethane (PU) foam offers benefits as a hydroponic grow media such as tunable physical properties and reduced CO<sub>2</sub> emissions compared to the industry standard, Rockwool. Despite these benefits, the non-recyclable nature of PU foam as a thermoset plastic poses challenges for sustainability and end-of-life considerations. Discarded substrates, comprising both plastic and plant biomass, present a recycling challenge as traditional chemical and mechanical methods are unsuitable. This study aims to explore biological methods as a potential solution for PU recycling.

Biodegradation products are made up of polymer fragments and metabolites hence analysis by MALDI ToF offers a simultaneous examination of both the polymer, polymer fragments and the degrader. Liquid culture degradation of both foam and low molecular weight water soluble PUs was performed using wild bacterial communities. MALDI ToF analysis of supernatant indicated the fatty acid cleavage from ethoxylated castor oil polyol foams. Strains of *Geobacillus thermoleovorans* were isolated from the bacterial colony which exhibit the production of appropriate enzymes, substantiating this observed ester bond cleavage. Additionally bacterial communities were successful at utilizing PUs as the sole carbon source in minimal media at 65°C.

Given the widespread use of PU as a highly valuable and abundant plastic material, gaining a comprehensive understanding of the biodegradable factors holds great potential. This integrative approach offers MALDI ToF MS as a method for comprehensive and detailed analysis method of tracing both polymer and metabolite components in the biodegradation of polyurethanes.

## CHEMICAL RECYCLING OF SILICONES

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The exceptional mechanical and thermal properties of silicones as well as their low toxicity make them the materials of choice for numerous applications. The raw material is quartz from which pure silicon metal is obtained via metallurgy to then form chlorosilanes that can be hydrolyzed/polymerized into silicones. In a circular economy context, the chemical recycling of silicones to recover the monomers essential for their industrial synthesis is particularly relevant. It saves about 70% of the energy needed to manufacture virgin material by avoiding the metallurgy step from native quartz. This leads to a minimal carbon footprint from the chemical recycling of silicones.

We have recently developed two original catalytic recycling processes for depolymerizing silicones. The first one uses a ligand-potassium silanolate complex in a very effective catalytic process allowing chemical recycling of silicones into cyclic monomers from many substrates including silicone wastes.<sup>1</sup> The process, which requires only a small amount of catalyst, operates over a wide temperature range to efficiently produce the mixture of cyclosiloxanes (D3/D4/D5, efficiency up to 99%). The second developed chemical recycling process of silicones goes further upstream in the silicone production chain allowing for the depolymerization of a variety of silicone substrates (oils, gums, resins and even cross-linked elastomers and actual silicone wastes) into chlorosilane monomers.<sup>2</sup> It requires a metalloid source of chlorine and a small amount of a metallic catalyst and operates at low temperature (< 60°C). Depending on substrates, almost quantitative yields in SiMe<sub>2</sub>Cl<sub>2</sub>, SiMe<sub>3</sub>Cl and/or SiRMeCl<sub>2</sub> have been obtained.

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2. WO2023222749A1.

### RECYCLING OF ORTHOPEDIC PRODUCTION SCRAPS FOR THE ADDITIVE MANUFACTURING OF ORTHOSES

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The Non-Governmental Organization *Humanity and Inclusion* (HI) has been using Fused Filament Fabrication (FFF) since 2017 to manufacture prosthetics and orthotics in low-income countries. The first outcomes were promising but the reliance on imported filaments from Europe has led to logistical issues while increasing financial and environmental costs. This project aims to recycle plastic waste into 3D-printing filament for local orthopedic device manufacturing in Togo.

First, a selective study was conducted to determine the most appropriate material based on criteria such as availability, recyclability, printability and mechanical properties. Polypropylene (PP) was retained for its semi-rigidity, ensuring comfort and support to the patient. Local sources of PP were identified in the orthopedic centers of Lomé, where thermoforming production scraps of PP and PE sheets are usually thrown away. Both materials were blended to obtain the desired properties: PP improves the flowability during printing and the mechanical resistance of the blend while PE enhances its ductility and the stability of the deposited layer. The compatibility between both phases was enhanced during processing due to high shear rate and temperature conditions. The most promising blend was later transformed into 3D-printing filaments and scale 1 prototypes of ankle-foot orthosis were printed during 15 hours long.

Durability assessments of the orthotics were also conducted, first by focusing on the ageing resistance under Togo weather conditions. The study highlighted the sensitivity of recycled PP to photo-oxidation reactions, requiring the addition of stabilizers during recycling. In the next phase, the 3D-printed devices will be tested on a test-bench that reproduces the walk conditions, in order to evaluate their fatigue resistance.

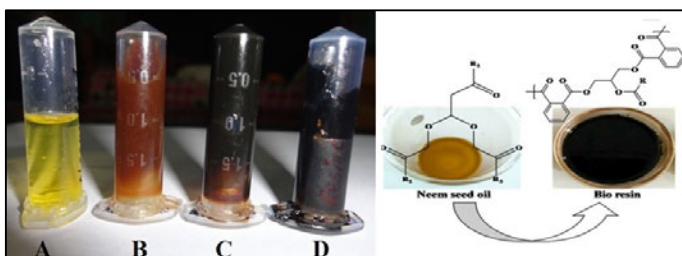


**PLANT OIL: A GREEN PLATFORM FOR DESIGNED  
POLYMERS AND NANOCOMPOSITES WITH VERSATILE  
APPLICATIONS**

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Plant oils such as cotton seed oil (CSO) and neem seed oil (NSO) were exploited in the synthesis of alkyd resin for coating<sup>1</sup> and in pesticide application for agriculture.<sup>2</sup> Alkyd resins (Fig. B, C, D) based on purified NSO and CSO were synthesized by two-stage alcoholysis–polyesterification reaction of this oil by reaction with phthalic anhydride and maleic anhydride. The reactions were tuned by using CuO nanoparticles. The oils and oil based synthesized alkyd resins were characterized by using physicochemical characterization, GC-MS, GPC, FTIR and <sup>1</sup>H NMR spectroscopic analysis. Resins were cured by blending with epoxy resin and hardener. The coating performance tests revealed that CSO and NSO based coatings showed anticorrosive properties. Both CSO and NSO were found to be good sources of renewable raw material having the potential to synthesize plant oil based alkyd resins, their nanocomposites for different industrial applications.



**Fig.** Plant oil and alkyd resins synthesized

1. Das, P., Sharma, N., Puzari, A., Kakati, D.K., Devi, N., *Polymer Bulletin*, 78:457–479, 2021.
2. Devi, N., Maji T.K., *Journal of Applied Polymer Science*, 113(3):1576–1583, 2009.

### VALORIZATION OF TPU WASTE AS FILTERING MEMBRANES FOR WATER POLLUTANTS

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A thermoplastic polyurethane (TPU) waste from the livestock industry was valorized obtaining functional electrospun nanofibers membranes.<sup>1</sup> To that end, magnetite nanoparticles coated with oleic acid (MNP) were synthesized and added, varying their content, into dissolved TPU, obtaining different TPU/MNP dispersions, which were subsequently electrospun. The morphological and mechanical properties, as well as the magneto response of the membranes were characterized. It was seen that magnetic membranes with homogeneous defect-free nanofibers were obtained. Moreover, MNPs were distributed throughout the membrane and they turned out to be an effective reinforcement, as membranes with higher modulus were obtained as the MNP content increased. Finally, the organic dye absorption capacity of the membranes was evaluated by filtering a methylene blue (MB) solution through the membrane that was placed in a ring-shaped support and measuring the absorbance of MB before and after filtration by UV spectroscopy. It was observed that the absorbance decreased after filtration. In this way, it was concluded that electrospinning was a feasible processing technique to valorize TPU waste, and that it was possible to provide the membranes with different properties and functionalities depending on the nature of the added nanoparticles.

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### REBIOPOLYOL-NEW COMPONENT FOR SYNTHESIS OF POLYURETHANE FOAMS

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Polyurethane foam is one of the most versatile polymeric materials widely used in the construction industry as thermal insulation. Due to the need to increase the energy efficiency of buildings, the demand for highly efficient thermal insulation materials is growing. According to the idea of a circular economy, raw materials from waste sources should be used for the synthesis of environmentally friendly polymer biomaterials.

This research was carried out on the possibility of using new components - rebiopolyols for the synthesis of rigid polyurethane foams. Rebiopolyols were obtained in the chemical recycling reaction of polyurethane biofoams obtained from biopolyols with different chemical structures. The influence of new biocomponents on the foaming process of polyurethane systems, the cellular structure and the physico-mechanical properties of new polyurethane foams for use as thermal insulation materials was analyzed.

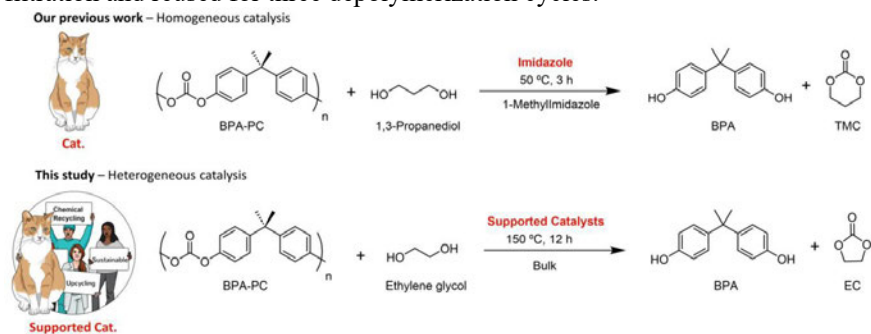
***Acknowledgements:** This research was funded by the National Research Center in Poland (Narodowe Centrum Nauki, NCN) under contract number UMO-2021/43/D/ST5/01222.*

## HETEROGENEOUS CATALYTIC SYSTEM FOR ADVANCING PLASTIC CIRCULAR ECONOMY

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Chemical recycling emerges as a pivotal strategy in combatting the escalating global issue of plastic waste pollution.<sup>1</sup> Efficient catalysts designed for depolymerizing plastics offer a promising avenue to address this challenge. Through depolymerization, the recovery of monomers or valuable intermediates becomes feasible, facilitating their reintroduction into the production chain and thereby enabling a circular economy. In this study, three different commercially available supported catalysts were employed. They were used to depolymerize bisphenol A-based polycarbonate (BPA-PC) via the glycolysis of carbonate linkages under bulk conditions. The procedure resulted in the formation of ethylene carbonate, as depicted in **Figure 1**.<sup>2</sup> Through process optimization, a remarkable 99% depolymerization of BPA-PC was achieved. Additionally, the supported catalysts could be readily recovered via filtration and reused for three depolymerization cycles.



**Figure 1.** Upcycling of BPA-PC through heterogeneous catalysis.<sup>2</sup>

- Jehanno, C., Alty, J. W., Roosen, M., De Meester, S., Dove, A. P., Chen, E. Y.-X., Leibfarth, F. A., Sardon, H. *Nature*, 603:803–814, 2022.
- Olazabal, I., Luna, E., De Meester, S., Jehanno, C., & Sardon, H. *Polymer Chemistry*, 14: 2299–2307, 2023.

## ENHANCING STYRENE RECOVERY AND UPCYCLING OF THE RUBBER PHASE OF HIGH IMPACT POLYSTYRENE

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High impact polystyrene (HIPS) is a two-phase polymeric material that consists of a free polystyrene (PS) matrix and rubber particles, occupying a substantial portion of plastic waste.<sup>1,2</sup> To recover styrene from HIPS via pyrolysis, several challenges must be overcome first, like low styrene yield (<50%) and char formation due to the presence of rubber.<sup>3</sup> To tackle these challenges, a green fractionation process using ethyl acetate (EtOAc) as an efficient solvent to separate rubber from the free PS matrix in HIPS is envisioned and carried out under mild conditions (Fig. 1). Molecular dynamic simulations revealed that PS is more stable in EtOAc than the rubber particles, resulting in the fractionation of PS. The subsequent pyrolysis of the fractionated PS led to a 20% increase in styrene selectivity compared to the pyrolysis of untreated HIPS. The revalorization of the rubber particles was then accomplished by ethenolysis metathesis, in which after 4 h at 100 °C, polybutadiene was split to produce 1,5-hexadiene as a major product and isolated PS, which was further thermally degraded, achieving a styrene selectivity of 70%.<sup>4</sup>



**Figure 1.** HIPS revalorization process.

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## DETERMINATION OF THE CLEANING EFFICIENCY FOR CONTAMINATED HDPE USING SOLVENT-BASED RECYCLING

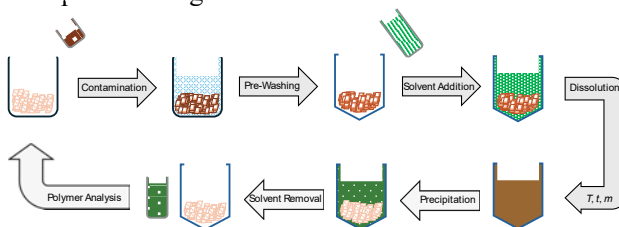
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Global plastics production is at an all-time high, with over 400 million tons produced annually, but only around 9.5 % is produced by circular means.<sup>1</sup> Further improvements are necessary to increase this number in all recycling sectors.

This work focuses on the solvent-based recycling of high-density polyethylene (HDPE) using a dissolution-precipitation process.<sup>2</sup> To evaluate the method a so-called challenge-test is performed, where virgin HDPE flakes are contaminated with a known surrogate cocktail.<sup>3</sup> The experimental procedure is depicted in Figure 1.



**Figure 1:** Experimental setup for the challenge-test.

The process is tested by the variation of the dissolution temperature ( $T$ ), the dissolution time ( $t$ ) and the amount of solvent ( $m$ ) utilizing Design of Experiments (DoE). The performance is then investigated through the analysis of the recycled polymer. Therefore, the remaining contamination is measured using Gas Chromatography with Flame Ionization Detection (GC-FID) and the molecular weight distribution is determined by High Temperature – Size Exclusion Chromatography (HT-SEC).

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2. Zhao Y.-B., Lv X.-D., Ni H.-G., Chemosphere 209, 707–720, 2018.
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## NOTES

## **POSTERS**





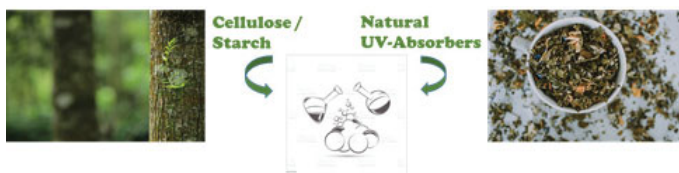
## P-01

### MODIFIED CELLULOSE AS AN EFFECTIVE UV ABSORBER

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The research results to be presented show an innovative, cost-efficient way of functionalizing nano-/micro-fibrillated cellulose for use in sunscreen.



**Figure:** Production of biogenic/biodegradable UV absorbers from cellulose and phenolic acids from plant extracts. (photos: [www.pexels.com](http://www.pexels.com))

Efficient, resource-saving esterification of polysaccharides such as cellulose or starch with phenolic acid derivatives provides biogenic and biodegradable UV protection for use in cosmetics and home & personal care products.<sup>1</sup> To enable cost-effective production, phenolic acid extracts from a novel microwave-based extraction process are used.<sup>2</sup> The resulting raw material of functionalized cellulose or polysaccharides should not only show an outstanding UV absorption profile, but also very good emulsifying or thickening properties that allow it to be used in different cosmetic formulations. In this way, a multivalent material is created that offers the opportunity to substitute several synthetic fossil oil-based ingredients from cosmetics and home & personal products.

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## P-02

### **BIOSYNTHESIS OF HIGHLY FLEXIBLE LIGNOSULFONATE–STARCH BASED MATERIALS**

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<sup>c</sup>*Austrian Centre for Industrial Biotechnology (ACIB), Konrad Lorenz Strasse 20, 3430 Tulln an der Donau, Austria*

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The need to replace polymers from fossil sources with bio-based renewable sources is increasingly imminent. This work reports on the synthesis of biofilms obtained from the polymerization of lignosulfonates using laccase as a biocatalyst and blending with starch. The effect of the reaction conditions on the formation of stable starch-lignosulfonate polymers was evaluated by monitoring changes in viscosity, molecular weight (Mw), and fluorescence measurements. Enzymatic polymerization led to molecular weights of about 400 kDa and viscosities of ca. 1.00 Pas and decreases in lignosulfonates-OH groups by about 46% after 1 h of reaction carried out at pH 7 and adding starch at the end of the polymerization reaction. Additionally, the effect of the starch concentration on the mechanical, thermal, and water absorption properties was studied. As a result, the addition of up to 7% starch was found to improve the mechanical properties of the lignosulfonate films as indicated by the increase in elongation at break, tensile strength, and Young's modulus, reaching values of 157%, 1.19 MPa, and 0.22 MPa, respectively. This study demonstrated a green alternative for creating 100% biobased films composed of starch and lignosulfonates.

## P-03

### MICROBIALLY SYNTHESISED POLYESTERS FOR BIOBASED TEXTILE FIBRES

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Polyester fibres are the predominant raw material in the textile industry, which significantly contribute to global carbon emissions. Their annual global production exceeds 60 million metric tons, equating to over 570 kg of carbon emissions.<sup>1</sup>

To support the industrial transition from fossil-derived to biobased polymers, we propose a sustainable approach to polyester fibre manufacture, integrating organic waste valorisation, microbial synthesis, and eco-friendly wet spinning. Polyhydroxyalkanoates (PHAs) are a group of linear fossil-free polyesters synthesised by microbes for carbon and energy storage. PHAs have been successfully synthesised from two different microbes, *C. necator* and *H. mediterranei*, as demonstrated by thermal and spectral analysis, with coffee waste and green solvents serving as a viable carbon source and for polymer isolation, respectively.

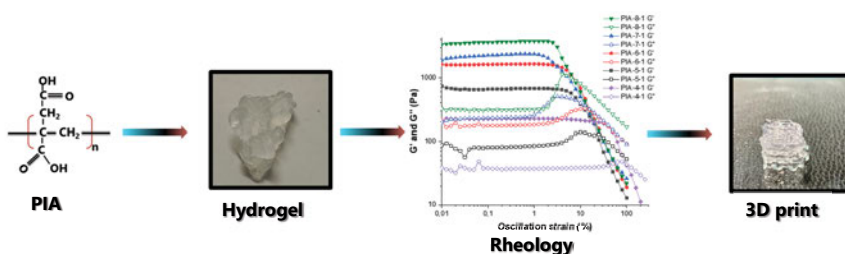
An eco-friendly method was also developed for the wet spinning of individual textile fibres from poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). Commercial grade PHBV fibres were wet spun from a 16 wt% solution in 1,3-dioxolane into an ethanol bath. The resulting fibres exhibited an average diameter of  $57 \pm 12 \mu\text{m}$  (n=200), an ultimate tensile strength (UTS) of up to 6 GPa, and could be continuously collected with lengths exceeding 1 m. Wet spinning trials are ongoing using PHBV microbially synthesised in-house from coffee waste.

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## HYDROGELS BASED ON RENEWABLE POLY(ITACONIC) ACID FOR EXTRUSION–3D PRINTING

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3D printing technologies have been widely explored for the rapid design and fabrication of hydrogel constructs, which are required for biomedical applications and functional devices.<sup>1</sup> In this study, a new hydrogel ink for extrusion–3D printing has been developed. The physically crosslinked hydrogel has been prepared of a mixture of poly(itaconic) acid (PIA) and Laponite, which has been further optimized to provide ideal rheological behavior for the extrusion and gel-setting process.<sup>2</sup> The rheological characteristics of the hydrogels favorable for 3D printing such as yield point and flow point were established. In the second part of the study, the formulated hydrogel was subjected to 3D printing of multiple-layer-scaffold model under the optimized printing conditions. After printing, the structure was subjected to additional physical crosslinking using calcium chloride to fix the shape of the object.



**Figure 1.** General procedure for hydrogel ink optimization and extrusion-3D printing.

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## P-05

### BIO-BASED RECYCLABLE THERMOSETTING POLYURETHANES BY DIELS-ALDER CHEMISTRY

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Thermoset polyurethanes (PUs), thanks to their adjustable chemical and physical structure, have exceptional properties and versatility. As a result, they are used in a wide variety of industries and applications. However, their widespread use also generates a large amount of waste, which, due to their low biodegradability, creates an environmental problem. Many efforts are underway to develop effective strategies for tackling the PU waste issue. Recently, the incorporation of dynamic covalent bonds in their structure has emerged as a promising alternative to make PUs more recyclable and reprocessable.<sup>1</sup>

The novelty of this study consists in the engineering of a triol containing three thermo-reversible Diels-Alder (DA) adducts (Triol-DA) in its structure, and its use as a crosslinking agent for PUs.<sup>2</sup> Different Triol-DA contents were employed in combination with a commercial bio-based polyol and polymeric methylene diphenyl diisocyanate (pMDI) in order to synthesize various formulations of PUs, from flexible to rigid. The thermo-reversibility of the DA (r-DA) was evaluated by differential scanning calorimetry (DSC) and stress relaxation tests. The mechanical and thermo-mechanical behavior was analyzed by bending or tensile tests and dynamic-mechanical analysis (DMA). Finally, recyclability and reprocessability were evaluated by compression processing.

Thereby, the results obtained within this study demonstrate a promising avenue for enhancing PU recyclability through dynamic covalent chemistry, offering insights into the development of sustainable thermoset materials.

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## P-06

### BIODEGRADATION OF ALIPHATIC POLYURETHANE FOAMS: FACTORS OF CHEMICAL COMPOSITION AND SUPRAMOLECULAR STRUCTURE

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The current global problems associated with the environmental impacts of plastics production are leading scientists to develop new types of polymers that are designed to allow degradation after their useful function has ended. Polyurethane foams, produced in large volumes across the world, are a typical example of thermosets, whose chemically cross-linked structure makes their physical recycling practically impossible. Traditional polyurethane foams, predominantly based on aromatic isocyanates, are resistant to biodegradation and prone to generating microplastic particles through photo-oxidation. We have recently designed fully aliphatic polyurethane foams (derived from polyester polyols and aliphatic isocyanates) that show great potential as biodegradable alternatives.<sup>1,2</sup>

Herein, we present the preparation of diverse aliphatic polyurethane foams with variable chemical composition resulting in various cellular structure, distinct supramolecular arrangement and thermo-mechanical properties. These foams were subjected to biodegradation in soil and in liquid media containing the fungus *Fusarium solani*. The progress of biodegradation was monitored via respirometry complemented by periodic structural evaluations using FTIR and WAXS methods.

**Acknowledgements:** *The authors acknowledge financial support from the Czech Science Foundation (project No. 24-10651K).*

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**STUDY ON THE HUMIC ACID BASED HYDROGEL MEMBRANE**

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Natural polymers offer distinct advantages for building crosslinked hydrogels due to their diverse structures and rich potential for physical interactions.<sup>1</sup> Humic acid (HA), a naturally occurring biopolymer, possesses various oxygen-containing functional groups like hydroxyl, carboxyl, carbonyl, and amino groups after activation.<sup>2</sup> These groups provide ample opportunities for molecular modification and the creation of tunable functionalities within three-dimensional crosslinked networks. In this work, a self-assembled hydrogel membranes based on the humic acid was prepared using glutaraldehyde as crosslinker. These membranes utilize sodium humate (NaHA) and polyvinyl alcohol (PVA) as the primary materials, forming a hydrophilic network. Our findings demonstrate that incorporating sodium humate (NaHA) into hydrogel membranes significantly improves their mechanical properties compared to pure PVA-based hydrogels. Furthermore, by adjusting the content of NaHA, PVA, and the crosslinking agent, we can precisely regulate the physical and mechanical properties of the hydrogel membranes. This crosslinking method enhanced water retention, slow release, and degradability, making it suitable for agricultural mulch film applications.

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## P-08

### BIOPOLYMERIC CHITOSAN/POLYDOPAMINE FILM AS AN SORBENT FOR THE PRECONCENTRATION OF TRACE METALS IN BIOLOGICAL SAMPLES

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In this study, a sustainable sample pretreatment approach involving a bio-based composite film composed of chitosan (CS) and polydopamine (PDA) was successfully applied to the preconcentration of trace levels of copper (Cu) and chromium (Cr) in biological samples. After the biosorption of Cu and Cr ions, trace metal concentrations in the samples were determined by atomic absorption spectrophotometry. The morphology and surface chemical characteristics of the CS/PDA sorbent films were meticulously examined through a number of analytical techniques, including Fourier-transform infrared spectroscopy and scanning electron microscopy. Our findings clearly demonstrate the abundance of diverse functional groups, such as catechol, hydroxyl, and amino moieties, on the surface of the CS/PDA film. These functional groups have been revealed to increase the extraction efficiency of various metals through a spectrum of interaction mechanisms, including complexation, electrostatic forces, cation- $\pi$  interactions, and diffusion. The constructed approach achieved a good analytical performance with low limits of detection for the analytes of interest. To rigorously assess the precision and practicality of our proposed approach, we subjected it to real urine samples. The obtained relative standard deviation for both Cr and Cu in all urine samples was less than 5%, affirming that the sample matrix did not significantly impede the performance of the CS/PDA sorbent film. Our proposed approach exhibited good reusability, delivering satisfactory results over seven consecutive extraction and desorption cycles, thus underlining its inherent sustainability and applicability in practical settings.

**POLY(2-ISOPROPENYL-2-OXAZOLINE) BRUSHES  
AS A PLATFORM FOR VERSATILE SURFACE  
FUNCTIONALIZATION**

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2-Isopropenyl-2-oxazoline (IPOx) is a significant double functional monomer with numerous applications.<sup>1</sup> However, until now there are no conditions which allow for precise control of surface-initiated PIPOx brush growth under the conventional Copper mediated reversible-deactivation radical polymerization (Cu-RDRP) conditions. In this study, we demonstrate that IPOx can be polymerized through Cu-RDRP with unprecedented control using 11-(trichlorosilyl)undecyl-2-chloropropanoate initiator and CuCl/CuCl<sub>2</sub> with HMTETA or Me<sub>4</sub>CYCLAM catalytic system in an aqueous medium from silicon surface. The potential of PIPOx brushes is then exemplified by incorporating different functionalities on the surface via modification of pendant 2-oxazoline rings using different carboxylic acids<sup>2</sup> under optimized reaction conditions. Hydrolysis of the oxazoline rings with hydrochloric acid is also achieved in this work. Importantly, functionalization with azide-bearing carboxylic acids enabled the brushes to participate in copper-catalyzed alkyne–azide cycloaddition reaction (CuAAC). In addition, we also show that the prepared PIPOx brushes can be transformed into well-defined ATRP macroinitiators for subsequent grafting of a different polymer thereby yielding “bottle-brush” brushes with precisely controlled structure. Taken together, the optimized PIPOx brush polymerization and modification procedures provide a robust and versatile avenue for imparting functionality on a surface.

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### THE PHYSICAL CHARACTERIZATION OF POLY(3-HYDROXYBUTYRATE-*co*-4-HYDROXYBUTYRATE) BLENDS WITH CELLULOSE ACETATE BUTYRATE DEPENDING ON COMPOSITION OF 4HB COMONOMER

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Among the biodegradable plastics, microbial polyhydroxyalkanoates (PHAs) have attracted research and commercial interests worldwide because they can be used as biodegradable thermoplastics and also because they can be produced from renewable resources.<sup>1</sup> Although several types of PHAs have been identified to possess commercial value, poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) [P(3HB-*co*-4HB)] as the latest generation of PHA family has become the focus of interest because its mechanical properties can be controlled by the composition of P(3HB-*co*-4HB).<sup>2,3</sup> This copolymer shows more flexible and less crystalline with increase content of 4HB because the introduction of 4HB units induces defects in the crystal lattice.<sup>31</sup> In this study, P(3HB-*co*-4HB) and cellulose acetate butyrate (CAB) blends were prepared through melt blending method. The four different 4HB content of P(3HB-*co*-4HB) were used to investigate how the 4HB content affects to the properties of the blends. The glass transition temperature of the PHAs in the blends were increased and the melt temperatures of those were depressed as the CAB content increased. The tensile properties of the semi-crystalline PHAs showed more ductile as the CAB content increased 0 to 60 wt.-%. The 4HB content of the P(3HB-*co*-4HB) relates to the miscibility with the CAB, and the partial miscibility of the P(3HB-*co*-4HB) and CAB was confirmed.

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## P-11

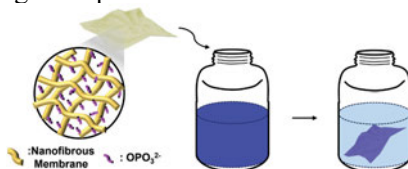
### MODIFIED FISH GELATIN NANOFIBROUS MEMBRANE FOR ULTRA-FAST CATIONIC DYE REMOVAL

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Nanofibrous membranes are specific materials with fiber diameters ranging hundreds of nm and can exhibit fast adsorption behavior due to their high specific surface area to volume ratio. In this study, we fabricated a nanofibrous membrane with very fast adsorption capacity for cationic dyes using fish-derived gelatin. Fish gelatin aqueous solution has a low gelation temperature and high water solubility, making it possible to successfully convert it into nanofibers through aqueous solution electrospinning.<sup>1</sup> To provide moisture stability to nanofibers and strongly enhance their affinity for cationic dyes, glucose-6-phosphate was added as a natural crosslinking agent. This sugar phosphate/fish gelatin membrane exhibited an impressive methylene blue removal capacity of 58.36 mg g<sup>-1</sup> and demonstrated rapid adsorption equilibrium within 15 minutes. The cationic dye removal capacity stems from powerful electrostatic interactions between the adsorbent and the cationic dye, facilitated by the phosphorylated groups in gelatin nanofiber (**Fig. 1**).<sup>2</sup> Additionally, even after 6 regeneration cycles, the membrane maintained an efficiency of over 81%, highlighting its potential for long-term application and excellent stability, even under low pH conditions during desorption.



**Figure 1.** Cationic dye removal by electrostatic interactions between phosphorylated groups of membrane and cationic dye.

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## P-12

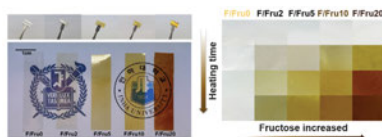
### MULTIFUNCTIONAL FRUCTOSE-CROSSLINKED FIBROIN FILM WITH DEVELOPED BETA-SHEET STRUCTURE FOR FOOD PACKAGING

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Fibroin from silk is a natural protein fiber renowned for its impressive mechanical strength, biocompatibility, and antibacterial properties. In addition, it can be converted into various forms through solution-based polymer processes, expanding the availability of natural biopolymer resources and piquing interest in diverse applications. In this study, multifunctionality was successfully imparted to fibroin film through an innovative fructose crosslinking process (Figure 1). By inducing a beta sheet structure within the film, the physicochemical properties of the fibroin film could be effectively controlled. Notably, these resulting films exhibit exceptional mechanical strength, boasting a tensile strength of 115 MPa and a Young's modulus of 2.17 GPa, surpassing previously reported fibroin-based films. Additionally, the F/Fru film offers superior transparency, UV shielding ability, water resistance. The multifunctionality of this F/Fru film was able to improve food storage stability when applied to food packaging materials. This high-performance fibroin film with a developed beta sheet structure will be an excellent replacement for existing petrochemical-based polymers.



**Figure 1.** Optical images and the color change of film at different reaction times of fructose-crosslinked fibroin films.

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## P-13

### ENVIRONMENTAL-FRIENDLY MEMBRANES MADE OF BIODEGRADABLE POLYMERS: INNOVATIVE TECHNIQUE FOR REGULATING TUBULAR OR FLAT-PLATE PORES

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Non-degradable polymers are posing a threat to ecosystems and humanity by causing environmental destruction. One way to mitigate this risk is by replacing membranes, produced annually for water treatment and air purification purposes, with biodegradable polymers.<sup>1</sup> This study focuses on an innovative method for fabricating a biodegradable membrane, specifically poly-L-lactic acid (PLLA), by utilizing patterned substrates. The precise regulation of tubular or flat-plate pores within membranes was successfully achieved using a patterned cap, comprising high-thermally-conductive Ti alloy pins and low-thermally-conductive polyethylene (PE). This was carried out by employing one-directional cooling equipment for the thermally-induced phase separation (1D-TIPS) technique.<sup>2</sup> Notably, a porous structure characterized by well-aligned flat-plate pores and a sandwich panel skeleton was fabricated using a cosolvent system (benzene/dimethyl carbonate). It is anticipated that the developed innovative technique will serve as a novel and promising method for fabricating intricate porous structures that go beyond conventional membranes.

**Acknowledgements:** *This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (Ministry of Science and ICT, MSIT) (No. RS-2023-00245547).*

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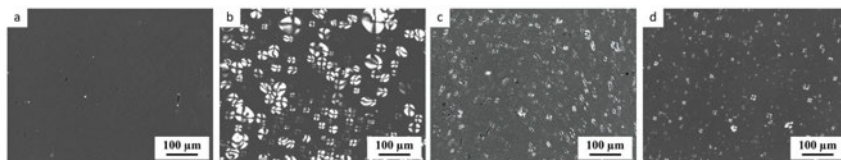
## THERMOPLASTIC STARCH: INFLUENCE OF BOTANICAL ORIGIN AND PREPARATION CONDITIONS ON MORPHOLOGY AND PROPERTIES

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Our previous studies showed that the processing of wheat starch via a two-step preparation procedure in mild conditions results in a highly homogenous thermoplastic starch (TPS).<sup>1</sup> In this contribution, our method was tested on different starches from different botanical origins (cereals, tubers, and legumes). All starches were processed by solution casting (at 65°C for 15 min), followed by melt mixing in a chamber of a twin-screw mixer (120 °C and 60 rpm for 8 min). The preparation conditions (time and temperature) were further optimized for each specific starch type. The reliability of our method was investigated by comparing the morphological and mechanical properties of the obtained TPS's. Non-plasticized starch granules in the TPS matrix were visualized by polarized light microscopy PLM (Fig.1). The impact of starch homogeneity on stiffness and viscosity was provided by dynamic mechanical analysis (DMA) and instrumented microindentation hardness testing (MHI).



**Figure 1.** PLM micrographs showing thin sections of all of prepared TPS's: (a) wheat, (b) potato, (c) bean, and (d) tapioca starch.

*Acknowledgment:* Projects TN02000020 (TA CR) and NU21-06-00084 (AZV CR).

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### ITACONIC ACID AS RENEWABLE BUILDING BLOCK FOR THERMOSETTING RESINS

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Over the last decades, biomass-derived chemicals have received considerable attention as alternative and renewable building blocks in the development of bio-based polymers. To this end, extensive research has been conducted regarding the development of bio-based thermoplastics such as polyester and polyamides.<sup>1</sup> However, research on thermosets, especially on epoxy resins, is far more limited and focused merely on feedstocks such as vegetable oils, lignin and lignin derived phenolic molecules such as vanillin.<sup>2</sup>

In this work, we have developed epoxy resins, of high biobased content, and studied their properties upon thermal and UV induced polymerization. Biomass derived itaconic acid, an unsaturated dicarboxylic acid, was utilized as monomer for the synthesis of epoxy resins. Identification and characterization of the epoxy monomers was conducted by NMR, FTIR (ATR) and EEW titration. The properties of crosslinked resins were evaluated by means of DSC, TGA, DMA and FTIR and were compared to the respective conventional BPA based epoxy resin, cured under same conditions.

**Acknowledgements:** *This research has received funding from the European Union's Horizon Europe research and innovation programme under Grant Agreement No. 101058699 (Project FreeMe).*

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### UV-TREATMENT OF GELATINE FILMS

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Currently, there is an increasing demand for the reduction of non-biodegradable plastics. Simultaneously, the demand and research in the synthesis of biodegradable films and packaging materials from natural renewable sources are growing. The aim of this study is the producing of gelatin films, prepared by casting of solution with subsequent drying, intended for use as food packaging materials. A 20% gelatin-water solution was used for preparation of films. Afterwards films were divided into two series with the addition of 30 or 40 wt. % of glycerol with the role of plasticizer. Gelatin was extracted from chicken feet, which are by-products of the poultry industry. The films underwent accelerated UV-aging at the temperature of 35 °C and relative humidity of 50 %. Samples were analyzed before and after various irradiation intervals. The characteristics were monitored by analysis of solubility and swelling, vapor permeability, spectrophotometry, Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The obtained results indicate that samples with a higher plasticizer content exhibited greater hydrophilicity. UV-exposition of the samples led to bond formation, correlating with the obtained results by FTIR analysis, resulting in a significant reduction in free volume of samples. Strengthening the structure prolonged the desired ability of the film to resist water penetration and reduced its vapor permeability. Spectrophotometric changes were indicated and manifested in slight darkening, yellowing, and increased haze. Thermal stability remained unchanged by UV-exposition. When in contact with food, it is necessary to ensure that packaging is non-toxic and safe for health. In conclusion, the production of gelatin films as food packaging from underutilized raw materials of the poultry industry crosslinked by UV irradiation appears to be a cost-effective and promising option for food preservation and shelf-life extension.

### RESEARCH ON THE RESISTANCE OF PLA TO COSMETIC PRODUCTS

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Biodegradable polymers are an interesting and constantly developing area of research. This applies, among others, to their applications in various fields, including the cosmetics industry. Society, along with growing ecological awareness, places more and more emphasis on the development and use of materials that fulfil technical functions, but are also environmentally friendly.<sup>1</sup> Cosmetic products that contain various chemicals may affect biodegradable polymers. It is therefore important to conduct resistance tests that can estimate the possible adverse effects of a cosmetic product on a biodegradable polymer, which may occur during the use of cosmetic product packaging.<sup>2,3</sup>

The aim of the work was to analyse the influence of natural model cosmetics on selected properties of poly(lactic acid). Cosmetics are made from fat, alcohol or an acidic environment. The scope of work included the determination of mechanical properties and visual assessment. Samples aged for 8 weeks at room temperature and 45 °C were tested.

Based on the conducted research, it was found that the use of PLA as packaging for cosmetic products may be significantly limited. The ongoing degradation processes result in a significant reduction of mechanical properties. This may lead to a failure to meet the required properties. A particularly unfavourable effect was observed for cosmetics based on alcohol and at elevated temperatures.

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### **POLYMERIC DRUG DELIVERY SYSTEMS: BRIDGING THE GAP BETWEEN MODERN DAY TOOLS AND NATURAL POLYMERS**

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Polymeric drug delivery systems in the form of nano-particles, micro-particles, micelles, hydrogels nano-fibers and nano-sponges are widely used in the field of pharmaceuticals for treatment of numerous diseases.<sup>1</sup> Over the decades, synthetic polymers have been considered as first choice because of their tunable properties and ease of fabricating delivery systems. However, in the recent years natural polymers and their derivatives have gained significant attention in the pharmaceutical research due to their biodegradability, cost-effectiveness, and potential for chemical modification. These advantages make them attractive alternatives to synthetic polymers.<sup>2</sup> In that context, we picked a natural polymer, arabinoxylan (extracted from cornhusk) and explored its gelling properties in first part of our recent investigations. On one hand this natural mucilage can form highly viscous solutions and gels even at a low concentrations (0.5–1.5% w/v), and on the other hand it exhibits thixotropic behavior, i.e. possess ability to recover its gel structure once the applied stress is removed. Apparently, it seems a promising gelling agent for topical delivery systems such as emulgels. In the second part of the investigation, we are in the process of exploring the potential of arabinoxylan in oral drug delivery via developing mucoadhesive nanoparticles. With the extension in residence time, the aim is to increase the bioavailability of critical drugs that can help in decreasing the dose size or the dosing frequency. The outcomes until now are very promising in term of their potential for clinical applications.

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## P-19

### DEVELOPMENT OF BIODEGRADABLE HYDROGEL-BASED BIOINKS FOR 3D PRINTING

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In the emerging field of bioprinting, there is a growing interest in polymeric materials specifically designed to produce bioinks for tissue engineering. In this context, photocrosslinking of water-soluble biodegradable polymer precursors to form hydrogels is a promising strategy due to its precision and rapid curing. Recently, visible blue light has been preferred over conventional UV light due to its significantly lower cell cytotoxicity.<sup>1</sup>

Here we present hydrogel inks based on fully synthetic biodegradable methacryloyl polymers, including synthetic poly(*N*<sup>5</sup>-2-hydroxyethyl-L-glutamine)-*ran*-(*N*<sup>5</sup>-ethylmethacrylate-L-glutamine) (PHEG-MA) and hyaluronic acid methacryloyl (HA-MA). These inks are capable of photocrosslinking using a natural light-sensitive system containing riboflavin as photoinitiator and L-arginine as co-initiator under blue light at a wavelength of 450 nm. The hydrogels were prepared with different concentrations of riboflavin (0.1-0.2 wt%) and L-arginine (1-2 wt%) and their yield, swelling capacity and mechanical properties were evaluated. To improve printability, several polysaccharide-based additives were incorporated into the ink formulation. The effect of the additives on ink rheology was investigated. Successful printing was achieved using an extrusion-based Cellink Bio X bioprinter with a temperature-controlled or electromagnetic droplet (EMD) printhead coupled with a photocurable toolhead.

**Keywords:** Bioprinting, Bioinks, Photocrosslinking, Hydrogel, Riboflavin, blue light.

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### CHITOSAN-BASED COATINGS FOR THE WATER-PROOFING OF WOOD

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Wood is one of the oldest building materials and is currently becoming increasingly popular again due to the raised awareness for environmental issues. Wood is hygroscopic and porous, i.e. it not only absorbs moisture from the atmosphere, but also actively and quickly sucks up large amounts of water through the capillary system particularly via the end grain. This leads to dimensional changes, but above all the wood becomes susceptible to rot. As a result, for many applications the wood needs to be protected from moisture.

While a large number of well-established petrochemical products are widely used for this purpose, there are also traditional natural finishes available. Linseed oil, which is rich in linoleic acid, is a prominent example, although it requires multiple layers and several days to fully harden by autooxidation in air. In addition, increased use could interfere with the food chain.

We have recently developed an alternative coating for wood based on chitosan, derived from food-industry waste, and itaconic acid, which is produced in large scale by fermentation of sugars or industrial wastes such as glycerol. The coating is applied from aqueous solution and adheres nicely on wood surfaces due to the structural similarity of chitosan and cellulose. Heating the applied solutions polymerises the itaconate anion into an anionic polyelectrolyte. Ion pairing of the two polyelectrolytes, chitosan polycation and polyitaconate, crosslinks the chitosan chains. The resulting interpolyelectrolyte complex precipitates in the form of a water-insoluble film on the wood surface upon drying. The films were found to adhere very well to the wood surface, enhancing the wood properties, while remaining both bio-based and biodegradable. Thus, a hydrophobic coating that reliably seals the end grain against liquid water can significantly prolong the woods lifespan, and protect it from various forms of biological degradation.

**A MODEL OF GELATION  
IN ASPARTATE-AMINE-ISOCYANATE SYSTEM:  
EFFECT OF SIDE REACTIONS AND UNEQUAL REACTIVITIES  
ON GEL POINT AND NETWORK STRUCTURE**

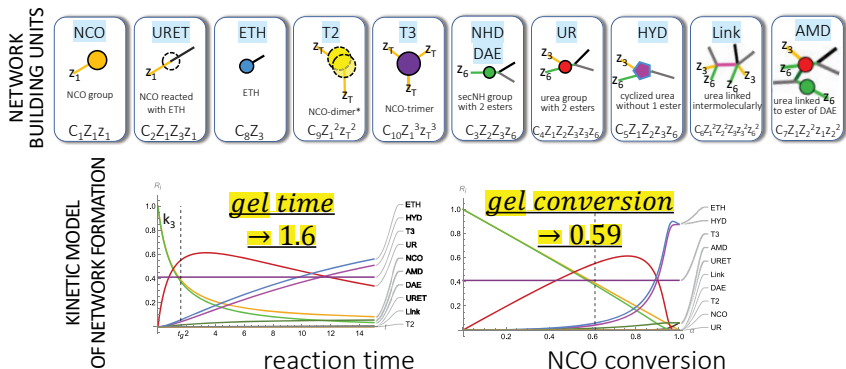
M. Dušková Smrčková<sup>a</sup>, A. Sharma<sup>a,b</sup>, S. Natour<sup>a</sup>, O. Kočková<sup>a</sup>,  
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The polyaspartate-based polyurea networks, PU-ASPEs, have been gaining importance in applications such as coatings, sealants, and polyelectrolytes for reductions of volatile solvents, process energy, and level of heavy metal catalysts. To interpret the crosslinking behavior in PU-ASPEs, we have derived a conjunct model based on kinetic module of crosslinking process, and fed its output into a statistical module based on theory of branching processes. We were able to predict the gel conversions, gel times, development of network structure features with conversion.



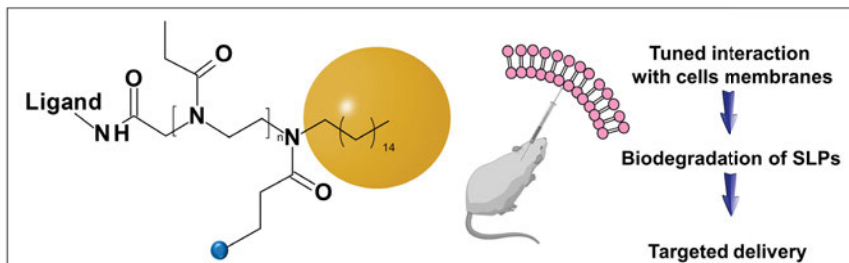
**Acknowledgment:** We acknowledge the Institute of Macromolecular Chemistry for providing institutional support (RVO: 61389013).

**BIODEGRADABLE SOLID LIPID PARTICLE CARRIERS  
FOR POLYMER-LIGAND CONJUGATES**

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We have developed solid lipid particles based on a cholesterol/tetradecanol mixture for carrying water-soluble amphiphilic poly(2-oxazoline)-ligand conjugates.



**Scheme:** Biodegradable solid lipid particles

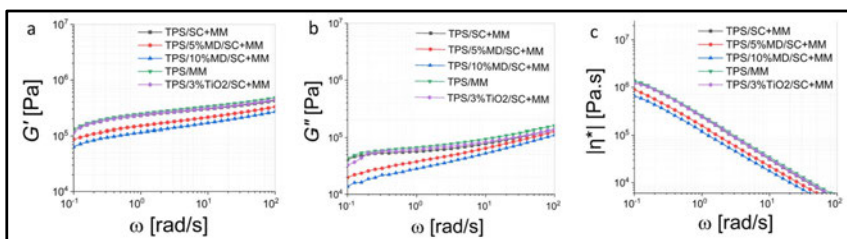
The biodegradability of the SLPs' core material serves to temporarily mask the hydrophobic block of poly(2-oxazoline), enabling the active targeting of cell membrane receptors with the ligand. Subsequently, the particle core decomposes, leading to non-specific binding of the hydrophobic block with the cell membrane. This strategy fosters synergy between specific and non-specific binding, thereby enhancing the targeting efficiency with the ligand.

## CHARACTERIZATION OF SOLID THERMOPLASTIC SYSTEM MADE FROM WHEAT STARCH WITH ADDITION OF MALTODEXTRIN FOR BIO-MEDICAL APPLICATIONS

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We prepared thermoplastic starch (TPS) from wheat starch powder, glycerol and water using our two-step preparation protocol. Maltodextrin oligomer (MD) was added to reduce the viscosity of the TPS.<sup>1</sup> The lower viscosity should decrease the processing temperature, resulting in better preservation of antibiotics activity in TPS/ATB systems.<sup>1,2</sup> TPS systems with and without MD were prepared by solution casting (SC: at 67°C-70°C until gelatinization) followed by melt mixing (MM; at 60 rpm at 120°C for 8 min). Morphology of TPS samples was visualized by light microscopy and SEM microscopy. Rheological and thermomechanical properties were characterized by rheometry. The addition of MD (Fig. 1) decreased both modules ( $G'$  and  $G''$ ) as well as the complex viscosity  $|\eta^*|$ , which suggested that the material could be processed at lower temperatures.



**Figure 1.** Frequency sweeps from oscillatory shear flow rheometry: (a) Storage modulus  $G'$  and (b) loss modulus  $G''$  (c) absolute values of complex viscosities at 120°C and strain of 0.1%.

**Acknowledgment:** Projects TN02000020 (TA CR) and NU21-06-00084 (AZV CR).

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### APPLICATION OF WASTE COFFEE GROUNDS AS POLY(VINYL CHLORIDE) MODIFIER

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Coffee is a product that is widely known and loved around the world. Statistics show that coffee consumption is increasing year on year. Global coffee production reached 168.5 million 60-kilogram bags as of 2021/202.<sup>1</sup> The highest coffee consumption based on data from the International Coffee Organization was recorded in Finland, i.e. 12 kg per person, while in Poland it is approximately 3 kg per person and in the Czech Republic 4.3 kg per person.<sup>2</sup> Every cup of this beverage generates waste, which can also be reused in the modification of polymer plastics under the assumptions of a zero waste industry.

Although poly(vinyl chloride) is one of the oldest and widely used large-volume polymers, there is little information in the current literature on the use of waste coffee beans for its modification and the properties of such composites.

In this study, PVC composites with waste coffee beans were characterised. Their structure and physical-mechanical and thermal properties were evaluated. Based on the analysis of the results obtained, it was concluded that this waste could be a valuable filler for PVC modification.

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## ACTIVE FILMS REINFORCED WITH CHITIN DISSOLVED VIA NATURAL SOLVENTS

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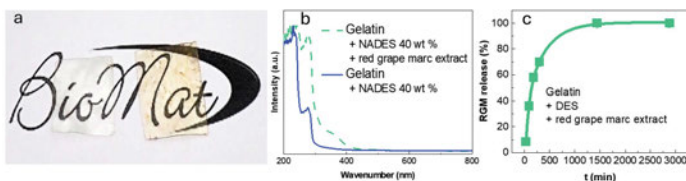
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A new and innovative strategy was explored in this study to dissolve chitin, valorized from fruit fly pupae, which was used as reinforcement in gelatin films. Choline chloride and citric acid were used as natural deep eutectic solvent (NADES) that, additionally, acted as plasticizer in gelatin films. Gelatin films with 0, 20, 40, 60 and 80 wt % NADES were characterized and those with 40 wt % NADES were selected to prepare active films with red grape marc. In particular, the films with 40 wt % NADES showed high UV protection, tensile strength of 10 MPa and elongation at break of 31 % due to the interactions observed between the components of the formulation by FTIR analysis. Those films prepared with red grape marc as antioxidant showed an inhibition capacity of 73 %. It is worth noting that these films were prepared by compression molding, a rapid and cost-effective processing method for industrial scale implementation. Therefore, this methodology arises as an environmentally conscious alternative, using valorized and biodegradable materials.



**Figure 1.** a) Film without red grape marc extract (left) and film with red grape marc extract (right). b) UV-VIS spectra of the film with and without the antioxidant. c) Release of grape marc extract over time.

### **BIOBASED POLYURETHANE PREPOLYMERS FOR SUSTAINABLE PLANT GROWTH MEDIA PRODUCTION**

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With the explosive growth in protected cultivation, there has been an increased demand for growing media. This trend is expected to continue in the future, with growing media production predicted to grow by 420% by 2050. Despite the expected growth in conventional media production, there is still predicted to be a shortfall in the market, with a gap of 65Mm<sup>3</sup> yr<sup>-1</sup> to be taken up by "new" growing media<sup>1</sup>. Conventional growing media mixes often contain a large peat-based component and as the growing media industry looks to "depeat", alternatives will need to be found. Many components have been suggested and used to some success, including compost, coco coir, wood chips, wool, wood fibre, biochar, and rice hulls. These components, often bio-waste products, bring environmental advantages over finite resources such as peat but suffer from variability in terms of physical and chemical properties due to their organic nature and varying sources.<sup>2</sup> This variability leads to variability in growth, a professional grower's nightmare.

This project looks to homogenous biobased byproducts for use as growing media using novel biobased polyurethane prepolymers (bPUPs). Although polyurethane prepolymers have long been used in growing media applications, advances in biobased isocyanates and biobased polyols allows for the generation of new, all biobased prepolymers. We have focused on the prepolymers based on PDI (pentamethylene diisocyanate) and a range of biobased polyols. A design of experiments approach is used to optimise reaction temperature and isocyanate index of bPUPs.

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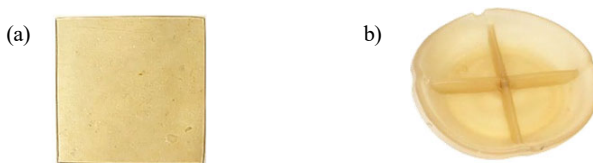
### PLASTICISING STARCH WITH DEEP EUTECTIC SOLVENTS: A SUSTAINABLE APPROACH FOR PRODUCING RECYCLABLE AND BIODEGRADABLE PLASTICS

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The effort to replace non-degradable petrochemical plastic has become a major concern for environmental scientists and organisation. One approach is to modify natural biodegradable polymers, such as starch, to create potential bio-based alternatives to synthetic polymers.<sup>1</sup> However, the plasticisation of starch is challenging due to the extensive number of hydrogen bonding between its chains. The use of a green deep eutectic solvent (DES) to plasticise starch and enhance its mechanical properties was followed by the optimisation of production factors and parameters (Figure 1). These efforts were aimed at creating environmentally friendly, recyclable, and biodegradable starch-based plastics with properties comparable to some commercial synthetic plastics.<sup>2,3</sup> The study demonstrated that starch plasticised with DES exhibited improved mechanical properties, making it a promising approach for the development of sustainable plastic materials.



**Figure 1:** Sheet of plasticised starch-DES (a), and a vacuum moulded recycled sample (b).

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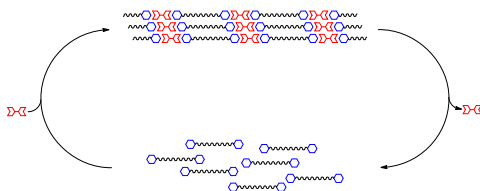
## SUSTAINABLE POLYESTERS DESIGNED FOR RECYCLING ON DEMAND

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The recyclability of common polymer materials is usually challenging. This is where the concept of recycling on demand comes into play. The aim is to design next-generation engineering polyesters that combine good material properties with a convenient ability to be easily recycled and reused.<sup>1</sup> Established recycling processes for polycondensates are based on solvolysis down to the monomer. This work targets oligomers as desired degradation products to optimize the energy efficiency of the process. Therefore, dynamic covalent bonds (DCBs) are introduced into the polyester chains to selectively obtain oligomers by heat or catalytic activation.<sup>2</sup>



**Figure 1:** principle of recycling on demand.

The polyesters were synthesized in a sustainable melt polycondensation process. The DCBs were introduced either directly during polycondensation or subsequently by reactive compounding. The resulting materials were analyzed by nuclear magnetic resonance spectroscopy, thermogravimetric analysis, dynamic scanning calorimetry and size exclusion chromatography. Based on the obtained results, further optimization towards closed-loop recyclable engineering polyesters and possible processing conditions are being investigated.

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**POLYPROPYLENE WASTE SOLVENT-BASED RECYCLING:  
NOVEL APPROACH FROM *IN-SITU* SPECTRAL ANALYSIS**

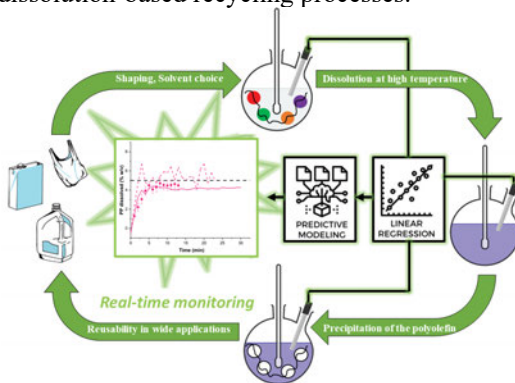
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In the past thirty years, significant efforts have been dedicated to the recycling of plastic waste. This is motivated by the increased collective awareness and concerns about the environmental impact of plastics, besides economic benefits. From the different recycling techniques, solvent-based recycling is the most promising because it offers the possibility to recover a “virgin” polymer from plastic waste, free of all additives. We propose to use different analytical techniques to describe the solvent-induced decrystallization step and to monitor different parameters during the dissolution of polypropylene. For example, we show the potential of *operando*-DSC and *in situ* spectroscopic techniques (MIR, NIR and Raman) to be useful for the understanding and monitoring of dissolution-based recycling processes.



**Figure 1.** Overview of the monitoring of the dissolution-based recycling process.

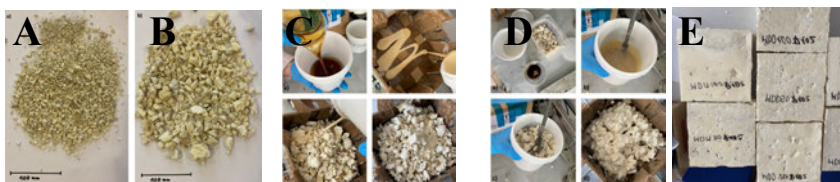
**MOLDED RIGID POLYURETHANE FOAMS MADE FROM POST-CONSUMER WASTE FOAMS USED IN REFRIGERATION EQUIPMENT**

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**Aim of the study**

The present study was designed to test the feasibility and develop a method for reusing post-consumer foam waste from refrigeration equipment in the production of rigid polyurethane foams, and to determine the physical and mechanical properties of the resulting products.



**Figure 1.** A) small recyclates fraction; B) large recyclates fraction; C) synthesis via “flooding” method; D) synthesis via “blending” method E) Example photo of synthesised polyurethane composite foams.

It was shown that the use of post-consumer polyurethane foams affects the final properties of the product in different ways. Parameters such as brittleness and thermal stability coefficient deteriorated slightly, but some composite materials outperformed polyurethane reference materials with a corresponding degree of overload. One of the primary applications could be thermal insulation that does not have high strength requirements.

**Future perspectives**

A key issue would be to develop improvements in the flooding method to ensure that the filler particles are better surrounded by the polyurethane reaction mixture. Adhesion analysis between filler particles and the polyurethane matrix.

## P-31

### SCAFFOLDS OF POLYURETHANE AND CELLULOSE ACETATE NANOFIBERS

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The production of cultured meat requires the use of 3D scaffolds, which serve to mimic the extracellular matrix. The surface properties of the material are modulated to a state where adsorbed proteins can maintain bioactivity. In this work, new scaffolds based on polyurethane and cellulose acetate were produced by electrospinning technique. The results showed that fibers in the range of nanometers were obtained. Mechanical measurements from dynamic mechanical analyses (DMA) indicated that increasing the speed rotation of the collector led to an enhancement of fiber orientation, which also increased the stiffness of both acetate and polyurethane thermoplastics.

**Keywords:** scaffolds, polyurethane, cellulose acetate, mechanical stiffness, cultured meat.



### RECYCLED POLYURETHANE FOAMS AS NEW ARTIFICIAL SOILS

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Artificial soils are becoming increasingly important<sup>1</sup> from pressures of producing commercially available soils that are not harmful to the environment, such as peat,<sup>2</sup> for future plant growth. Polyurethanes present themselves as a possible avenue of a novel artificial soil<sup>3</sup> that can be adapted to suit plant or environmental needs through bespoke synthesis and recycling. Polyurethanes are produced from a reaction between a polyol and a diisocyanate, resulting in an extremely versatile polymer with applications ranging from adhesives to foams, that have been used for artificial soils.<sup>3</sup> This has been achieved through effective rational design of the multitude of components that can be included into a polyurethane, from aliphatic/aromatic polymeric backbones to the surfactants and catalysts used in the synthesis, these factors create a rich and varied material for use in future soils.<sup>3</sup> These new soils can ideally target the water uptake and airflow needs of the plants grown in the for applications such as hydroponics.

Currently, polyurethane foam is shaped into products through subtractive manufacturing, where waste foam is removed and discarded. Industrial methods have already capitalized on utilizing these discarded pieces in new products. These discards are glued back together using a polyurethane prepolymer, compressed and steamed to create a new “rebond” block.<sup>4</sup> These rebonded foams are used in seats, crash mats and beds. This work looks at how these rebonded foams can be used as a recycled material for artificial soils, utilizing a waste product and altering factors such as the type of polyurethane used and the synthesis of the prepolymer to produce the next generation of artificial soils.

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### **ON-DEMAND CHEMICAL RECYCLING OF CARBON FIBER REINFORCED PLASTIC: ECO-FRIENDLY EPOXY RESIN FROM NATURAL SOURCES**

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A widely used material in the industry is epoxy resin of the Bisphenol A (BPA) type. However, its toxic and non-degradable nature has spurred demand for an eco-friendly alternative. In response, we develop a novel epoxy resin sourced from natural materials, enabling chemical recycling and suitable for high-performance applications. This new epoxy resin, derived from vanillin and raspberry ketone, is synthesized through an environmentally friendly process involving L-proline-catalyzed aldol condensation followed by epichlorohydrin coupling. The resulting thermosetting plastic, made with this natural resin, exhibits impressive tensile and flexural strength, along with a high crosslink density. Moreover, when applied to carbon fiber-reinforced plastic, it demonstrates exceptional strength. Importantly, these innovative epoxy resin-based plastics can be fully degraded through oxidation and decomposition processes. Thus, our natural resin holds significant promise as a sustainable and degradable alternative to BPA-type epoxy resin.

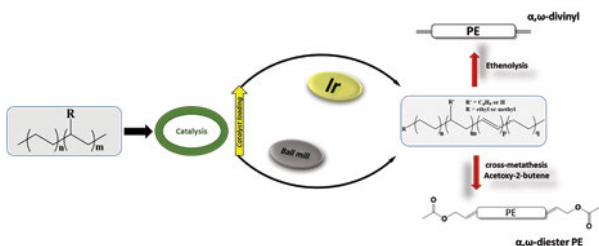
**PE FUNCTIONALIZATION TOWARDS METATHETIC  
DEPOLYMERIZATION USING IR-CATALYSIS  
AND MECHANOCATALYSIS**

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The extensive Sp<sup>3</sup> C–C bonding in PE hampers their natural degradation or facile chemical recovery. Thermolysis and hydroconversion strategies require either high temperatures and/or lead to mixtures of hydrocarbons which are difficult to valorize as such, require further refining to yield new chemicals. Installation of internal unsaturation on the PE backbone allows for lower (<100 °C) temperature selective cleavage into better-defined value-added chemicals (telechelic PEs) by metathesis. Iridium catalysis has been proven efficient for the selective functionalization/dehydrogenation of PE. To manage issues related to the preciousness of Iridium we showed in the present work that Ir-catalyzed PE-cycloalkene transfer dehydrogenation in *p*-xylene provides a thermomorphic system that allows for the recycling of an active Ir-complex. The system is effective for different grades of PE. Up to 4.2 % vinylene units were installed on a post-consumer HDPE which is the highest yield of unsaturation ever reported with Iridium.

We also investigate the possibility of performing a solvent-free dehydrogenation of PE in a ball miller under mechano-catalytic conditions. This utilizes low catalyst loading at a much shorter reaction time while avoiding high temperatures (reflux of toxic aromatics).

Cleavage of these unsaturated polyethylenes by cross-metathesis afforded telechelic divinyl or diester products with 86 % and 91 % conversions respectively.



### OXIDATIVE CHEMICAL RECYCLING OF CARBON FIBER REINFORCED PLASTICS WITH ENERGY EFFICIENCY

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Chemical recycling of carbon fiber-reinforced plastic (CFRP) utilized meta-chloroperoxybenzoic acid (*m*CPBA), a representative oxidizing agent. The optimal decomposition conditions for the epoxy (EP) resin in CFRP were investigated by varying *m*CPBA concentration and reaction time. The most efficient decomposition occurred in a 1.5 M *m*CPBA solution at 40 °C. Under these conditions, 2 g of waste CFRP completely decomposed within 6 hours with 100 mL of 1.5 M *m*CPBA. The Arrhenius equation analysis revealed a decomposition rate constant of  $4.27 \times 10^{-1} \text{h}^{-1}$ , confirming rapid decomposition. Tensile strength measured 4.4 GPa, 93.6% of virgin carbon fiber (v-CF), and electrical conductivity reached 590 S/cm, 95% of v-CF. Furthermore, the interfacial shear strength (IFSS) of the recovered carbon fibers (r-CF) using EP resin and polyamide 6 (PA6) was analyzed. For EP resin, the IFSS of r-CF was 88 MPa, a 26% increase compared to v-CF. In the case of PA6 resin, IFSS values were 80 MPa for r-CF, a 17% improvement over v-CF. The analysis emphasizes that the r-CF derived in this study exhibits superior physical properties and favorable IFSS compared to r-CF obtained through various recycling methods, making it a promising candidate for regenerating composites from r-CF. Remarkably, the recycling process in this study was implemented at 40 °C, the lowest temperature among existing recycling technologies. The recorded energy consumption during the recycling process is 35 MJ/kg, establishing it as the most energy-efficient method compared to other existing recycling methods.

### POLYMER BLEND COMPATIBILIZATION USING BLOCK COPOLYMER: THREE SIMILAR SIMPLE MODELS

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Properties of polymer blends can be improved by compatibilization, a modification decreasing interfacial tension  $\gamma$  between immiscible components. Suitable compatibilizers are block and graft copolymers with blocks compatible with related components of polymer blends. Knowledge of compatibilization efficiency is crucial for polymer materials preparation. Although many models including sophisticated ones exist, relatively simple models are welcome for practical use. We dealt with calculations based on the theory of Leibler<sup>1</sup>(L). This model was extended by Noolandi<sup>2</sup> and Hong (N) or Retsos<sup>3</sup> and Anastasiadis (R). We removed the approximation of bulk copolymer concentration equality with that in the whole blend. We estimated and compared compatibilizer effect quantified by relative decrease in interfacial tension  $\Delta\gamma/\gamma$  using their methods in our recent work,<sup>4</sup> in particular  $\Delta\gamma/\gamma$  dependence on chain and blocks lengths, interface to volume ratio and Flory-Huggins interaction parameters  $\chi$  in individual models.

The (N) modification leads to higher calculated  $(-\Delta\gamma/\gamma)$  than for (L) model, the (R) to slightly stronger one for longer copolymer chains and slightly weaker one for shorter copolymer chains. In all mentioned models, the calculated  $(-\Delta\gamma/\gamma)$  reaches its maximum  $(-\Delta\gamma_x/\gamma)$  with respect to copolymer chain length for its length comparable with homopolymer chain length. In dependence on  $\chi$ ,  $(-\Delta\gamma_x/\gamma)$  reaches its minimum for certain  $\chi$  value, increasing markedly for higher positive  $\chi$  and slightly for lower  $\chi$ .

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### CHEMICAL RECYCLING OF COMMERCIAL POLYURETHANE FOAMS BY GLYCOLYSIS

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The chemical recycling of currently used polymeric materials is one of the most promising routes to industrial circularity. Namely, the automotive industry employs many macromolecular materials, including polyurethane (PUR) products that are difficult to reuse or mechanically recycle since they cannot be melted or dissolved. Glycolysis is a chemical process using certain polyols (typically containing/similar to glycerol) to deconstruct the formed macromolecular site of the thermoset, resulting in the liquid raw recycled polyol production. This liquid recycled mixture can serve as a reactant for additional PUR manufacture. The formed recycled polyol exhibits unique material properties depending on the used nucleophile. This work summarizes the reactivity and structural characterization comparisons of differently produced recycled polyols. The nucleophiles used for the glycolysis were different low molecular glycols (LMG) and coconut oil glycerides (COG). The viscosity increases of recycled polyol with LMG reached 400% compared to the original foam polyol, while the COG recycled polyol exhibited an apparent viscosity upsurge of 39% (at 25 °C). The reactivity was not affected by the foamed system with 20 w% of LMG recycled polyol. On the contrary, COG-formed recycled polyol reaction times (cream and rise) decreased by approximately 30% (the system is more reactive). These results correspond with the different amine values of recycled polyols (44.5 mg KOH/g for LMG and 76.8 mg KOH/g for COG) – the higher the amine values, the more reactive the system. The structural differences are also observable from the FTIR spectra of DEG and COG recycled polyols (especially the presence of multiple C=O stretching and C–O stretching signals in COG polyols referring to the ester presence in the mixture). Both recycled polyols were incorporated into the original standard solution, and their functional properties are yet to be studied.

**Keywords:** Chemical Recycling, Glycolysis, Polyurethane, PUR, Glycerides, Polyols.

### RECYCLING AND VALORIZATION OF POLYESTER (PET) TEXTILE WASTE THROUGH VITRIMER CHEMISTRY

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The 21<sup>st</sup> century is often referred to as the “Age of Plastics” where the mass consumption of disposables, particularly textile leads to excessive pollution. Global fiber production has almost doubled from 58 million tons in 2000 to 113 million tons in 2021. Among the synthetic fiber production, polyester fibers (polyethylene terephthalate or PET) represent 54% of the market, being the most used fiber worldwide.<sup>1</sup> Textile fiber recycling remains a challenge due to the low cost of virgin fibers and clothing collects issues, but also the fact that most of actual clothes are composed by blended fibers or multicomponent. Therefore, 70% of the textile waste is either incinerated either landfilled.<sup>2</sup> Hence, the development of novel textile recycling strategies is a crucial point to reduce the utilization of fossil resources and reduce the environmental footprint of synthetic fibers across their entire life cycle.

The use of vitrimer chemistry represents a promising approach to valorize textile waste in order to obtain high-value recycled products with enhanced properties. PET-based vitrimers were elaborated through reactive extrusion by adding bisphenol A diglycidyl ether (DGEBA) as crosslinker agent and the nature of transesterification catalyst was explored. Besides the use of ionic liquids as catalysts, this work presents the synthesis of innovative PET-based vitrimers systems using new generation of epoxidized ionic liquids<sup>3-4</sup> and hydroxyl ones which auto-catalytic effect.

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### **CLOSED-LOOP RECYCLING: MECHANICAL RECYCLING OF POLYPROPYLENE CUPS**

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The recycling of plastic products is an integral part of the life cycle of polymers. This work focuses on the mechanical recycling of polypropylene (PP) thermoformed cups used in the food industry. The prepared shredded flakes from the PP dairy products (e.g. yogurt) cups were used to produce regranulate in twin screw extruder. To maintain comparative quality, the virgin polypropylene, from which these cups are normally made, was also regranulated, as well as the same PP with 2 wt. % of titanium white (again based on the composition of the original cups). In addition, a 30% blend of recycled and pure PP was also prepared. Materials were then analyzed by capillary rheometry, wide angle X-ray scattering, differential scanning calorimetry, thermogravimetric analysis, spectrophotometry and mechanically tested by tensile and impact testing. It can be concluded that recycled PP shows slight decrease in viscosity, crystallinity and melting point, and a significant increase in crystallization temperature. Mechanical testing shows that the addition of recycled PP into virgin material significantly increases the impact toughness, while the recycled material alone does not show such a rapid improvement, and the tensile modulus and maximum tensile strength slightly decrease. The relative elongation decreases as well. The addition of 2 wt.% titanium white to the virgin material slightly increases the crystallization temperature and significantly promotes formation of  $\beta$ -phase, as well as increase in impact toughness. Thus, it plays a role of specific  $\beta$ -nucleating agent. All in all, the processing and performance properties of the recycled PP were found to be comparable to the virgin material while it is thus suitable for application to same products, i.e. thermoformed cups. The reuse of food cup recycled PP in new products is a simple and effective way to increase the circular economy of PP and reduce the cost of producing disposable packaging materials. However, the potential contamination of the material still needs to be eliminated. Logistics issues also remain open.



**MODIFICATION OF RECYCLED JUTE NONWOVEN  
MATERIAL WITH PANI/TiO<sub>2</sub> NANOCOMPOSITE  
FOR REMOVAL OF Zn<sup>2+</sup> ION FROM WATER**

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Pollution of water bodies with heavy metal ions and the generation of enormous quantities of textile waste, which is commonly burned or landfilled, pose serious environmental problems. Taking into account that recycling is one of the principles of the circular economy model, this study aimed to face these environmental issues by producing nonwoven sorbent (NWS) based on recycled carpet fringes made of jute fibers. NWS was in situ coated with polyaniline (PANI) to improve the sorption capability.

To overcome the problem of uneven PANI coating of jute fibers, PANI synthesis was carried out in the presence of TiO<sub>2</sub> nanotubes (NTs), which regulate the aniline polymerization process. The influence of PANI/NTs nanocomposite on the sorption of Zn<sup>2+</sup> ions was evaluated. The sorption capacity of untreated and PANI/NTs treated NWS was investigated as a function of temperature, pH, and ion concentration. FESEM analysis revealed a uniform PANI/NTs coating on the surface of jute fibers. Raman and FTIR spectroscopy confirmed the presence of an emeraldine base form of PANI in nanocomposites. The modification of NWS with PANI/NTs coating resulted in considerably improved sorption efficiency. These sorbents withstand at least five sorption cycles without significant changes in Zn<sup>2+</sup> ions uptake.

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### REUSING COMPOSITES PRODUCTION WASTE INTO HIGH-ADDED VALUE APPLICATIONS

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Achieving circularity in structural composite materials is challenging as traditional recycling methods return short fiber material unlikely to be used in structural components and with serious difficulties to penetrate in other markets, especially in the case of glass reinforced composites.<sup>1,2</sup>

In this work, methods to cost-effective reuse of long fiber composite scraps in structural applications are explored. For instance, the production of dry fiber continuous roving and mats<sup>3</sup> or high-performance thermoplastic SMC (T-SMC) are studied.

For the T-SMC production unidirectional thermoplastic tape production waste is consolidated in a laminate with randomly oriented long fibers (>20 mm). In addition, to further enhance the material properties, the material is hybridized with continuous UD tape fiber inserts in the load direction.

Results show that reusing of the manufacturing offcuts can lead to very competitive material solutions.

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### QUANTIFYING CLIMATE-FRIENDLINESS: CARBON FOOTPRINT OF BIOCOMPOSITES THROUGH LIFE CYCLE ASSESSMENT

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Cradle-to-gate life cycle assessments (LCAs) of the newly developed, laboratory-scale polyamide (PA)/starch and polylactic acid (PLA)/starch biocomposites, with varying content of potato starch as the biofiller (ranging from 0 to 70 wt.% and 0 to 50 wt.%, respectively), were executed. The results indicated that the progressive addition of potato starch as the biofiller into the PA and PLA matrices significantly reduced the total carbon footprint of the PA/starch and PLA/starch biocomposites, achieving a maximum reduction of 43% and 18% with the highest starch content of 70 wt.% and 50 wt.%, respectively. Moreover, the newly developed PA/starch biocomposites demonstrated distinctive carbon footprint reductions compared to reference fossil-based polyamides of polyamide 6 (PA6), polyamide 12 (PA12), and polyamide 6.6 (PA6.6), as well as composites of polyamide 610 (PA610)/80 wt.% PLA modified by reactive extrusion (REX-PLA) and polyamide 40 (PA40)/30 wt.% glass fibers. Similarly, the carbon footprint of the newly synthesized PLA/starch biocomposites was successfully diminished in comparison to reference fossil-based plastics of high impact polystyrene (HIPS), acrylonitrile butadiene styrene (ABS), and PA6.6, respectively. Based on these findings, the PA/starch and PLA/starch biocomposites can be argued to contribute to advancing the development of a more climate-friendly future for plastics.

**STRAIGHTFORWARD SYNTHESIS OF COMPLEX POLYMERIC ARCHITECTURES USING NATURAL SUBSTRATES**

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In this study, we developed a new strategy for the synthesis of complex polymeric architectures (CPAs) with ultra-high chain density via the modification of highly functional natural substrates. This strategy uses the rapid and clean introduction of initiation sites for copper-mediated reversible-deactivation radical polymerization (Cu-RDRP) into different substrates through their reaction with trichloroacetyl isocyanate (TAI).<sup>1</sup> Through an extensive optimization study, we created a library of Cu-RDRP conditions affording well-controlled TAI adduct-initiated polymerization of different monomer classes (styrene, acrylates, methacrylates) in a wide molecular weight range. Importantly, using comprehensive NMR and triple-detection SEC studies, we proved conclusively for the first time that the TAI-based initiation sites act as trifunctional, effectively amplifying the substrate functionality and affording CPAs with unprecedentedly high chain density in straightforward protocols utilizing *in situ*/one-pot approaches. The great utility of the TAI strategy in the synthesis of natural-synthetic hybrid copolymers was exemplified using different precursors, including  $\beta$ -cyclodextrin ( $\beta$ -CD) and various cellulose substrates. In this way,  $\beta$ -CD-based stars with an extremely high number of arms and cellulose-based bottle-brushes with ultra-high grafting density were obtained in solution, and spatially controlled surface-initiated grafting of different cellulose-based substrates was demonstrated. In summary, the TAI strategy unlocks an access to a whole new group of unique CPAs based on natural substrates.

*Acknowledgment:* Financial support from the Institute of Macromolecular Chemistry, CAS, is gratefully acknowledged.

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**METAL-IMPRINTED POLYMER HYDROGEL BASED  
ON COLORIMETRIC AZO-QUINOLINOL FOR SELECTIVE  
DETECTION AND SEPARATION OF COBALT(II) IONS  
FROM AQUEOUS SOLUTIONS**

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We propose a technique for simultaneous detection and separation of cobalt established in a selective coordination-based colorimetric probe in Metal Imprinted Polymer Hydrogel (MIG). Especially, the N,N'-dimethylacrylamide (DMA), (E)-2-((4-(Diazenyl(8-hydroxyquinolin-5-yl))phenyl)(methyl)amino)ethylacrylate (M1) are copolymerized by free radical copolymerization to yield the polymeric probe [p(DMA-co-M1)] (designated as P1). M1 contains a selective 1:1 Co(II) binding site. P1 exhibited a sensitive and selective colorimetric response to Co(II) in aqueous media that could be detected with the naked eye through a yellow to red color change. The separation behavior in that MIG was evaluated with Hydrogel (HG), demonstrating a better MIG response to Co(II) separation and the success of imprinting. The selective separation of Co(II) in presence of an approximately 10-fold excess of Fe(II) ion present in excess, was studied. The selectivity of MIG has been modified through metal ion imprinting technique for its potential application of radioactive waste in nuclear industry.

**Keywords:** Co(II) ions, Polymeric probe, Colorimetric sensor, Metal-Imprinted polymer hydrogel, Metal separation

### COMPREHENSIVE DATA ANALYSIS OF PYROLYSIS-BASED CHEMICAL RECYCLING OF MIXED PLASTIC WASTE THROUGH PRINCIPAL COMPONENT ANALYSIS (PCA)

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Principal Component Analysis (PCA) is a multivariate statistical technique widely used for dimensionality reduction (DR) and data visualization.<sup>1</sup> It facilitates the transformation of complex datasets into a new coordinate system, allowing for a comprehensive understanding of underlying patterns and relationships.<sup>2</sup> In this study, we apply PCA to analyze the extensive datasets obtained from the pyrolysis-based chemical recycling of mixed plastic waste. Our research aims to produce high-quality pyrolytic oil suitable for integration into the petrochemical supply chain, thereby enhancing the circularity of plastic products. By employing PCA, we identify the most significant variables impacting the recycling process and explore their interrelationships. This abstract elucidates the development and implementation of a tailored PCA model for our specific research context. Through the integration of PCA, we gain valuable insights into the intricate dynamics of the recycling process, enabling informed decision-making and optimization strategies. Our findings contribute to advancing the efficiency and sustainability of chemical recycling initiatives, aligning with the principles of circular economy in the plastics industry.

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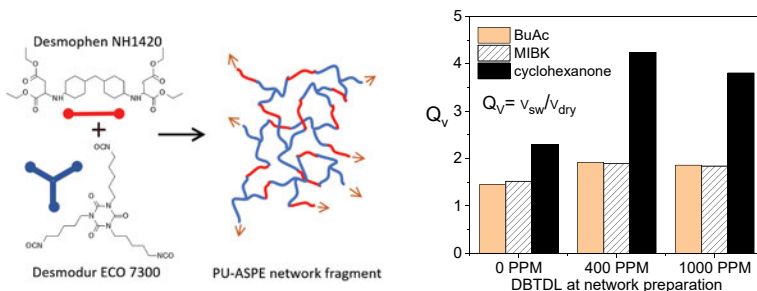
## INVESTIGATING THE STRUCTURE OF POLYASPARTATE - BASED POLYUREA NETWORKS BY SWELLING: EFFECT OF TRANSITION OF UREA BONDS ON NETWORK DENSITY

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Polyaspartate-based polyurea networks, PU-ASPEs, are eco-friendly alternatives to thermosetting systems such as epoxies and polyurethanes. We studied the curing mechanisms and structure of PU-ASPE networks based on aspartate-ester Desmophen® NH1420 and bio-based tri-isocyanate Desmodur® eco N 7300 (Covestro).



The networks prepared without dibutyltin dilaurate (DBTDL) revealed the lowest swelling indicating the highest crosslink density. On contrary, in presence of DBTDL swelling increased. The results suggest that the DBTDL has significant impact on the network structure. We further link this finding to the consecutive transition of urea groups into the hydantoin cycles by intramolecular deesterification. We hypothesize the effect of DBTDL in aspartate-amine – isocyanate cure is highly selective.

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**ADVANCING SUSTAINABILITY: BIO-BASED POLYURETHANE FOAMS DESIGNED FOR ENHANCED RECYCLABILITY**

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Polyurethane (PUR) foams play a pivotal role in various industries due to their versatile properties. Yet, despite their widespread use, their recycling rate remains low despite the increasing emphasis on circular economy principles.

This study focuses on advancing sustainability by designing PUR foams with enhanced recyclability, based on renewable raw materials. By integrating bio-based polyols derived from succinic acid (SA) into the foam's composition, we aim to reduce environmental impact and foster a more circular approach to material usage.

Through solvolysis experiments, we investigate the influence of SA-based polyols bearing hydrolysable ester linkages on the chemical recyclability of the PUR foams. Our results demonstrate a significant improvement in the recyclability of the foams through glycolysis upon the incorporation of SA-polyols, highlighting their potential to contribute to a circular economy and address the concerns surrounding plastic waste.<sup>1</sup>

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### HYDROPHOBIZATION OF CELLULOSE FOR PACKAGING APPLICATIONS

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Cellulose is being explored as a low-cost and circular alternative to synthetic plastics for disposable objects, with the aim of reducing environmental pollution. However, its processing and hydrophilic nature limit its use for packaging. The first technological challenge was accepted by the Italian company Sacmi, which successfully developed a new technology to mould dry cellulose fibres, allowing them to produce complex objects like cellulose-based caps for bottles. 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 are vegetable oils that have the ability to harden, forming a solid and continuous film through a process of oxidative polymerization. This property is due to the presence of unsaturated double bonds in the fatty acid chains present in these oils. 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) and Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) were conducted on samples subjected to various polymerization processes to obtain information on the degree of curing of the system and to optimize the treatment conditions. Cellulose fibers treated with oil 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).*

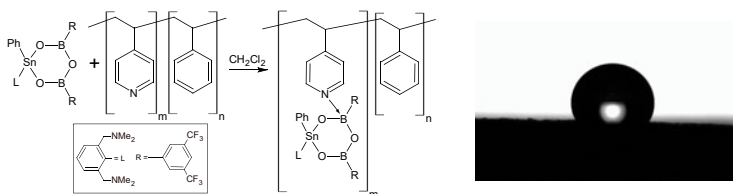
## HYDROPHOBIC FILMS BASED ON METALLABOROXINE POLYMERS

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In the current context of green chemistry, there is a growing pressure to find new non-fluorinated alternatives of hydrophobic polymers and thus seeking of new hydrophobic polymers is thus hot topic. Motivated by the study reporting the synthesis of new N-boroxine-PDMS, that allowed to generate new superhydrophobic formulation with SiO<sub>2</sub>, we developed new polymers based on metallaboroxines as good film forming materials.<sup>1</sup> These new polymers were used for the preparation of thin layer by spin coating at Si, SiO<sub>2</sub> and polyethylene surfaces. The layers were characterized by the help of SEM, VASE, XRF, UV-VIS spectroscopy and finally their WCA were determined.



**Figure 1:** Example of new metallaboroxine based hydrophobic polymer with WCA 125°.

**Acknowledgements:** Authors would like to thank the Czech Science foundation for the financial support (GA23-06548S).

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**METALLABOROXINES: SYNTHONS FOR THE HYBRID  
INORGANIC-ORGANIC POLYMERS**

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Nowadays, the development of inorganic-organic hybrid polymers are of great attention due to the mechanical properties and the thermal stability of the inorganic component with the flexibility, ductility and processability of the organic component. Recently, we have reported the synthesis of N→M intramolecularly coordinated metallaboroxines (MBOs, where M = Ga, Sn) having the central six membered ring MB<sub>2</sub>O<sub>3</sub>.<sup>1</sup> Advantage of suggested MBOs is their facile synthesis, so variety of functional groups may be easily introduced and some functional groups may be even further modified. Our preliminary tests demonstrated that stanna-boroxines L(Ph)Sn(O<sub>3</sub>B<sub>2</sub>(3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub> (L = {2,6-(Me<sub>2</sub>NCH<sub>2</sub>)-C<sub>6</sub>H<sub>3</sub>}<sup>-</sup>) can interact thanks to the Lewis acidity of boron atom with N-bases and allow to form N→B coordination bond. Based on this, we synthesized coordination polymers derived from poly(4-vinylpyridine) and poly-(4-vinylpyridine-co-styrene). MBOs have also been incorporated into oligomeric or polymeric chains by Schiff-coupling of L(Ph)Sn(O<sub>3</sub>B<sub>2</sub>(4-CH=O-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub> and LGa(O<sub>3</sub>B<sub>2</sub>(4-CH=O-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub> with various diamines such as 1,4-benzenediamine, ethylenediamine or amine-terminated siloxane.

***Acknowledgements:** Authors would like to thank the Czech Science foundation for the financial support (GA23-06548S).*

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### **CHEMICAL STRUCTURE, MORPHOLOGY AND SURFACE PROPERTIES OF SUSTAINABLE POLYURETHANES WITH MODIFIED HARD SEGMENTS**

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Plastics are currently key players in the global materials market. Among them, polyurethanes (PUs) - materials characterized by a segmented structure - have become more widespread. They can be found in foamed form (polyurethane foams) and solid form (thermoplastics or thermosets). In light of the latest scientific findings, there is a focus on developing sustainable green plastics.<sup>1</sup>

The presented work is a respond to the current demand of the plastics market for materials synthesized with bio-derived components. New thermoplastic bio-poly(ether-urethanes) (bio-TPUs) with approximately 80% bio-component content were synthesized using a two-step (prepolymer), solvent-free method. The synthesis included bio-polyol poly(trimethylene glycol), bio-1,3-propanediol, and a mixture of diisocyanates: hexamethylene diisocyanate (HDI) and partially bio-derived diisocyanate (containing 32% of green carbon). Four series of bio-TPUs with variable content of bio-based diisocyanate in the mixture (0%, 10% and 20%) were developed.

In order to verify the chemical structure and morphology of the obtained materials different techniques were used: ATR-FTIR spectroscopy, X-ray diffraction and SEM microscopy. The hydrolytic stability in acidic and basic environments and the wetting angle with water and ethylene glycol were also tested.

The test results showed that the modification of the hard segments of the bio-TPUs affects the material properties. Increasing the bio-diisocyanate content resulted in a decrease in the degree of phase separation. In addition, significant differences in surface morphology and wetting angle values were observed, depending on the bio-diisocyanate content.

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### **PIONEERING DEVELOPMENT OF ULTRATHIN NANOFIBROUS MEMBRANES FOR TISSUE ENGINEERING APPLICATIONS**

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In the realm of tissue engineering, there exists a pressing demand for ultrathin and highly porous membranes of minimal thickness to serve as transient replacements for basal membranes. These membranes play indispensable roles in facilitating cell cultivations and supporting cell transfer into tissue lesions during transplantations.

In this study, poly( $\gamma$ -benzyl-L-glutamate) (PBLG) was utilized as a biocompatible and biodegradable synthetic polymer. Various concentrations (ranging from 0.2 g/mL to 0.4 g/mL) of dissolved PBLG in dichloropropane with 1 wt% trifluoroacetic acid solvents were prepared. PBLG-based nanofibrous membranes were fabricated via electrospinning at room temperature following parameter optimization [flow rate (250  $\mu$ L/h), voltage (7 kV), gap between the needle and collector (10 cm)]. Scanning electron microscope observations were conducted to evaluate morphological characteristics and fibre width. Additionally, profilometric measurements were performed to monitor membrane thickness variation as a function of areal density.

Our results reveal a significant linear correlation between fibre diameters and both concentration and flow rate. Concentrations below or above the optimized concentration ( $C_{\text{Opt}} = 0.35$  g/mL) led in increased beads density and instability of the Taylor cone, respectively. Through manipulation of various parameters, we successfully generated high-quality samples with high porosity (>85%) and low thicknesses of up to 1.5  $\mu$ m, with average fibre diameters around 0.5  $\mu$ m. These findings hold promise for addressing critical challenges in regenerative medicine.

***Acknowledgments:** The authors would like to thank the European Regional Development Fund (No. CZ.02.01.01/00/22\_008/0004562 Project "Excellence in Regenerative Medicine") for providing financial support.*

**DISSOLVABLE MICRONEEDLE AND MICROCARRIER  
FOR CONTROL RELEASE OF DRUGS AND CELLS  
IN BIOMEDICAL APPLICATION**

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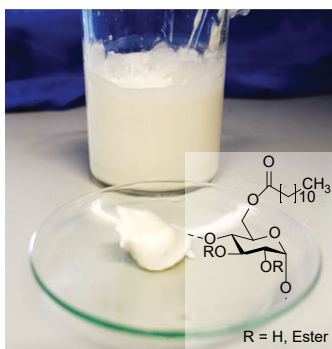
To modify mechanical strength and stability, we synthesized redox sensitive crosslinking agents and applied them to the polymer composite hydrogel. We created a dissolvable microcarrier and microneedle (MN) for use as biomedical device and API carrier since the aforesaid hydrogels dissolve in specific situations. We created a redox/thermo-responsive dissolvable gelatin-based microsphere for cell proliferation and high-quality cell harvesting in our initial investigation. Interestingly, diselenide crosslinked microspheres coated with PNIPAm-ALA5, enhancing cell attachment and proliferation. After adding 25 mM 1,4-dithiothreitol (DTT) and reducing the temperature (4°C), cells detached after 15 min. Thus, the microsphere generated in this work proved useful for non-enzymatic cell detachment and might be employed for cell multiplication and collecting high-quality live cells for tissue engineering or cell treatment. The second method used IPN hydrogel to make MN arrays by consecutive photoionic crosslinking sodium alginate and sulfobetaine methacrylate with N, N'-methylenebisacrylamide and Ca<sup>2+</sup> ions. The MN array allowed skin penetration and boosted IPN hydrogel mechanical strength in tensile and compression testing. A disulfide-crosslinked IPN hydrogel was used to make the MNs' detachable backbone, which was readily removed by disulfide bond cleavage with DTT and ethylenediaminetetraacetic acid solution. The dual drug-loaded MN patch was left in the skin for steady drug release. In vivo tumor suppression experiments on glioma-bearing C57BL/6 mice showed that LPS/DOX@MNs significantly increased immune response and inhibited tumors, demonstrating their synergistic immunochemotherapeutic benefits. Thus, MN-mediated combination immunochemotherapy offers targeted sustained administration and a potential novel strategy for synergistic therapeutic benefits.

## MULTIVALENT RAW MATERIALS FROM ENZYMATICALLY MODIFIED POLYSACCHARIDES

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An innovative and efficient method for substituting fossil raw materials in the home and personal care/cosmetics sector will be presented.



**Figure 1:** Enzymatically modified starch with outstanding emulsifying properties for oil-water mixtures with high oil content.

In a pilot project at the Fraunhofer IAP,<sup>1</sup> it was shown that lipase-catalyzed modification of starches is possible and that these subsequently exhibit very good emulsifying properties. In addition, an analogous modification of cellulose demonstrated its performance as a thickening agent. These biogenic, harmless basic materials are used at the Fraunhofer IAP in creams, lotions and ointments. A database of the emulsifying behavior and the thickening effect depending on the degree of modification and mixing enables a broad portfolio for the substitution of partially questionable raw materials in the home and personal care sector with modified polysaccharides. The

results generated will also be applied to the field of bio-based paints and varnishes.<sup>2</sup>

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**ENZYME DRIVEN RESTRUCTURALIZATION  
OF THE SURFACE OF BIODEGRADABLE POLYESTER  
MICROFIBERS**

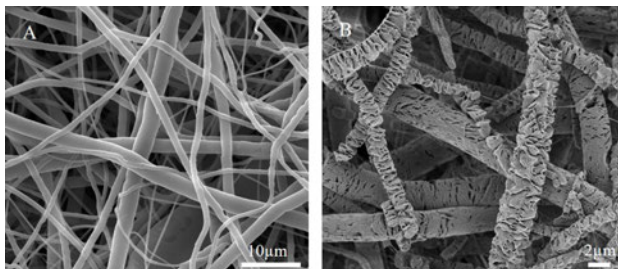
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Micro- and nanofibrous materials have great potential for use in tissue engineering, as their structure mimics the native extracellular mass (ECM). Nanofibrous materials have suitable properties for ECM replacement, namely large porosity and a large active surface ("surface to volume ratio") enabling protein adsorption and subsequent cell adhesion and proliferation. Planar nanofibrous layers with small fiber diameters are especially suitable for the treatment of chronic and acute wounds. However, despite all the advantages of nanofibrous scaffolds, the need to increase their bioactivity is becoming increasingly apparent. One possibility is further structuring of the fiber surface. Presented work deals with partial enzymatically catalyzed degradation used to change the surface structure of fibers based on biodegradable polyesters. The change in fiber morphology is very specific (Fig.1) with respect to its composition and can be controlled by enzyme selection and optimization of the enzymatic degradation process.



**Fig. 1:** SEM images documenting the microfiber material without (A) and after partial enzymatic degradation (B).

*Acknowledgements:* Work was supported by GAČR project n. 23-05154S.



### HYDROGEL IMMOBILIZATION OF DOPA DIOXYGENASE FOR ENHANCED CATALYSIS OF L-DOPA TO BETALAMIC ACID

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Enzymes offer high catalytic activity and substrate selectivity, enhancing productivity, reducing energy consumption, and limiting pollution. However, challenges like high purification costs, sensitivity to environmental factors, poor stability, and non-recoverability arise. Immobilization techniques, such as using hydrogels, can effectively tackle these issues. Alginate hydrogels, being biodegradable and biocompatible, were employed to encapsulate DOPA dioxygenase, an enzyme extracted from *Mirabilis jalapa* (MjDOD). MjDOD catalyzes the oxidation of L-DOPA, yielding yellow betalamic acid with an absorption peak at 430 nm. Our study assessed the enzyme's activity, stability, and reusability with varying temperature and pH, in hydrogel matrix by measuring absorbance at 430 nm. Scanning electron microscopy revealed the structure of the alginate hydrogels. Immobilized MjDOD displayed comparable activity and stability to its soluble form, retaining over 75% activity through seven cycles of reuse. Kinetic analysis showed a  $V_{max}$  of 16.00  $\mu\text{M}/\text{min}$  and a  $K_m$  of 364.2  $\mu\text{M}$  for the immobilized MjDOD.

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**STUDY OF LITHIATION  
OF 1,1-DIMETHYL-3-(4-OXO-4H-CHROMEN-6-YL) UREA,  
SYNTHESIS OF VARIOUS DERIVATIVES**

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2-Amino-4H-chromenes are important class of compounds found in many natural products<sup>1</sup> and are widely used as cosmetics, pigments,<sup>2</sup> and agrochemicals.<sup>3</sup> They also show a variety of biological activities, including anticancer,<sup>4</sup> antiinflammatory,<sup>5</sup> antimalarial,<sup>6</sup> and pesticidal activities.<sup>7</sup> A few synthetic methodologies have been developed till now for the synthesis of 2-amino-4H-chromenes by using various catalysts and additives. Recently Perumal and co-workers reported indium (III) chloride as a Lewis acid catalyst for the synthesis of (2-amino-3-cyano-4H-chromene-4-yl) phosphonic acid diethyl ester structural motif.<sup>8</sup> Lithiation of 1,1-dimethyl-3-(4-oxo-4H-chromen-6-yl) urea will be investigated under various reaction conditions. The *preliminary* results obtained to date with these substrates using n-BuLi as the lithium reagent and benzaldehyde as the electrophile offer great potential. In order to establish a general process a range of other lithium reagents (*sec*-BuLi, *t*-BuLi, LDA), electrophiles (benzophenone, acetophenone, acetone, cyclohexanone, D<sub>2</sub>O and *N,N*-dimethylformamide) and temperature (-78, -20 and 0 °C) are required to investigate their effects on the selectivity of lithiation.

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### SUSTAINABLE AND SCALABLE ROUTES TO BLOCK COPOLYMERS VIA CU-MEDIATED REVERSIBLE-DEACTIVATION RADICAL SOLUTION POLYMERIZATION

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While Cu-mediated polymerization has proven to be a method to engineer complex polymer microstructures in the lab for research applications, efforts are still required to scale-up the chemistry in a cost-effective manner for commercial production<sup>1</sup>. We are developing a robust process that is compatible with current operating practices and the wide range of acrylates and methacrylates used to produce acrylic coatings resins. Our process runs at low temperatures (40 to 60 °C) and low solvent content using inexpensive reagents to produce block copolymers to high conversion (> 90%) with a reaction time under 4.5 h. The one-pot process uses the same semi-batch operating strategy and reaction times used commercially to produce random acrylic copolymers by conventional free-radical polymerization at much higher operating temperatures. These mild operating conditions for the Cu-mediated process are enabled by using ascorbic acid as an environmentally benign reducing agent to speed up the reaction while also reducing the level of copper catalyst in the final solution to less than 50 ppm.<sup>1</sup> The advantages of the process will be outlined using the 12 Principles of Green Chemistry.<sup>2</sup> The process has been developed using methyl acrylate (MA) and diethylene glycol di(ethylene glycol) methyl ether methacrylate (DEGMEMA) as representative acrylate and methacrylate monomers. The efficient production of acrylate-acrylate (MA with either butyl acrylate or 2-methoxyethyl acrylate) and DEGMEMA-MA methacrylate-acrylate block copolymers has been demonstrated. Work is ongoing to further reduce the copper levels in the process while maintaining robust operation, as well as to demonstrate the ability to operate the process with functional monomers.

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### SYNTHESIS AND PROPERTIES OF SUSTAINABLE BIOPOLYURETHANES

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Polyurethanes (PU) rank as the 6th most produced polymers globally and find extensive application across various fields owing to their versatile properties.<sup>1</sup> The use of bio-based raw materials for PU obtaining thus opens the path to sustainable material utilization across various industrial sectors and minimize negative environmental impact. An essential strategy entails incorporating monomers rich in green carbon for material synthesis.

The main aim of this study was to obtain materials with high content of green carbon, by incorporating plant-derived monomers. A series of bio-based poly(ether urethane)s (bio-PU)s were synthesized using 100% bio-based polyol polytrimethylene ether glycol (PO3G) and the low-toxic diisocyanate, dimethyl diisocyanate (DDI), along with bio-based 1,3-propanediol (PDO) as a chain extender. The procedure of the materials synthesis was conducted using two methods: the one-shot method and the prepolymer method. Bio-PU)s were prepared at three different molar ratios of [NCO]/[OH]: 0.95, 1.0, and 1.05. The obtained materials underwent investigations of their chemical structure and selected thermal, processing, and physical (including mechanical) properties. These materials with a high bio-based content can be effectively acquired and may serve as substitutes for petroleum-based materials.

***Acknowledgements:** The financial support for this study from the Gdansk University of Technology by the DEC-9/RADIUM/2023 grant under the Radium Learning Through Research Programs—'Excellence Initiative-Research University' program is gratefully acknowledged.*

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**RING-OPENING METATHESIS POLYMERIZATION OF CYCLIC  
OLEFINS CATALYZED BY RUTHENIUM COMPLEX  
CATALYTIC SYSTEM**

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Ring-opening metathesis polymerization (ROMP) is a powerful tool for fabricating macromolecular materials by precisely controlling the microstructures that show excellent physical and mechanical properties.<sup>1</sup> Ru(II) alkylidene complexes are used as initiators that have shown remarkable benefits to stereospecific ROMP.<sup>2,3</sup> However, for practical use, alkylidene complexes are not required to be isolated and introducing appropriate supporting ligands is important. In this regard an *in-situ* approach has been adopted for ROMP of cyclic olefin using RuCl<sub>3</sub>-L<sub>n</sub>, and Ru(NO)Cl<sub>3</sub>.xH<sub>2</sub>O-L<sub>n</sub>, systems in conjunction with tri-isobutyl aluminum (tri-<sup>t</sup>BuAl) as cocatalyst, where L<sub>n</sub> represents tricyclohexylphosphine (L<sub>A</sub>) and 1-(naphthalen-2-ylmethyl)piperidine (L<sub>B</sub>). It has been observed that RuCl<sub>3</sub>-L<sub>A</sub> and RuCl<sub>3</sub>-L<sub>B</sub> demonstrated 100% and 92% conversion of NB to polynorbornene (PNB), respectively in CB at 60 °C yielding high molecular weight PNB. Ru(NO)Cl<sub>3</sub>.xH<sub>2</sub>O-L<sub>A</sub> has shown 98% conversion of NB to PNB. Higher activities have also been demonstrated for butyl-norbornene (Bu-NB). However, when tested for functional monomer, i.e., methyl-norbornen (Me-NB), lower conversions have been obtained under identical experimental conditions.

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## P-61

### SUSTAINABLE HETEROBIMETALLIC CATALYSIS FOR POLY(THIO)ESTER SYNTHESIS

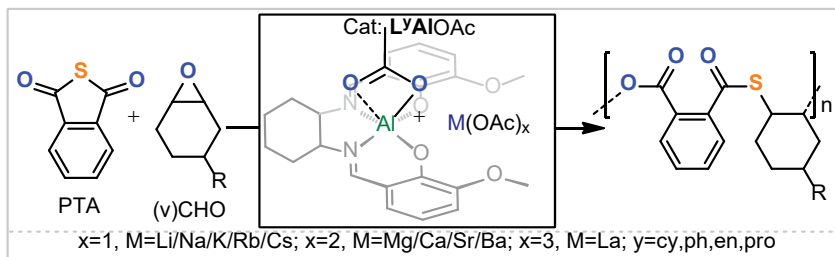
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Heteroatom containing polymers are susceptible to faster degradation than current commodity polymers comprising an all-carbon backbone, due to the presence of reactive centres in the polymer main-chain. In this regard, moving from oxygenated polymers like polyester and polycarbonates to sulfur containing analogues imparts additional desirable thermal and optical properties onto the polymers while further enhancing their degradability. The ring-opening copolymerisation (ROCOP) of cyclic thioanhydrides with epoxides results in poly(ester-thioesters) from alternating enchainment of the two monomers. In this work, we show that bimetallic Al(iii) catalysis displays improved rates, greater monomer tolerance and linkage selectivity for thioanhydride/epoxide ROCOP than analogous Cr(iii) catalysis,<sup>1</sup> resulting in the synthesis of novel terpolymers with CO<sub>2</sub> and high  $M_n$  materials with functional vinyl substituents for post-polymerisation modification.<sup>2</sup>



**Fig.:** Outline of the current work; R=H (CHO), CH=CH<sub>2</sub>(vCHO).

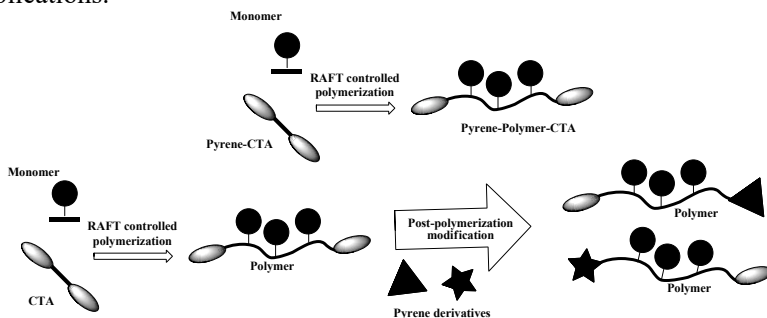
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## PRECISION BY RAFT POLYMERIZATION: ADVANCING PYRENE-BASED POLYMERS FOR DIVERSE MATERIAL APPLICATIONS

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Polymers are essential in numerous everyday applications but often face challenges regarding precision during traditional manufacturing. RAFT (Reversible Addition-Fragmentation Chain Transfer) polymerization offers a sophisticated solution, enhancing control over the polymer synthesis process.<sup>1</sup> In parallel, chemosensors are increasingly critical in detecting specific analytes via observable changes in properties such as absorption, emission, or conductivity.<sup>2</sup> These sensors are particularly valuable in biological settings where fluorescent chemoreceptors, utilizing mechanisms like pyrene excimer formation, emit fluorescence upon binding to target analytes.<sup>3</sup> In this study, the pyrene molecule was incorporated into the polymer structure either through RAFT polymerization or via post-polymerization modification. This integration enhances the development and functionality of new polymer-based materials across various possible applications.



**Figure.** Schematic illustration of the synthesis of functional polymers.

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### ATRP DERIVED COPOLYMERS FOR POLYESTER STABILIZATION AND RECYCLING ENHANCEMENT

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PLA is a good example of polyester as it is bio-derivable, biodegradable, easily reprocessable, and it has PS-like mechanical properties, so it is durable but brittle.<sup>1</sup> The material is valuable, and it should not be wasted on compost until it is not crucial. However, it is not efficiently mechanically recycled due to polymer degradation (hydrolytic and thermo-oxidative via radicals) occurring at elevated temperatures necessary for polymer processing.

In this work, macromolecular, multifunctional, and reactive additives for polyester recycling, were proposed, using PLA as an example. The first generation of additives was synthesized by Activator ReGenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP) of methacrylates, including glycidyl methacrylate (GMA). As epoxy groups can react with carboxylic acids, obtained copolymers can act as polyester chain extenders. Moreover, different elastic polyols were used as ATRP macroinitiators to positively impact PLA's mechanical properties, mainly impact strength. The second generation of reactive additives was obtained by opening some of the epoxide rings present in the additives with primary and/or secondary antioxidants. The additives were reactively extruded with PLA and their positive effect on recycling was proved by the viscosity measurements recorded during the experiment and by GPC analysis of the extruded materials.

*Acknowledgements: Research was funded by POB Technologie Materialowe of Warsaw University of Technology within the Excellence Initiative: Research University (IDUB) programme.*

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## P-64

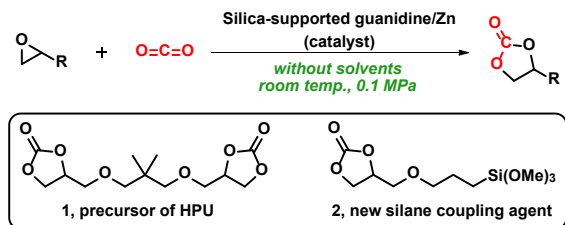
### DEVELOPMENT OF A SILICA-SUPPORTED CATALYST FOR THE EFFICIENT SYNTHESIS OF CYCLIC CARBONATES

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Cyclic carbonates are valuable materials with a wide variety of applications including electrolyte solvents in lithium-ion batteries, precursors of polycarbonates, resin plasticizers, and so on. Hydroxypolyurethanes (HPU), which are produced by reacting cyclic carbonates with polyamines, have been attracting much attentions as safer alternatives to traditional isocyanate-based polyurethanes.<sup>1</sup> The cycloaddition reaction of carbon dioxide (CO<sub>2</sub>) to epoxides in the presence of a catalyst is one of the most promising ways to produce cyclic carbonates.<sup>2</sup> This transformation is also recognized as an effective tool for CO<sub>2</sub> utilization.

In this study, we have developed a silica-supported guanidine-zinc complex as a catalyst for the synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>. This catalyst was prepared by immobilization of a guanidine-functionalized alkoxy silane and zinc bromide onto silica gel. The supported complex exhibited high catalytic performance even at room temperature under atmospheric pressure without any solvents. This method was also applicable for the synthesis of valuable cyclic carbonates including a bifunctional cyclic carbonate **1** (precursor of HPU) and as an alkoxy silane bearing a cyclic carbonate moiety **2** (silane coupling agent).



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### CATALYTIC CONVERSION OF CO<sub>2</sub> TO CYCLIC CARBONATES USING IONIC LIQUIDS FOR SUSTAINABLE CHEMICALS

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Herein, we present CO<sub>2</sub> as a renewable feedstock for the synthesis of cyclic carbonates by reacting it with various epoxy monomers derived from bio-based as well as petrochemical feedstocks. Imidazolium metal-free and metal-based ionic liquids (ILs) was found to be efficient catalysts of epoxy-carbon dioxide cycloaddition reaching high conversions (98%) under either supercritical CO<sub>2</sub> conditions (7.7 MPa, 80 °C, 1 h) or microwave irradiation (110 °C, 70 W, 2.5 h). The resulting cyclic carbonates can be easily aminolyzed to synthesize  $\beta$ -hydroxyurethanes.<sup>1</sup> Comprehensive and detailed mechanistic insights provided by Density Functional Theory (DFT) elucidated the IL-catalyzed CO<sub>2</sub>-epoxy reaction pathway.

**Acknowledgement:** *The research was supported by the Czech Science Foundation (GACR No. 22-05244S) and the Grant Agency of Charles University (GAUK No. 413022).*

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### **POLY(HYDROXYURETANE) FUNCTIONALIZED WOOD-DERIVED CARRIERS FOR CO<sub>2</sub> ADSORPTION**

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Currently used technologies of carbon dioxide capture are based upon hydroxides, ion-exchange resins or immobilized amines adsorption. Approach of active amine entrapment in poly(hydroxyurethane) molecules was proposed in our previous work for carbon capture adsorbents.<sup>1,2</sup> Our research show that immobilizing PHU CO<sub>2</sub> adsorbent on a carrier properly depends on few rules. Contact surface with carbon dioxide containing gas must be maximized for best efficiency, but sufficient flow must be maintained. Adsorbing layer must be thick enough to ensure longevity but thin enough to avoid idle adsorbing material and allow for fast regeneration. It is not an easy task, but proper carrier might deliver all those benefits. Wood-derived/cellulose carriers offer high enough surface area with big pores for proper diffusion of gas. In this work amines immobilized within poly(hydroxyurethanes) structure were synthesized from five-membered cyclic carbonates based on Bisphenol A diglycidyl ether, diglycidyl ether and trimethylolpropane triglycidyl ether, then coated onto different wood-derived carriers such as microcrystalline cellulose, delignified wood. Poly(hydroxyurethanes) syntheses and thermal degradation mechanisms were explored by FTIR, 1H and 13C NMR spectroscopy. Adsorption efficiency was recorded, surface and structure were analyzed for polymer deposition with SEM, surface area and pore distribution was measured and adsorption/desorption processes were analyzed using TGA and DSC.

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## DEGRADABLE BISPIPERIDONE DERIVATIVE AMINE NETWORKS

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The increasing need for a responsible use of nature's resources requires a circular economy of polymers. Among several recycling strategies, dynamic covalent chemistry (DCC) is gaining in importance.<sup>1</sup> Compared to aldehydes as electrophilic building blocks, ketones are less often used in amine-carbonyl chemistry and in the context of DCC as they are usually less reactive. Here, we report three bis(piperidin-4-one) derivatives with tunable electrophilicity as reactive, ketone-based monomers for dynamic, degradable polymer formation with amines.<sup>2-4</sup> Using model compounds besides polymerizations, the contribution of aminal, hemiaminal, imine and enamine units are determined. Imine and enamine units are found as predominantly species according to NMR and IR spectroscopy. Degradation occurs in aqueous solutions of different pH values and allows bispiperidone recovery.

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### IN-SITU NIR SPECTROSCOPY IN REACTIVE EXTRUSION OF POLYHYDROXYURETHANES

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Poly(hydroxyurethane) (PHU) chemistry is a promising sustainable alternative for specialty applications compared to conventional isocyanate-based polyurethanes. However, typical batch synthesis of PHU systems suffers from diffusion limitations and catalytic challenges, hindering its efficiency. Although the reactive extrusion (REX) technique shows promise in mitigating these issues,<sup>1</sup> its optimization for PHUs remains unexplored due to the absence of reliable real-time analytical tools.<sup>2</sup>

Therefore, we focused on establishing a methodology for continuous, in-situ near-infrared (NIR) spectroscopic monitoring of model REX synthesis of PHUs. We demonstrated the influence of the REX processing parameters by NIR-tracking of monomer depletion and verified the findings through FTIR, NMR, and MALDI-ToF analysis of the products. Hence, our study validated NIR monitoring as an effective tool for advancing REX technology to produce PHU prepolymers, applicable as e.g. precursors for coatings.

**Acknowledgements:** *Funding from the European Union's Horizon RIA programme (project SIMPLI-DEMO, GA. No 101058279).*

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### INCORPORATING BIOBASED MONOMERS INTO A TERPOLYMER DYNAMIC NETWORK

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Global thermosets production in 2021 was about 49.2 million tons accounting for 12.6% of global plastic production, while the European one was about 6.9 million tons accounting for 12.1% of total plastic production.<sup>1</sup> Thermosets are cross-linked materials with enhanced thermo-mechanical stability and better chemical, wear, and creep resistance properties than thermoplastics. Therefore, these network materials are employed in many advanced lightweight applications, such as aerospace, automotive, wind turbine, and thermal insulation.<sup>2</sup> Unfortunately, they also have a drawback: they cannot be reshaped, reprocessed, or recycled.

Dynamic covalent networks overcome this issue due to the presence of exchangeable chemical bonds activated by simple external stimuli, such as light or heat, making them fully reprocessable.<sup>2-4</sup>

The ever-increasing number of dynamic exchange mechanisms, coupled with the wide variety of monomers exploited to obtain polymer chains, enables the tailored synthesis of advanced materials with desired mechanical properties for specific applications.

In this study, we present a new dynamic network formed through the dissociative amide-imide exchange mechanism on a terpolymer containing also a biobased monomer.

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### SPECIFICALLY MODIFIED BIO-CHAR INFUSED BASED VITRIMERIC THIOL FRAMEWORKS FOR ANTI-CORROSIVE COATINGS

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Microwave triggered vitrimeric coating were developed as pre-eminent futuristic approach for sustainable development of coating industry. To protect the exorbitant assets from micro-cracking, damages, getting fatigued due to prolonged uses and weathering conditions, self-healable materials are the revolutionary choices.<sup>1</sup> Herein, a generous strategy was introduced to develop microwave assisted vitrimeric composite system incorporated with specifically modifies bio-char as nano-filler. The developed composite displays excellent self-healing efficiency when irradiated with microwave via transesterification exchange mechanism.<sup>2</sup> The composite also demonstrates the reliable thermo-mechanical properties along with noticeable stress relaxation ability, indicates a fast bond exchange reaction in the matrix. The composites exhibit amazing shape-memory properties in the presence of thermal as well as microwave stimuli. The excellent anti-corrosive properties of highly transparent coating system are validated through electro impedance spectroscopy *via* tafel plots and high hydrophobicity makes these smart composites insightful into the engineering and application as shielding coatings in marine applications.<sup>3</sup>

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## P-71

### **AN APPROACH BASED ON SUSTAINABILITY IN THE DEVELOPMENT OF CRYOGENIC INSULATION FOR SPACE AND ON-GROUND APPLICATIONS**

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Cryogenic insulation is a necessary and effective tool to prevent undesired heat gain and save energy. It is used for liquefied natural gas (LNG) carriers as well as insulation for space launchers' cryogenic propellant: liquefied hydrogen (LH2) and liquefied oxygen (LOX) tanks. Also the EU has set the goal of producing a Zero-emission airplane by 2035. Rigid polyurethane (PUR) foams are one of the best materials for cryogenic insulation due to their light weight, good mechanical properties, and low thermal conductivity. LSIWC has many years of experience in developing cryogenic insulation using more and more environmentally friendly components and blowing agents. Recent years research focuses on PUR foams produced using polyols from recycled and renewable resources as well as using the next-generation blowing agents with low global warming potential (GWP). As with many industries, there is a growing emphasis on sustainability. Studies of rigid PU foams from bio-based feedstock are growing each year. Second-generation feedstock, such as tall oil (TO), is more favourable as it is produced as a side stream of cellulose production. Using our developed approach to cryogenic insulation calculations and design, we have replaced petro-chemical polyols with polyols from renewable materials (TO polyols). Another essential component of rigid PUR foams is the blowing agent. Many physical blowing agents have a negative effect on global warming and ozone layer depletion. Currently, 4th generation blowing agents are allowed in Europe according to the REACH regulations.

The research shows the possibility that by combining more environmentally friendly catalysts and foaming agents it is possible to obtain PUR material, which in the future can serve as cryogenic insulation in LNG transportation or in aerospace technologies.



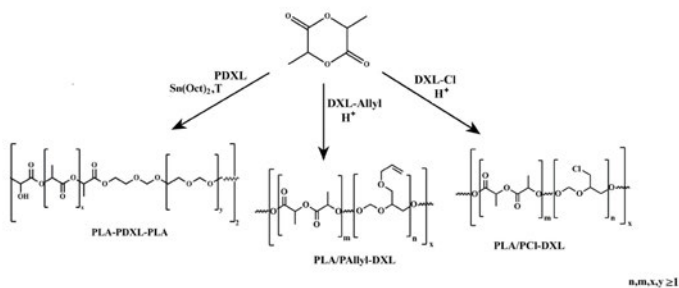
## POLYLACTIDE MODIFICATIONS: TOWARDS SUSTAINABILITY

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The rapid pace of industry development is correlated with the mass production of synthetic polymers. However, the increase in the production of non-degradable polymeric materials has a negative impact on the environment, constantly intensifying the issue of waste accumulation. Consequently, increasing attention is being devoted to the search for new materials that would not only mitigate environmental risks but also exhibit the ability to undergo accelerated degradation or recycling. In this context, polylactide (PLA) as an alternative to traditional synthetic polymers, widely used, is gaining significance. However, this material has flaws, and challenges associated with its properties require further research. For this purpose, in our studies acetal units were introduced into the polyester chain via cationic copolymerisation or coordinative polymerisation. Statistical or block copolymers of L-lactide with various acetals were obtained. Furthermore, it has been demonstrated that copolymers containing chloromethyl or allyl groups exhibit susceptibility to further modification of the polymer chain, enabling the formation of more complex structures.<sup>1</sup>



**Scheme 1.** Synthesis of lactide copolymers with various cyclic acetals.

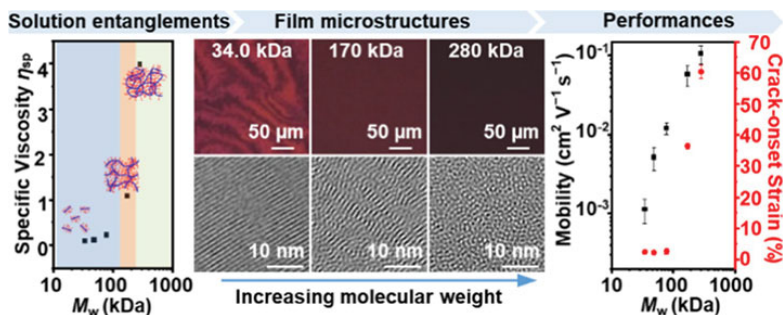
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## MORPHOLOGY DESIGN FOR HIGH PERFORMANCE STRETCHABLE CONJUGATED POLYMER FILMS

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The conjugated semiconducting polymers are important materials for flexible and stretchable electronic devices such as field-effect transistors (OFET), organic light-emitting diodes (OLEDs), and organic solar cells (OPVs) with excellent opto-electric properties, low-cost solution, large-area processing, and light weight. In order to meet the requirements of wearable devices, stretchable conjugated polymer films should combine high carrier mobility with stable stretchability. However, although some polymer semiconductors with high carrier mobility have relatively low crystallinity, their rigid molecular structure limits their inherent flexibility and stretchability. Therefore, how to prepare polymer films with high electrical and mechanical properties is one of the core problems to realize stretchable electronics. We solved these problems by increasing the molecular weight above the entanglement molecular weight and by solution-phase structure and assembly pathways in a controllable fashion. Finally, we design a stretchable conjugated polymer film with a percolation network structure with optimized mechanical/electrical properties, which provided a basis for the construction of fatigue-resistant electronic devices.



**FLAME RETARDANT POLYLIMONENE CARBONATE: MATERIAL INNOVATION AS A GAME CHANGER**

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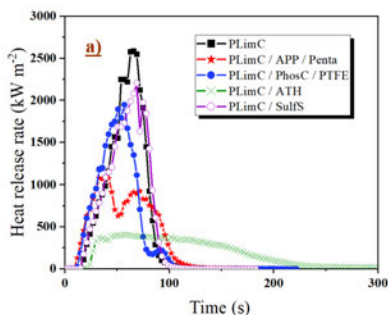
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The global plastic industry relies on fossil-based materials, presenting environmental challenges. A sustainable polymer namely poly(limonene carbonate) (PLimC), made of limonene oxide and CO<sub>2</sub> as two monomers from non-food sources, shows advances in various applications where additives such as flame retardants (FRs) are crucial to comply with fire safety measures.

The variety of FRs is wide, and therefore the approach involved conducting a comparative study of four different halogen-free flame retardant systems that are conventionally used in polycarbonates and polyolefins. The objective is to understand which FR enhances the flame resistance of PLimC most effectively. The primary task of the project is to conduct experimental evaluations to analyze the thermal properties, flammability, and fire behavior of each system. This data will offer valuable insights towards the advancement of safer and more sustainable materials.



**b)**

	PLimC / APP / Penta (wt.-%)	PLimC / ATH (wt.-%)
<i>PLimC</i>	70	50
<i>Ammonium polyphosphate - APP</i>	20	-
<i>Pentaerythritol - Penta</i>	10	-
<i>Aluminium Hydroxide - ATH</i>	-	50

	PLimC / PhosC / PTFE (wt.-%)	PLimC / SulFS (wt.-%)
<i>PLimC</i>	83.6	99.6
<i>Phosphorus compound - PhosC</i>	16	-
<i>Polytetrafluoroethylene - PTFE</i>	0.4	-
<i>Sulfonate salt - SulFS</i>	-	0.4

**Figure 1.** a) Cone calorimeter results (heat release rate vs. time) for the PLimC and with the four FRs systems b) Composition (wt.-%) of the systems used in the study.

### ENHANCING THE OXIDATION STABILITY OF $Ti_3C_2T_x$ MXENE FOR USE AS AN ANTI-CORROSION COATING

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MXene is a two-dimensional material that is being used in various fields such as energy storage, electromagnetic shielding, sensors, and corrosion protection. However, MXene suffers from poor oxidation stability. This leads to a short lifetime and poor performance. This is especially critical in the field of polymer/MXene nanocomposites anti-corrosion, where MXene is used to prevent corrosion by blocking the oxidizing media. To overcome this issue, various studies have been conducted to prevent oxidation by treating the surface of MXene with silanol,<sup>1</sup> using polyanionic salts at the edges of MXene to block the penetration of oxidizing media,<sup>2</sup> or using chelating agents to block the penetration of oxidizing media.<sup>3</sup> In this study, various antioxidation methods for  $Ti_3C_2T_x$  MXene were compared by UV-Vis spectroscopy, Raman spectroscopy, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), and the most effective method was determined and selected. The  $Ti_3C_2T_x$  MXene antioxidized by the selected method is expected to form a stable polymer/MXene nanocomposite by interaction with the polymer. In addition, the oxidation stability of MXene is enhanced, which is expected to improve the anti-corrosion performance of the polymer/MXene nanocomposite coating.

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## ATOMIC LAYER DEPOSITION OF SOLID-STATE ELECTROLYTE FOR HIGH LITHIUM-ION BATTERY PERFORMANCE

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With increasing demand for cost-effective and environmentally friendly energy solutions, lithium-ion batteries (LIBs) have gained prominence as stable energy storage devices in various sectors such as electric vehicles, portable electronics, and aerospace. Consequently, extensive research is underway to enhance the electrochemical performance of batteries and explore new materials and manufacturing methods to meet evolving environmental and technological demands. In this pursuit, atomic layer deposition (ALD) emerges as a promising coating technology, capable of depositing uniform, ultrathin films with controllable thickness and composition at the atomic level<sup>1</sup>. Leveraging ALD, issues like aggregation in cathode slurries of lithium-ion batteries can be addressed, leading to improved battery performance<sup>2</sup>. Thus, ALD holds significant potential to revolutionize the future of the battery industry. This paper delves into the sophisticated structure formation of solid-state electrolytes utilizing ALD, contributing to the advancement of battery technology.

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**MXENE- BASED MATERIAL FOR ADVANCED APPLICATION**

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MXenes are relatively new two-dimensional (2D) materials with the formula  $M_{n+1}X_nT_x$ , where M represents a transition metal, T represents carbon and nitrogen and  $T_x$  is =0, -OH, -H or  $-F^1$ . MXenes materials possess unique physicochemical properties such as metallic conductivity allowing high electron transfer, redox active centres enabling electrochemical activity, unique optical properties such photothermal, plasmonic response and surface-rich tunable functional groups suitable for an easy interfacial modifications and (bio)compatibility. We and others revealed that suitable modifications leading to the enhanced stability of MXene against oxidation. Modification can be modulated and tunable towards targeted advanced applications. This contribution will provide application of MXenes-based materials such as detection small bioactive molecules, biomarkers, glycan enrichment, photothermal actuator and utilization as liquid marble for a controlled movement, self-assembly, light-induced release, and water evaporation system.

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### **MXENE/PEDOT:PSS NANOCOMPOSITE FILM WITH HIGH CONDUCTIVITY AND SELF-ADHESIVE PROPERTIES FOR REAL-TIME HEALTH MONITORING**

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Wearable electronic devices have the potential to accurately and rapidly measure physiological signals when attached to the user's body. This is expected to play a crucial role in electronic skin, healthcare monitoring, and human-machine interface fields.<sup>1</sup> However, achieving a wide sensing range, fast response/recovery time, and skin compliance simultaneously to measure small electro-physiological signals on the skin remains a significant challenge. In this study, we fabricated a nanocomposite film with high electrical conductivity and excellent self-adhesiveness using solution-processed conductive MXene, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), polydimethylsiloxane (PDMS), and polysorbate 80 (Tween 80). MXene with abundant surface functional groups was used as a conductive filler to provide high conductivity similar to metals.<sup>2</sup> PEDOT:PSS enhanced the conductivity through chemical and structural interactions with MXene.<sup>3</sup> PDMS was utilized as an elastomer to provide excellent skin compliance and self-adhesiveness, and Tween 80, a nonpolar surfactant, was employed to achieve uniformity in the composite. The homogeneous formation of the nanocomposite film was confirmed using Fourier transform infrared spectroscopy, x-ray diffraction, scanning electron microscopy, transmission electron microscopy, and Raman spectroscopy. The electrical properties of the film were evaluated using an oscilloscope and a Keithley multimeter. With high electrical conductivity and excellent self-adhesiveness, the prepared nanocomposite film is expected to accurately measure physiological signals, including electrocardiograms and electromyography.

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**MOLECULAR DYNAMICS SIMULATION FOR EVALUATING  
CHEMICALLY AMPLIFIED RESIST DEPROTECTION  
AND LINE EDGE ROUGHNESS IN NANOLITHOGRAPHY**

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In photolithography, chemically amplified resists (CARs) are widely used photoresists.<sup>1</sup> However, with the shift to Extreme Ultraviolet (EUV) lithography, photon scarcity poses challenges. Reduced photon counts from EUV exposure can increase Line Edge Roughness (LER), impacting semiconductor performance. To address this, resist materials and chemical formulations are crucial.

To tackle this problem, a simulation of the deprotection process in CARs was implemented using all-atomic molecular dynamics. Protons were substituted with Li ions to overcome simulation challenges. When Li ions approached the protected group, a deprotection reaction occurred, closely resembling experimental FTIR results. By dividing reactions into masked and unmasked areas, resulting LER during development was measured. Exploring various PAG and polymer combinations, trends for reducing LER were identified, providing strategies for optimization.

This research offers valuable insights into optimizing the design of chemically amplified resists in the era of EUV lithography, where precise control over LER is of utmost importance for advanced semiconductor fabrication.

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**UNVEILING THE INFLUENCE OF CHEMICAL STRUCTURES  
ON PHOTO ACID GENERATOR DYNAMIC PROPERTIES  
IN PHOTORESISTS VIA MOLECULAR DYNAMICS  
SIMULATION**

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Our research tackles the challenge of photoacid generator (PAG) diffusion in chemically amplified resists (CARs) during photolithography's post-exposure bake (PEB) phase. Our approach melds quantitative analysis, measuring ion diffusion rates using statistical mechanics, and qualitative assessments, exploring structural influences on diffusion dynamics. Crucially, we focus on the role of pairwise interactions in influencing ion movement within the polymer matrix.

Leveraging these insights, we establish a screening methodology to evaluate PAGs, rating them based on their diffusion traits, considering ionic mobility and interaction energies. This methodology prioritizes the diffusion characteristics that are critical for maintaining micro-pattern integrity.

This research conducts computational simulation with experimental calibration to ensure our theoretical findings are grounded in reality. These molecular-level understandings serve to enhance photolithographic techniques, enabling the selection of PAGs that heighten the performance of CAR resists.

By bridging the gap between theoretical simulations and practical photolithography demands, our work pushes forward semiconductor manufacturing, underpinning the enhancement of microelectronic device production. Overall, the study enriches our understanding of PAG diffusion, emphasizing the substantial effect of molecular interactions on photolithographic outcomes and paving the way for CAR resist optimization tailored to the semiconductor industry's evolving needs.

## SOFT MICRON-SIZED POLYPEPTIDE MICROGELS: PREPARATION, CROSSLINK DENSITY, TOPOGRAPHY, AND NANOMECHANICS IN SWOLLEN STATE

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We report the innovative preparation of soft micron-sized polypeptide microgels by horseradish peroxidase (HRP)-mediated crosslinking in inverse suspension. The microgels were based on poly[*N*<sup>5</sup>-(2-hydroxypropyl)-L-glutamine)-*ran*-(*N*<sup>5</sup>-propargyl-L-glutamine)-*ran*-(*N*<sup>5</sup>-(6-aminohexyl)-L-glutamine)]-*ran*-(*N*<sup>5</sup>-[2-(4-hydroxyphenyl)ethyl]-L-glutamine)] (P2HPG-Tyr). We tested effect of surfactants sorbitan monooleate (SPAN 80), polyoxyethylenesorbitan trioleate (TWEEN 85), and dioctyl sulfosuccinate sodium salt (AOT), on microgelation in inverse suspension without, or with pre-emulsification step. The crosslinking employing SPAN 80, and 1-hour pre-emulsification yielded high-quality, spherical, and colloidally stable  $\sim 80 \mu\text{m}$  P2HPG-Tyr microgels. We immobilized these large swollen hydrated P2HPG-Tyr microgels on Mica and glass substrates for the topography and nanomechanical measurements by atomic force microscopy (AFM). The topography analyses revealed surface irregularities of the P2HPG-Tyr microgels. The AFM proved the viscoelasticity and softness of P2HPG-Tyr microgels documented with Young's moduli in range of tens of kPa. Finally, the crosslink density was evaluated revealing the concentrations of elastically active network chains (EANCs) in the range from  $0.717 \times 10^{-3}$  to  $0.946 \times 10^{-3} \text{ mol/cm}^3$ .

**THE ROLE OF SILVER NANOPARTICLES IN PVA-G-PMA  
NANOFILMS AND ITS PERFORMANCE IN TERMS OF OPTICAL  
ACETONE DETECTION**

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Easy and fast detection of flammable and hazardous vapors of the acetone is important due to the harm that it can cause. Here, an easy and efficient optical detection is developed based on composite thin films consisting of silver nanoparticles (AgNPs) synthesized through a “green” method and poly(vinyl alcohol-graft-methyl acrylate) copolymer matrix. The hybrid films were deposited via spin-coating of dispersions prepared by blending of copolymer solutions and AgNPs synthesized using water extract of lavender based on by-products of the essential oil industry. Optical properties and sensing performance of the films with different AgNPs volume fractions were studied by UV-VIS-NIR spectroscopy through monitoring the reflectance change and calculating swelling degree. The role of the nanoparticles’ weight concentration in the films and their impact on the optical response toward acetone was studied along with the nanoparticles size, size distribution, concentration, and morphology via DLS and TEM methods. An optimal value of AgNPs concentration around 1.2 wt % in the films was found, at which, the substantial enhancement of sensing responses toward acetone vapors was observed.

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## EXPLORING MR-TADF VIA COMBINATORIAL CHEMISTRY WITH BREADTH FIRST TREE SEARCH

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TADF (Thermally Activated Delayed Fluorescence) material, which is called as a third-generation OLED, is attracting attention because of its efficiency and economic feasibility.<sup>1</sup> Especially, multi-resonance type TADF material shows high color purity and oscillator strength, and is currently attracting attention as a very promising TADF design method.<sup>2</sup>

As AI technology has recently developed, research using machine learning techniques in the field of material discovery is increasing, and its feasibility is being verified in practice.<sup>3</sup> However, this ML-assisted material discovery has the intrinsic limitation that the property distribution of the material it generates is dependent on data used for training.

As an effort to overcome these limitations, there are cases where combinatorial chemistry via reinforcement learning has been applied. In those case, results were reported that the method was somewhat effective in extrapolating and finding materials with extreme physical properties.<sup>4,5</sup>

In this study, we apply Breadth first tree search from the perspective on Fragment Based Drug Discovery to explore the optimal Deep Blue Multi-resonant TADF material that can be synthesized. This method can be extended to reinforcement learning.

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**TOUGH AND TEMPERATURE-RESPONSIVE NANOCOMPOSITE  
HYDROGEL BASED ON POLY(N-ISOPROPYLACRYLAMIDE-  
CO-SODIUM METHACRYLATE) / CLAY: POTENTIAL  
ENVIRONMENTAL APPLICATION**

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Hydrogels able to respond to a stimulus, such as  $T$  or pH, by a distinct change in the degree of swelling are attractive for potential use as drug delivery systems, sensors or biosensors, actuators, or super-absorbents. Currently, an important topic is the removal of hazardous heavy metal ions from wastewater, which are released as industrial pollution. In this work, we developed a simple method to prepare a tough and ultra-extensible hydrogel with an ultra-fast response to temperature and pH and with a high potential to adsorb heavy metals, by using poly(N-isopropylacrylamide) (PNIPAm), sodium methacrylate (SMA, co-monomer), and Laponite RDS clay platelets. The obtained hydrogels showed excellent mechanical and tensile properties due to the specific physical crosslinking by clay, in combination with ultra-long polymer chains.

PNIPAm exhibits a distinct temperature responsiveness, while a small amount (1.5 mol%) of SMA co-monomer introduced a strong pH response and an enhanced efficiency of removal of metal cations. The hydrogels have been demonstrated to successfully adsorb Cr(VI) from aqueous solutions, and the introduction of SMA increased the removal efficiency and stability, achieving efficiency values up to 99.93%. This work can promote the development of new adsorbents for Cr(VI) from wastewater. Their excellent mechanical and tensile properties make possible using them as water treatment material in various sizes and shapes.

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**CHITOSAN/GRAPHENE  
OXIDE/VANILLIN@CARBOXYMETHYL CELLULOSE  
FOR THE ADSORPTION OF NSAIDS FROM WASTEWATERS**

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The COVID-19 pandemic has increased NSAID consumption, necessitating their removal from wastewater.<sup>1</sup> Adsorption, a sustainable and cost-effective method, is ideal for this. Chitosan (CS), a non-toxic, biodegradable polymer, is enhanced by vanillin and graphene oxide (GO) for improved adsorption due to GO's large surface area.<sup>2,3</sup> Combining CS, GO, vanillin, and carboxymethylcellulose (CMC) creates a low-toxicity, biocompatible compound with high adsorption capacity for diclofenac. Characterized by FTIR, SEM, XRD, and BET, the compound's optimal adsorption conditions (pH, temperature, contact time) were determined through batch experiments.

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### EXPLORING THE IMPACT OF VARYING ACN CONTENT IN HNBR ON MISCIBILITY, MORPHOLOGY, AND DISPERSION IN BATTERY SLURRY THROUGH MD SIMULATION

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Lithium-ion batteries (LIBs) are pivotal for modern energy storage, serving various sectors from smartphones to electric vehicles and renewable energy integration.<sup>1</sup> Their advancement relies on optimizing electrodes, electrolytes, and separators, with cylindrical cells standing out for their durability, safety, and efficiency.<sup>2</sup> This study examines a multi-component cathode battery slurry's phase behavior, morphology changes, and dispersion levels. The slurry, composed of PVDF as binder, HNBR with varying ACN content as dispersant, NMP as solvent, and CNT/GRA as conductive agent, underwent comprehensive analysis. Various techniques, including visualized imaging and RDF analysis, were employed. Results show that increasing ACN content in HNBR enhances miscibility with PVDF, while low ACN content leads to phase separation. Conversely, higher ACN content in HNBR negatively affects dispersion. These insights into molecular aggregation and morphology of the slurry are also applicable in the separator slurry's dry-coating process, where the dried morphology plays a crucial role and will be discussed in future studies.

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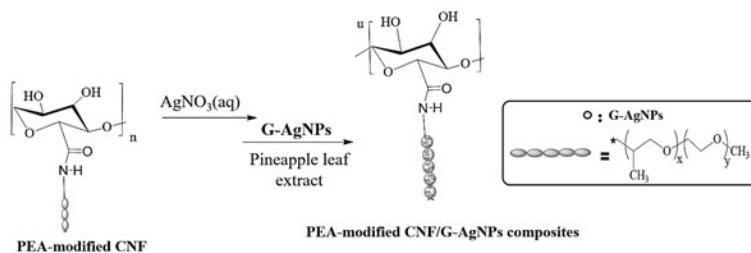
**SUSTAINABLE CELLULOSE NANOFIBER COMPOSITES FOR THIRAM DETECTION BASED ON SURFACE-ENHANCED RAMAN SPECTROSCOPY**

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This study utilizes the by-product of the juice industry (carrot pulp fiber) to prepare cellulose nanofiber (CNF)<sup>1</sup>, chemically modifies it with polyetheramine (PEA), and incorporates green eco-friendly silver nanoparticles (G-AgNPs)<sup>2</sup> to design functional CNF for surface-enhanced Raman spectroscopy (SERS)<sup>3</sup>. The results show that the PEA-modified CNF with G-AgNPs has significantly higher sensitivity in detecting thiram than CNF without PEA modification and without G-AgNPs. Moreover, there is a good linear relationship between the intensity of thiram Raman spectra and its concentration ( $R^2=0.9972$ ). The SERS-functional CNF synthesized in this study not only improves the detection technology for agricultural products but also increases the recycling value of discarded plant fibers, making it an environmentally friendly, green, and sustainable material.



**Figure 1.** PEA-modified CNF/G-AgNPs composites.

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## P-88

### A NOVEL COORDINATION POLYMER FOR PROTONIC MEMRISTORS WITH HIGH MIXED PROTON-ELECTRON CONDUCTIVITY

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In this presentation, a novel mixed proton-electron conductor derived from a coordination polymer is introduced, aimed at advancing polymer nanotechnologies for sustainability. This material is produced via a solution-based synthesis method and showcases a distinctive dual conductivity profile with exceptionally high values. The molecular architecture of the material is distinguished by a dense network of hydrogen bonds and d- $\pi$  conjugation, which enable efficient and simultaneous transport of protons and electrons. Moreover, when converted into a gel form, the material displays memristive properties and synaptic plasticity. These features establish it as a promising candidate for protonic memristors, which are crucial for sustainable developments in the growing field of artificial intelligence. The versatility and potential of this material underscore its capacity to forge new directions in the development of functional sustainable polymers.

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**TUNING THE CRYSTALLINITY OF EU-DOPED  
POLY(L-LACTIC ACID) MICROSPHERES FOR TUMOR  
TREATMENTS**

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In recent years, there has been significant interest in utilizing poly(L-lactic acid) (PLLA) microspheres infused with a rare earth radioisotope as an alternative to conventional methods for personalized internal radiotherapy and diagnostics. These polymeric microspheres are biodegradable, biocompatible, and do not cause adverse reactions in the patient's body as they do not sediment within the organs.<sup>1</sup> This research investigates a new method to control the crystallinity of both pristine PLLA microspheres and those doped with Europium by ranging the emulsification temperature from 20 to 80°C. Through x-ray diffraction and calorimetry, the crystalline fractions were determined for both undoped and Eu-doped microspheres, ranging from 16% to 35%, and from 30% to 50%, respectively. By analysis of the vibrational modes, it was possible to hypothesize a model in which the combined action of the emulsification temperature and the presence of Eu affect the ratio of amorphous to  $\alpha$ -phase crystalline components within each PLLA microsphere.<sup>2</sup> Moreover, unlike bulk materials, the microspheres do not exhibit infrared-active changes in the molecular unit following exposure to x-rays,<sup>3</sup> making them suitable for radiotherapy and diagnostics. These findings present opportunities for innovative methods to synthesize radiation-resistant and biodegradable microspheres with tuned crystallinity.

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## P-90

### DUAL-RESPONSIVE PHOTONIC MULTILAYERS IN COMBINATION WITH A SMARTPHONE APPLICATION AS HIGH-SECURITY ANTI-COUNTERFEITING DEVICES

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A new concept for dual-responsive one-dimensional (1D) photonic crystal (PC) multilayers is proposed herein. The novel PC-based systems rely on the humidity from the human breath and fluorescence triggered by  $Al^{3+}$  coordination to act as high-security anti-counterfeiting labels to be used in combination with a smartphone application. The dual-responsive patterned film is fabricated via the alternating deposition of photo-crosslinkable poly(2-vinylnaphthalene-co-benzophenone acrylate) and 51%-quaternized poly(4-vinylpyridine-co-benzophenone acrylate) onto a transparent polyethylene terephthalate substrate to obtain 1D PC multilayers, followed by the introduction of a poly([(2-hydroxybenzylidene)-4-vinylbenzohydrazide-co-benzophenonyl acrylate) top coating. The obtained system is then exposed to ultraviolet light irradiation through variously patterned masks. The patterned films exhibit vivid dual color transitions in high-humidity environments along with remarkable turn-on fluorescence, following the coordination of  $Al^{3+}$  ions upon spraying with a 1 wt%  $Al(NO_3)_3$  solution. Notably, the efficacy of the combination between the two-step security function of the flexible patterned multilayer films and a smartphone app was also demonstrated. The first level of security involves the determination of the RGB color value before and after a color change triggered by blowing onto the film. The second level of security involves the revelation of hidden fluorescent shapes under ultraviolet light irradiation after  $Al(NO_3)_3$  spraying.

**Keywords:** Anti-counterfeiting High-humidity Fluorescence 1D photonic crystals

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