Polymers 2022

New Trends in Polymer Science: Health of the Planet, Health of the People

25–27 May 2022, Turin, Italy

Program and Abstract Book

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Polymers 2022 - New Trends in Polymer Science: Health of the Planet, Health of the People

La Cavallerizza Reale

Turin, Italy

25 – 27 May 2022

Conference Chairs

Professor Francesco Trotta

Professor Pierangiola Bracco

Professor Marco Zanetti

Organised by

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25 – 27 May 2022, Turin, Italy

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Wednesday 25 May 2022: 08:15 - 13:10 / 14:30 - 17:50 / **Welcome cocktail: 18:45**

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Friday 27 May 2022: 08:30 – 13:05 / Closing Remarks: 13:05

Conference Program

Wednesday 25 May 2022

08:15 – 08:45 Registration Desk Open (Check-in)

08:45 – 09:00 Welcome
Chairs: Francesco Trotta, Pierangiola Bracco, and Marco Zanetti

Session Chair: Dimitri Bikiaris

09:00 – 09:35 **Rolf Mülhaupt** "From Hermann Staudinger to Sustainable Material Systems"

Session 1
Health of the Planet – Part I

09:35 – 09:55 **Pedro Luis de Hoyos-Martinez** "Synthesis of Biopolyols from Wood Residues for the Elaboration of Performing Polyurethane Foams"

09:55 – 10:15 **Enzo Pichon** "Waterborne and Bio-Based Non-isocyanate Polyurethane Dispersions: Towards Safer Polyurethane Coatings"

10:15 – 10:35 **Liudmyla Gryshchuk** "Influence of Recycled Polyurethane-Polyols on the Properties of Rigid Polyurethane Foams for Pre-insulated Pipes"

10:35 – 11:35 **Coffee Break & Poster Session A**

Session Chair: Alberto Frache

11:35 – 12:10 **Dimitri Bikiaris** "Progress and Critical Parameters for the Production of High Molecular Weight Poly(alkylene 2,5-furandicarboxylate)s Biobased Polyesters"

Session 1
Health of the Planet – Part II

12:10 – 12:30 **Louis Meunier** "Synthesis of PBT Vitrimers Through Reactive Extrusion - Effect of Flame Retardant Additives"

12:30 – 12:50 **Alberto Fina** "Phenoxy Resin-Based Covalent Adaptable Networks: A Recyclable Alternative to Epoxy Thermosets"

12:50 – 13:10 **Maddalena Bertolla** "Comparison of the Properties of a Random Copolymer and a Molten Blend PA6/PA6.9"

13:10 – 14:30 **Lunch**

Session Chair: Gaetano Guerra

14:30 – 15:05 **Claudio Gerbaldi** "Solid-Like Electrolytes for Safe, Ambient Temperature Operation of Alkali Metal Ion Batteries"

Session 2
Health of the People – Part I

15:05 – 15:25 **Maurice Brogly** "Structuration of Amphiphilic PE-b-PEO Copolymer Thin Films at Interfaces"

15:25 – 15:45 **Pierre Carmona** "Structure Evolution of Phase-Separated Biopolymer Films for Controlled Drug Delivery"

15:45 – 16:05 **Joong Ho Moon** "Conjugated Polymers for Intracellular Labeling and Delivery"

16:05 – 16:30 **Coffee Break**

Session Chair: Claudio Gerbladi

Session 1
Health of the Planet – Part III

16:30 – 16:50 **Niclas Conen** "Model Based Investigation of Sustained Ring-Opening Polymerization of Lactide With Non-toxic Zinc-Guanidine Catalysts"

16:50 – 17:10 **Christina Gkountela** "Exploring Enzymatic Polymerization Pathways for the Production of Aliphatic Polyesters"

17:10 – 17:30 **Viktoria Ilieva** "Biodegradation of Polyesters by Filamentous Fungi"

17:30 – 17:50 **Felice Quartinello** "Bioexploration Towards Novel Plastic-Degrading Microorganisms: Rumen Metagenomic Study for Synthetic Polyester Decomposition"

18:45 **Welcome Cocktail**

Thursday 26 May 2022

Session Chair: Francesco Trotta

08:30 – 09:05 **Gaetano Guerra** "Co-Crystalline and Nanoporous-Crystalline Polymers"

Session 3
Young Investigator Award Session – Part I

09:05 – 09:40 **Lei Fang (YIA Winner 2018)** "Conjugated Ladder Polymers and Polymer Networks: New Functions Imparted by Fused-Ring Constitution"

09:40 – 10:15 **Bernhard Schmidt (YIA Winner 2020)** "Double Hydrophilic Block Copolymers as an Avenue to Self-Assembly and Multi-Phase Systems"

10:15 – 11:15 **Coffee Break & Poster Session B**

Session Chair: Lei Fang, Bernhard Schmidt

Session 3
Young Investigator Award Session – Part II

11:15 – 11:35 **Athina Anastasaki** "Concurrent Control Over Sequence and Dispersity in Multiblock Copolymers"

11:35 – 11:55 **Mikelis Kirpluks** "Bio-Based Thermoset Polymer as Viable Alternative for Rigid Polyurethane Foams"

11:55 – 12:15 **Erlantz Lizundia** "Bio-Based Polymers Endow Environmentally Sustainable Energy Storage Systems With Long Lifespan"

12:15 – 12:35 **Matteo Bonomo** "Polyurethanes as Low Cost and Sustainable Moisture and Oxygen Barriers for Flexible Perovskite Solar Cells"

12:35 – 12:55 **Joost Brancart** "Sustainability of Dynamic Covalent Polymer Networks"

12:55 – 14:15 **Lunch**

Session Chair: Alberto Fina

14:15 – 14:50 **Katja Loos** "Advanced Nano-Composites Based on Poly(vinylidene fluoride) Block Copolymers"

Session 2
Health of the People – Part II

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Session 1
Health of the Planet – Part IV

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15:50 – 16:10 **Rachel Yerushalmi-Rozen** "Polymer and Solvent Mediated Nano-Cellulose Chiral Nematic Phases"

16:10 – 16:30 **Anna Sowińska-Baranowska** "Influence of Biofillers on the Crosslinking of Natural Rubber Compounds and the Performance of Vulcanizates"

16:30 – 16:50 **Coffee Break**

Session Chair: Katja Loos

Session 1
Health of the Planet – Part V

16:50 – 17:10 **Antonis Gitsas** "Electrical Conductivity and Crystallization Dynamics of EVA Nanocomposites in the Melt State"

17:10 – 17:30 **Silvia Lage-Rivera** "Enhancement of the Electrical Conductivity and Mechanical Properties of PLA/MWCNT Composite Thanks to a Natural Biopolymer: The Lignin"

17:30 – 17:50 **Alice Boarino** "PLA-Lignin Films for Sustainable Packaging"

18:45 **Bus to Gala Dinner**

Friday 27 May 2022

Session Chair: Roberta Cavalli

08:30 – 09:05 **Steven Kurtz** "Point of Care 3D Printing of PEEK for Orthopaedic Applications"

Session 2
Health of the People – Part III

09:05 – 09:25 **Elisa Guazzelli** "Single-Chain Folded Unimer Micelles for the Encapsulation and Release of the Anticancer Combretastatin A-4 Drug"

09:25 – 09:45 **Daniel Cuadra Rodriguez** "Well-Controlled Drug Delivery Systems Based on Polycaprolactone Hollow Fibers"

09:45 – 10:05 **Khalid Ferji** "Polymerization Induced Self-Assembly (Pisa): A Powerful Approach Toward Formulation of Advanced Nano-Objects of Polysaccharides-Based Copolymers"

10:05 – 10:25 **Mohammad Mamunur Rashid** "Sustainable Approach to Combine TiO_2 with Various Polysiloxane Matrices to

Produce Self-Sterilising, Uv-Protecting, Self-Cleaning, and Flame-Retardant Cotton Textiles for Technical Applications"

10:25 – 11:25	**Coffee Break & Poster Session C**

Session Chair: Massimo Lazzari

Session 1
Health of the Planet – Part VI

11:25 – 11:45	**Maria Laura Tummino** "Alginate and Alginate-Chitosan Hydrogels for Wastewater Remediation: Effect of Composted Biowaste-Derivative Addition"
11:45 – 12:05	**Jakub Łagiewka** "The β-Cyclodextrin Polymer Cross-Linked via 3,3',4,4'-Biphenyltetracarboxylic Dianhydride for Removal of Organic Dyes From Water"
12:05 – 12:25	**Claudio Cecone** "Sub-Micrometric Cross-Linked Mats and Fibrous Carbons Produced From Nades-Derived Beta Cyclodextrin-Based Polymers"
12:25 – 12:45	**Justyna Miedzianowska** "The Efficiency of Straw Modification Methods in Functionalization of Elastomer Composites"
12:45 – 13:05	**Bolesław Szadkowski** "Pro-ecological Hybrid Pigments Based on Natural Dyes and Mineral Supports as Multifunctional and pH Sensing Colorants for Polymer Composites"
13:05	**Closing Remarks**

Welcome by Francesco Trotta, Pierangiola Bracco, and Marco Zanetti

Dear colleagues and friends,

We are very proud and honored to announce the international conference *Polymers 2022 - New Trends in Polymers Science: Health of the Planet, Health of the People*, organized in collaboration with the MDPI open access journal *Polymers*. The conference will be held in Turin, Italy, on May 25–27, 2022.

Over the past 60 years, polymers have made an outstanding contribution to the development of modern society in every field. The substitution of traditional materials with tailored polymer systems in the most diverse applications has allowed us to overcome important technological challenges and improve the quality of life.

Today, however, polymeric materials face a new challenge: reconciling the technological progress and well-being of people with the preservation of the planet, from a circular economy perspective.

The purpose of the meeting is to bring together scientists from academia and industry to present leading-edge research on the advancements in polymer science and technology in all its main aspects, with a particular emphasis on those aiming to preserve and improve the health of the planet and of people, as per title. Both oral and poster contributions are welcome. The broad themes that will be addressed during the conference include synthesis, modification, and characterization of synthetic and natural polymers, polymers from green chemistry, polymer hybrids, nanocomposites, polymer biomaterials, polymers in drug delivery and tissue engineering, polymers for human health, bio-based and biodegradable polymers, polymer recycling and re-use, polymers for the environment, functional polymers, and polymers in energy, among others.

The conference follows the very successful meeting *Polymers 2018 - Polymers: Design, Function and Application* held in March 2018, Barcelona, Spain.

We look forward to welcoming you at the meeting in Turin!

Prof. Francesco Trotta, Prof. Pierangiola Bracco, and Prof. Marco Zanetti
Polymers 2022 Chairs

Conference Chairs

Professor Francesco Trotta
Department of Chemistry, University of Turin
Email: francesco.trotta@unito.it

Professor Pierangiola Bracco
Department of Chemistry, University of Turin
Email: pierangiola.bracco@unito.it

Professor Marco Zanetti
Department of Chemistry, University of Turin
Email: marco.zanetti@unito.it

Polymers (ISSN 2073-4360) is an international, open access journal of polymer science. It publishes research papers, communications and review articles. Polymers provides an interdisciplinary forum for publishing papers which advance the fields of (i) polymerization methods, (ii) theory, simulation, and modeling, (iii) understanding of new physical phenomena, (iv) advances in characterization techniques, and (v) harnessing of self-assembly and biological strategies for producing complex multifunctional structures. Scientists are encouraged to publish their experimental and theoretical results in as much detail as possible. Therefore, there is no restriction on the length of the papers. The full experimental and computational details must be provided so that the results can be reproduced.

Among other databases, *Polymers* is indexed by the Science Citation Index Expanded (Web of Science), MEDLINE (PubMed), and Scopus.

Journal Webpage: www.mdpi.com/journal/polymers
Impact factor: 4.329 (2020); 5-Year Impact Factor: 4.493 (2020)

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If you would like more information about open access or any of our services listed above, be sure to talk to us at the MDPI booth. See you there!

Polymers 2022 - New Trends in Polymer Science: Health of the Planet, Health of the People will be held in Turin, Italy, on 25 – 27 May 2022.

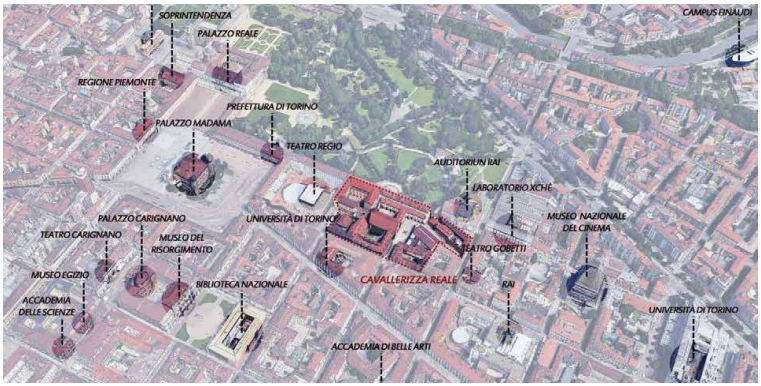
This conference seeks to bring together scientists from academia and industry to present leading-edge research on the advancements in polymer science and technology in all its main aspects, with a particular emphasis on those aiming to preserve and improve the health of the planet and of people.

Conference Venue

Torino is the capital of the Piedmont region, recently selected by Lonely Planet as the World's Top Region to Visit in 2019.

The symposium site "La Cavallerizza Reale" is in the heart of downtown Turin, close to the Royal Palace and other important buildings and monuments.

Address: Via Giuseppe Verdi, 9, 10124 Torino TO, Italy



Registration Desk

The desk for registration, information and distribution of documents will be open from 08:15 on 25 May 2022.

Certificate of Attendance

Upon request, the participants of the event will receive an electronic Certificate of Attendance by email once the event is concluded.

Venue Locations

Disclaimer

Delegates will receive a name-badge at the Information Desk, upon registration. The badge must be worn prominently in order to gain access to the congress area during all scientific and social events. Admission will be refused to anyone not in possession of an appropriate badge.

Insurance

The organizers do not accept liability for personal accident, loss, or damage to private property incurred as a result of participation in *Polymers 2022*. Delegates are advised to arrange appropriate insurance to cover travel, cancellation costs, medical, and theft or damage of belongings.

Gala Dinner

Thursday 26 May
Gala dinner is included in the full registration.

The conference dinner will be held at “Castello di Pavone”, one of the most beautiful Italian monuments and considered one of the most scenic and fairytale castles in the world. The Castle stands majestically on the top of a hill offering views of great beauty. The Castello di Pavone is located 30-40 min away from the conference venue. Free buses will be arranged.

Buses to Gala Dinner: 18:45h

MDPI contact persons during the event

Elena González

Email: elena.gonzalez@mdpi.com

Pablo Velázquez

Email: pablo.velazquez@mdpi.com

Ana Sanchis

Email: ana.sanchis@mdpi.com

Abstracts I

Invited and Short Talks

From Hermann Staudinger to Sustainable Material Systems

Rolf Mülhaupt

Freiburg Materials Research Center, FMF, of the Albert-Ludwigs-University of Freiburg, Germany

Hermann Staudinger is the father of macromolecular chemistry and bio-inspired chemical materials research. One hundred years ago, he made his vision public, which was revolutionary at the time but experimentally completely unproven. His vision was that both natural and man-made molecular materials are built according to the same blueprints. At that time, it was still believed that only nature but not man could synthesize biomaterials such as proteins. According to Staudinger's vision, a very large number of small monomer molecules are linked together by covalent bonds to form very long molecular chains, for which he coined the new term macromolecules. This concept was incompatible with the prevailing doctrine of colloid chemistry, which assumed that small molecules were only loosely connected but unable to form macromolecules. Moreover, crystallographers opposed Staudinger because they believed that only molecules with a maximum of 500 atoms could fit into a unit cell. The famous organic chemist and Nobel laureate of 1927, Heinrich Wieland, advised Staudinger at the end of the 1920s: "Dear colleague, abandon your idea concerning the existence of large molecules, organic molecules with a molecular weight above 5000 do not exist. If you clean your products like rubber, they will crystallize and turn out to be low-molecular weight substances". Staudinger persistently stood up against the heavy opposition of his colleagues and laid the foundation for the molecular design of polymeric structural and functional materials. His concept is still elementary in polymer chemistry and biotechnology alike. Back then, Staudinger also recognized that the system integration of macromolecules plays a central role in living systems. Today, we are beginning to equip passive synthetic material systems with the features of life by developing adaptive and smart material systems that can react energy-autonomously to changes in their environment by changing their properties. Thanks to Hermann Staudinger’s molecular design, the poor substitutes for ivory, silk and natural rubber developed during the pioneering days have evolved to enable tailoring of advanced structural and functional materials and systems. Trends and challenges in polymer research are illustrated by the example of polyethylene. What do polyethylene and aspirin have in common? Both molecules were discovered in 1898. This is where the similarity ends. Whereas aspirin is still produced today using the same process for the same application and even by the same company, the material polyethylene today has nothing in common with polyethylene one hundred years ago. Innovations in catalysis and process

engineering have revolutionized olefin polymerization and opened the door to sustainable advanced hydrocarbon materials. Polyefins are the clear leaders in both global plastics production and life cycle assessment. They are produced in highly energy- and resource-efficient solvent-free catalytic processes, can use renewable raw materials and their wastes can be easily recycled as materials, chemical feed stocks and energy. By controlling their molecular and supermolecular architectures, ethylene polymers are being tailored to meet the demands of highly diversified markets. Their applications range from fatigue-resistant pipes, recyclable packaging, elastomers and components of artificial hips to high-strength fibers that surpass the performance of Kevlar and even self-reinforcing and self-repairing all-polymer composites that are easily recycled, and even 3D printed. Versatile tailor-made polymers are essential for the sustainable development and help to ensure that humans regardless of their income can enjoy a better quality of life.

Synthesis Of Biopolyols from Wood Residues For The Elaboration Of Performing Polyurethane Foams

Pedro Luis de Hoyos-Martinez, Sebastian Barriga Mendez, Eriz Corro, Jalel Labidi

University of the Basque Country UPV/EHU

Nowadays polyurethanes are classified within the top-ranked polymers owing to their worldwide production and plethora of applications. This family of compounds is based on the reaction between polyols and diisocyanates to create urethane linkages. Accordingly, their industrial synthesis is considerably dependent on petrochemicals. Nevertheless, due to the depletion of fossil resources the current efforts are directed towards the employment of more renewable materials. In this respect, there is a tendency for the synthesis of plant-derived poylols, especially from lignocellulosic biomass. For this purpose, the implementation of liquefaction technology is preferred. This process consists in the cleavage of the biomass components of high molecular weight to obtain a liquid product rich in hydroxyl groups, which is designated as biopolyol. Considering the previous information, in this work it was carried out the synthesis of biopolyols together with the valorization of a wood residue (sawdust) for the elaboration of polyurethane foams with suitable insulating properties. Besides all the efforts were oriented towards the scaling up of the process and the potential transfer to the industry. It was observed that the biopolyols synthesized displayed suitable properties for their utilization in the foam preparation. In the end, it was possible the elaboration of two foams formulation based on these biopolyols at laboratory and industrial scale respectively. The mentioned foams presented good features for their application as insulators.

Waterborne And Bio-Based Non-Isocyanate Polyurethane Dispersions: Towards Safer Polyurethane Coatings

Enzo Pichon[1, 2], Andrij Pich[1, 2, 3], Katiren Bernaerts[1, 2]

1 Maastricht University
2 AMIBM/Sustainable Polymer Synthesis Group
3 RWTH Aachen University

Non-isocyanate polyurethanes (NIPUs) are polyurethanes (PUs) synthesized via alternative routes avoiding the use of isocyanate monomers. Usual isocyanate monomers are proven to be hazardous1, therefore the European Chemicals Agency (ECHA) is strongly restricting their industrial use. Transurethanization enables the synthesis of NIPUs via polycondensation of dicarbamate monomers with diols (and/or diamines)2. Therefore, bio-based NIPUs can reduce the impact of PU industry on both health and the environment.
In this work and for the first time, we report the synthesis of (partially) bio-based NIPUs of tunable molecular weights via transurethanization chemistry. To yield (partially) bio-based NIPUs, new dicarbamate monomers based on dimerized fatty-acid diamine and 2-methylpentamethylenediamine were synthesized. A bio-based polyol and an internal dispersing agent (IDA) were used as additional building blocks. Waterborne NIPU dispersions (WB NIPUDs) were prepared by neutralizing the IDA with a bio-based counter-ion and dispersing the NIPU in water via a procedure similar to the acetone process. Long NIPU chains were designed for adhesive layer applications in combination with bio-based PU top-coats, while telechelic NIPU chains were designed to be cross-linked into a top-coat. The properties (i.e. particle size and polydispsersity index, ζ-potential, stability) of the waterborne dispersions were compared to a commercial bio-based waterborne PU dispersion and exhibited lower particle size (90 nm) and similar ζ-potential (approx. +45 mV). The properties of the NIPU coatings/films were compared to an industrial PU coating.

Influence Of Recycled Polyurethane-Polyols on The Properties Of Rigid Polyurethane Foams For Pre-Insulated Pipes

Liudmyla Gryshchuk[1], Simon Unik[2]

1 Leibniz-Institut fuer Verbundwerkstoffe GmbH, Erwin-Schroedinger-Strasse 58, 67663 Kaiserslautern, Germany
2 Leibniz-Institut für Verbundwerkstoffe GmbH

Polyurethane (PUR) foams are widely used in many areas of industry, for example for pipe insulation.
In order to avoid the disposal of the PUR foams at the End of Life and to be able to reuse them instead, suitable and simple recycling processes are required. For this reason, the recycling of hard PUR foams was performed, and the influences of the recyclates on the new foams were investigated.
The starting material for the recycling process was fossil based rigid foam for pre-insulated pipes (industrial formulation) consisting on Component A (polyol blend), polyisocyanate as Component B and Component C (cyclopentane) as blowing agent.
For determination of the suitable recycling process for the reference (starting) rigid foam different methods were investigated. Recycling in microwave reactor by combination of glycolysis, aminolysis and acidolysis were determined as the fastest and most effective. In general were developed three recycling methods, which can be used for completely dissolving of the foam in short time and where the recyclate can be reused without additional purification and isolation of individual components from the mixture.
Obtained recyclates were used to substitute a part (up to 15%) of the Component A and a cup tests were carried out for comparison of the application-oriented processing (foaming) parameters for the reference foam and the foams with recyclate content. Good quality (without post-reaction shrinking) recyclates-containing PUR foams were tested to investigate the effects of the recyclate on the density and mechanical properties (the force required for 10% and 40% compression and the pressure module). For foam formulations containing recyclates were observed increasing of compressive strength values and Emod in comparison with reference foam.
Obtained results demonstrate the possibility of simplified use of recyclates as components of PUR foams preparation.
Acknowledgement
This work has been performed under the framework of the ReInvent project (Grant number 792049) funded by the H2020-BBI-JTI-2017 joint undertaking initiative.

Progress And Critical Parameters For The Production Of High Molecular Weight Poly(alkylene 2,5-urandicarboxylate)s Biobased Polyesters

Dimitrios Bikiaris

1 Aristorle University of Thessaloniki

Nowadays, most of the plastics and commodity materials in the global market that we use in our daily lives are derived from petroleum-based resources. The consumption of the latter is increasing steadily for many decades and it is estimated that till today, 9.1 bt of plastics have been produced worldwide, confirming our strong dependence on products prepared from non-renewable sources: oil, as well as other fossil fuels such as coal, natural gas, etc. In response to the awareness on several environmental and climatic global challenges associated with dwindling fossil resources and their imminent depletion, the surging energy demand and global warming, a large amount of recent research is focused on identifying renewable raw materials with the intention to gradually replace the industrially important fossil-based plastics. In a quest towards greener materials, many natural feedstocks, mainly cellulose, lignin and polysaccharides have been explored for the production of monomers that can be used to synthesize bio-based polymers. D-fructose and glucose are two of the most used starting materials, and they can be transformed via catalysis into furan derivatives, like 5-hydroxymethylfurfural (5-HMF) and 2,5-furandicarboxylic acid (2,5-FDCA), which is one of the most important biobased monomers for the production of biobased polyesters.

Today, although the majority of the series of furanoate polyesters have been synthesized and some of their properties are known, research and industry efforts are focused on the synthesis and study of poly(ethylene 2,5-furanoate) (PEF) and poly(propylene furanoate) (PPF). This is because they both have excellent properties, superior compared to poly(ethylene terephthalate) (PET), especially mechanical and gas barrier properties (against O2 and CO2) and can be used instead of PET in many applications, like food packaging. However, these polyesters are not yet commercialised and to this direction several problems should be solved. Those include the lack of large scale and production of high purity 2,5-FDCA, which directly affects the molecular weight of the produced polyesters, their mechanical properties and their coloration. Additional parameters like esterification and polycondensation temperature, time and catalyst content to produce high-quality polyesters are extensively studied the last years. More recent studies have focused on the production of copolymers with appropriate properties, like high Tg values and biodegradability. Nanocomposites are also under study, with several nanoparticles in order to enhance thermal stability, mechanical properties and gas barrier properties. All these efforts are contributing in overcoming the hurdles for the industrial production of poly(alkylene 2,5-furanoate)s and the availability of low price 2,5-FDCA on the market.

Synthesis Of PBT Vitrimers Through Reactive Extrusion - Effect Of Flame Retardant Additives

Louis Meunier, Sophie Duquesne, Fabienne Samyn, Valerie Gaucher, David Fournier

1 Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207 - UMET - Unité Matériaux et Transformations, F-59000, Lille, France

Bridging thermoplastics and thermosets families, the new class of materials called vitrimers shows great opportunities to develop recyclable alternatives to high performance thermosets. However, as their specificity relies on their bond exchange reactions capacity, the use of additives to functionalise such matrix may affect the exchange reactions and could thus be an issue. This work investigates how the presence of 20 wt.-% of flame-retardant additive will impact the performances of a poly (butylene terephthalate)-based vitrimer matrix (PBT vitrimer).

It was demonstrated that adding aluminium phosphinate (AlPi), a well-known halogen-free fire-retardant for PBT, during the synthesis by reactive extrusion of the vitrimer matrix (mixing PBT, epoxy and a Zn(II)-transesterification catalyst) does not prevent the formation of the vitrimer matrix and thus the bond exchanges reaction are maintained. The cross-linking density is nearly equivalent to the one of the pristine PBT-vitrimer counterpart and the dynamic exchange reaction kinetics is enhanced (ten times lower relaxation times).

It was also demonstrated that the flame retarded (FR) vitrimer presents equal, if not better, UL94 behaviour compared to PBT+AlPi thermoplastic. The vitrimer structure permits to limit the formation of drops during the test that could be detrimental. Moreover, recycling of the material by reprocessing was without impact on the Young's modulus.

On the other hand, it was also shown that a dynamic network can be formed in absence of catalyst demonstrating that AlPi may also act as transesterification catalyst. 31P and 27Al NMR analysis showed the modification of the environment of the phosphorous and aluminum atoms in the crosslinked part of the vitrimer.

Phenoxy Resin-Based Covalent Adaptable Networks: A Recyclable Alternative to Epoxy Thermosets

Francesca Portone[1], Giuseppe Soavi[1], Daniele Battegazzore[2], Chiara Paravidino[2], Alberto Fina[2], Enrico Dalcanale[1]

1 Department of Chemistry, Life Sciences and Environmental Sustainability (SCVSA) University of Parma, Italy
2 Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Alessandria, Italy

The environmental problems related to the non-recyclability of fiber-reinforced thermoset is bringing to the progressive substitution of thermoset matrices with thermoplastics. Unfortunately, the use of a thermoplastic matrix remains challenging for components operating well above room temperature. The recent introduction of dynamic networks, including vitrimers and other thermally reversible networks, may bridge the gap between thermosets and thermoplastics by combining the mechanical properties of the former with the ability of being reprocessed of the latter.
In this frame, a linear phenoxy resin was exploited in this work as a base polymer to prepare covalent adaptable networks exploiting hydroxyl function to produce crosslinking via different chemical routes.
Direct silylation with bis trialkoxysilane was explored, yielding highly crosslinked silyl ether exchangeable networks. As a second route, functionalization of phenoxy resin with acetyl acetonate (AcAc) moieties was carried out, at different concentrations of grafted AcAc. Such functional polymer was then reacted with aromatic or cycloalifatic diamines to produce vinylogous urethane-based dynamic networks.
The gel fractions at room temperature were determined by solvent extraction test and expectedly found dependent on the concentration of crosslinkers, up to fully crosslinked networks. Nonetheless, all formulations were confirmed easily re-processable via compression molding into plates and films. Thermal, mechanical and rheological test were carried out, to describe the evolution of materials properties as a function of the crosslinking density as well as the type of crosslinker between phenoxy chains. Recyclability of phenoxy based dynamic networks were also validated via successive remolding steps, exhibiting retained mechanical properties.
Materials developed in this work are therefore envisaged as possible alternative to conventional epoxy thermosets materials, including in structural applications.

Comparison Of The Properties Of A Random Copolymer And A Molten Blend PA6/PA6.9

Maddalena Bertolla, Michele Cecchetto, Anacleto Dal Moro, Mattia Comotto

Aquafil SpA

The properties of a copolymer depend on the way it is produced, even if the starting monomers are the same: block and random copolymers show different behaviors and the most suitable material depends on its final use.
This study compares a mixed molten blend PA6/PA6.9 and the copolymerization of its starting monomers. It is demonstrated that the mixing and melting of PA6 and PA6.9 produce a material with properties of a block copolymer, while the polymerization of caprolactam, hexamethylenediamine and azelaic acid produces a random copolymer.
A previous work showed that keeping the molten blend at 280°C for more than 8 hours moves the copolymer from block to random. The alternative method studied here ensures a higher flexibility and lower time to get several different random copolymers PA6/PA6.9, changing the monomers ratio in polymerization, using just one production line.
Different ratios PA6/PA6.9 have been produced with both techniques and characterized in terms of physicochemical, thermic and mechanical properties. The relative content and distribution of the monomers in the final dried copolymer has been studied with NMR.
For example, the random copolymer PA6/PA6.9 60/40 (by weight) is characterized by a low melting temperature (150°C), a heat deflection temperature of 30°C and an elongation at break higher than 200%. Those properties, different from the corresponding molten blend, are suitable in many fields where copolyamides are required. It can be used as an additive in PA6 thermoplastic compounding, elastomers production and hot melt adhesives.
A further advantage of random copolymers PA6/PA6.9 with respect to other additives is related to the chemical recyclability of the final product due to the high PA6 content, avoiding the use in hot melt adhesives of chemicals that could impact the recovery of the caprolactam monomer in the depolymerization process, like the aromatic rings present in rubbers.

Solid-Like Electrolytes For Safe, Ambient Temperature Operation Of Alkali Metal Ion Batteries

Marisa Falco, Francesca Colò, Gabriele Lingua, Elisa Maruccia, Lucia Fagiolari, Federico Bella, Giuseppina Meligrana, Claudio Gerbaldi

Politecnico di Torino

Standard commercial rechargeable batteries use liquid electrolytes, which are based on toxic and volatile organic carbonate solvents, and their flammability clearly raises safety concerns. The most striking solution is to switch on all solid-state designs exploiting polymers, ceramics, etc. To enhance low ionic mobility and stringent processing conditions, several approaches are proposed including the most promising in situ preparation of thermoset polymer electrolytes using solvent-free processes. Ionic conductivity/transport is directly linked to polymer chain mobility. It can be controlled through crystallinity reduction, which in turn increases the amorphous character of the polymer matrix, by means of addition of plasticisers, ceramic fillers, and proper crosslinking.

Here, an overview will be offered of recent developments on innovative polymer electrolytes for Li-/Na-based batteries by means of UV-induced photopolymerization, which is easily scalable, rapid, highly efficient and green, as the use of solvent is avoided. Crosslinking allows the incorporation of high amount of RTIL (e.g., imidazolium, pyrrolidinium) or tetraglyme and lithium salt (FSI–, TFSI– anion), leading to polymer electrolytes with remarkable homogeneity and robustness. To increase even more the cycling ability at (sub-)ambient temperatures, recent efforts are dedicated to the formulation of hybrid composite polymer electrolytes (CPEs), where the ceramic superionic conducting material is homogeneously embedded in the polymeric matrix. CPEs are stiff while preserving flexibility, are easily processed, and can be conceived to attain improved ionic transport and interfacial contact with the electrodes, showing enhanced cycling in real cell configuration.

Structuration Of Amphiphilic PE-B-PEO Copolymer Thin Films At Interfaces

Maurice Brogly, Sophie Bistac, Diane Bindel

Université de Haute Alsace

This work focus on the understanding of organization and crystallization of thin amphiphilic copolymer films1 directed by the surface chemistry of a metal substrate for biointerfacing. Various copolymers were adsorbed by spin-coating on metal substrates. The surface chemistry of the substrates was controlled by chemical grafting using thiols. The influence of the hydrophilic or hydrophobic nature of the substrate on the organization and structuration of PE–b–PEO copolymers of different compositions was then studied.

Characterization of thin films of copolymers requires the use of specific characterization techniques. Polarization-Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS) is an original vibrational spectroscopy that was used for "in situ" characterization of the copolymers. Indeed the polarization modulation of the incident IR wave increases the sensitivity of the spectral response, allowing determination of molecular orientation and structuring effects. Atomic Force Microscopy (AFM) analyzes were performed to access the surface morphology and distinguish amorphous and crystalline phases.

Chains orientations and conformations as well as surface morphologies were thus characterized in order to understand the competition between polymer/polymer and polymer/substrate interactions, as well as impact on the crystallization. This was explained by changes in the balance of polymer/polymer vs polymer/substrate interactions. Substrate surface chemistry alters the balance between these interactions significantly. In the case of amphiphilic PE-b-PEO diblock copolymers, an hydrophilic substrate favors the crystallization of the polar block whereas an hydrophobic substrate will favor the non-polar block crystallization. The modification of the crystalline phase content, morphology and molecular orientation of the crystalline structures of the adsorbed films reflects the strong competition between interfacial forces and intra and intermolecular forces.

Reference

1. Friction of PE-b-PEG diblock copolymers on model substrates, S. Bistac, D. Fischer, M. Brogly, in Surfactants in Tribology, Vol. 5, Section 1, G. Biresaw and K. L. Mittal Eds., CRC Press, Taylor and Francis Group, Boca Raton (2017)

Structure Evolution Of Phase-Separated Biopolymer Films For Controlled Drug Delivery

Pierre Carmona[1,2], Magnus Röding[1,3], Aila Särkkä[3], Christian von Corswant[4], Eva Olsson[5], Niklas Lorén[1,5]

1 Unit Product Design, Department Agriculture and Food, Division Bioeconomy and Health, RISE Research Institute of Sweden, Gothenburg, Sweden
2 Division Nano-and BioPhysics, Department of Physics, Chalmers University of Technology, Gothenburg, Sweden
3 Department of Mathematical Sciences, Chalmers University of Technology and Gothenburg University Gothenburg, Sweden
4 Oral Product Development, Pharmaceutical Technology & Development, Operations, AstraZeneca, Gothenburg, Sweden
5 Division Nano-and BioPhysics, Department of Physics, Chalmers University of Technology, Gothenburg, Sweden

Porous phase-separated ethylcellulose/hydroxypropylcellulose (EC/HPC) films are used to control drug transport in pharmaceutical pellets. The drug transport rate is determined by the 3D structure of the porous films that are formed as the water-soluble HPC leaches out. The films are applied on pharmaceutical pellets using fluidized bed spraying. However, a detailed understanding of the evolution of the phase-separated structure in the films is lacking. In this work, we have investigated EC/HPC films produced by spin-coating 1, which mimics the industrial manufacturing process. The aim of this work was to understand the structure evolution and coarsening kinetics during solvent evaporation and formation of the films. The structure evolution was characterized using confocal laser scanning microscopy (CLSM) and image analysis.

Here, we present a new method to slow down the process of solvent evaporation to follow the structure evolution in situ during phase separation, and a new image analysis procedure to monitor the time-dependent evolution of the curvature of the EC/HPC interface in bicontinuous structure. The effect of the EC:HPC ratio on the time-dependent evolution of the characteristic length scale, the structure growth rate and the curvature evolution will be shown. With the findings, it is possible to correlate the structure evolution to the governing phase separation and coarsening mechanisms 2. The findings of this work provide a good understanding of the mechanisms responsible for the morphology development and open for further tailoring of thin EC/HPC film structures for controlled drug release.

References:
1. P. Carmona, M. Röding, A. Särkkä, C. Von Corswant, E. Olsson and N. Lorén, Soft Matter, 2021, 17, 3913-3922.
2. P. Carmona, M. Röding, A. Särkkä, C. von Corswant, E. Olsson and N. Lorén, Submitted, 2022.

Conjugated Polymers For Intracellular Labeling And Delivery

Joong Ho Moon

Florida International Univ

p-Electron conjugated polymers (CPs) and oligomers are newly developed biomaterials exhibiting excellent photophysical and biophysical property. Using scanning probe and confocal microscopy, we have discovered that CPs with both hydrophobic and positively charged functionalities enter various cells very efficiently through various pathways including transiently formed pores on live cell membranes as well as traditional endocytosis pathways without causing cell viability inhibitions. By introducing biodegradable functional group along the backbone, we developed intracellularly degradable CPs and conjugated oligomer-based macrocycles for specific mitochondria and RNA labeling, respectively. Using a unique guanidine modulation chemistry through carbamoylation, CPs containing hydrophilic non charged side chains were developed. Carbamoylation of guanidine lowers pKa of guanidine dramatically, resulting in neutral charges in the physiological conditions. The resulting polymers exhibit excellent small interfering RNA complexation, diffusion through mucus layers, and efficient target gene knockdown in normal human bronchial epithelium cells. In this presentation, recent progresses toward functional protein delivery as well as antimicrobial activities will be discussed.

Model Based Investigation Of Sustained Ring-Opening Polymerization Of Lactide With Non-Toxic Zinc-Guanidine Catalysts

Niclas Conen[1], Martin Fuchs[2], Sonja Herres-Pawlis[2], Andreas Jupke[1]

1 RWTH Aachen University - AVT.FVT - Fluid Process Engineering
2 RWTH Aachen University - Bioinorganic Chemistry

Introduction

Poly lactic acid (PLA) is the most widely produced bio-based and fully biodegradable polymer in the world and has great potential in many applications from sustainable food packaging to advanced medical devices.1–6 Industrial Production of PLA takes place via ring-opening polymerization (ROP) of the cyclic dimer lactide applying stannous octanoate as catalyst.6–9 Although classified as food safe, toxic tin can be released in the environment during PLA degradation, as traces of the catalyst remain in the polymer matrix after ROP. Recently the harmlessness of several robust "asme"-type Zn catalysts for lactide ROP in bulk using robust guanidine-based ligands has been reported.10 Although high activities are observed for these catalyst systems, ligands can act as chain starter, which reduces the amount of active catalyst during the reaction. In this work, we investigate the influence of this phenomenon on quality characteristics, such as conversion, molecular weight distribution and dispersity.

Methods

A dynamic batch reactor model is developed and parametrized with experimental data. Population balance equations are set up for all relevant polymer species and solved implementing a method of moments.11 The generality of the model for the described catalyst class is validated using a second "asme"-type catalyst. We perform a model-based analysis on the influence of model and process parameters on conversion and molecular weight distribution.

Results

The simulation results show good agreement with experimental data for both catalysts applied. The initiation and propagation rate are important for high conversions and narrow molecular weight distributions that are crucial for competing with industrially applied catalysts. The model can be applied to determine performance criteria in order to compete with the industrial process and allows the determination of an optimal operating point.

References

1 M. Buggy, Natural fibers, biopolymers, and biocomposites. Edited by Amar K Mohanty, Manjusri Misra and Lawrence T Drzal, Polym. Int., 2006, 55, 1462.

2 D. Garlotta, A Literature Review of Poly(Lactic Acid), Journal of Polymers and the Environment, 2001, 9, 63–84.

3 S. Thakur, J. Chaudhary, B. Sharma, A. Verma, S. Tamulevicius and V. K. Thakur, Sustainability of bioplastics: Opportunities and challenges, Current Opinion in Green and Sustainable Chemistry, 2018, 13, 68–75.
4 M. S. Singhvi, S. S. Zinjarde and D. V. Gokhale, Polylactic acid: synthesis and biomedical applications, Journal of applied microbiology, 2019, 127, 1612–1626.
5 K. Hamad, M. Kaseem, M. Ayyoob, J. Joo and F. Deri, Polylactic acid blends: The future of green, light and tough, Progress in Polymer Science, 2018, 85, 83–127.
6 R. E. Drumright, P. R. Gruber and D. E. Henton, Polylactic Acid Technology, Adv. Mater., 2000, 12, 1841–1846.
7 M. J. Stanford and A. P. Dove, Stereocontrolled ring-opening polymerisation of lactide, Chemical Society reviews, 2010, 39, 486–494.
8 P. McKeown and M. D. Jones, The Chemical Recycling of PLA: A Review, Sustainable Chemistry, 2020, 1, 1–22.
9 S. Jacobsen, H. G. Fritz, P. Degée, P. Dubois and R. Jérôme, Polylactide (PLA)-a new way of production, Polym Eng Sci, 1999, 39, 1311–1319.
10 C. Lackmann, J. Brendt, T.-B. Seiler, A. Hermann, A. Metz, P. M. Schäfer, S. Herres-Pawlis and H. Hollert, The Green toxicology approach: Insight towards the eco-toxicologically safe development of benign catalysts, Journal of hazardous materials, 2021, 416, 125889.
11 Y. Yu, G. Storti and M. Morbidelli, Kinetics of Ring-Opening Polymerization of l l -Lactide, Ind. Eng. Chem. Res., 2011, 50, 7927–7940.

Exploring Enzymatic Polymerization Pathways For The Production Of Aliphatic Polyesters

Christina Gkountela, Stamatina Vouyiouka

1 Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Athens, Greece

Biocatalysis is a valuable tool to synthesize polymers in a sustainable, non-polluting way. The enzymatic polymerization of aliphatic polyesters (PEs) is herein studied through evaluating key process conditions such as the nature of monomers, the by-product removal rate, the presence of solvent. Firstly, the enzymatic synthesis of 1,8 octanediol-based PEs was conducted via solution technique (in toluene) to examine the effect of diacid monomer length (6, 12 and 14 C atoms) on polymerization rate [1]. The longer-chain diacids presented higher affinity with the used lipase (Novozyme 435), attributed to their increased hydrophobicity favoring diffusion into biocatalyst hydrophobic active sites. Molecular sieves were used to remove the polycondensation by-product (water), but the obtained polyesters presented low IV values (up to 0.189 dL/g), indicating the need for higher water diffusion rates. The high-boiling point diphenylether was therefore used as a solvent, permitting the application of vacuum and resulting in octanediol-based PEs of higher IV (up to 0.346 dL/g, Mn 8000 g/mol) [2]. The relevant family of polyesters, however, presented low Tm (58–75°C), and thus poly(butylene succinate) (PBS) with Tm at 114°C was examined as an alternative bio-based and biodegradable PE. The enzymatically synthesized PBS in diphenylether presented low IV (0.180 dL/g, Mn 3700 g/mol) due to its short-chain monomers and/or higher diol volatility which resulted in deviation from end groups stoichiometric balance. A two-step process was then conducted to prevent the 1,4-butanediol loss, with no however positive effect on the final Mn. To facilitate the scaling-up of PBS enzymatic polymerization, solventless systems were also examined using one- and two-step processes [3]; by tuning reaction temperature, time and vacuum pressure, metal-free PBS grades of Mn at ca. 3000 g/mol were synthesized with melting points in the vicinity of 105°C and high mass fraction crystallinities (ca. xc 75-80 %).

References

[1] S. N. Vouyiouka, E. Topakas, A. Katsini, C. D. Papaspyrides, and P. Christakopoulos, “A green route for the preparation of aliphatic polyesters via lipase-catalyzed prepolymerization and low-temperature postpolymerization,” Macromol. Mater. Eng., vol. 298, no. 6, pp. 679–689, 2013, doi: 10.1002/mame.201200188.

[2] M. Kanelli et al., “Production of biodegradable polyesters via enzymatic polymerization and solid state finishing,” J. Appl. Polym. Sci., vol. 131, no. 19, pp. 2–9, 2014, doi: 10.1002/app.40820.

[3] C. Gkountela, M. Rigopoulou, E. M. Barampouti, and S. Vouyiouka, “Enzymatic prepolymerization combined with bulk post-polymerization towards the production of bio-based polyesters: The case of poly(butylene succinate),” Eur. Polym. J., vol. 143, no. November 2020, 2021, doi: 10.1016/j.eurpolymj.2020.110197.

Biodegradation Of Polyesters By Filamentous Fungi

Viktoria Ilieva[1], Federica Spina[2], Giovanna Cristina Varese[2], Pierangiola Bracco[3], Marco Zanetti[3]

1 Dipartimento di Chimica, University of Torino
2 Mycotheca Universitatis Taurinensis, Department of Life Sciences and Systems Biology, University of Torino
3 Dipartimento di Chimica, NIS Interdepartmental, University of Torino

Biopolymers have gained increasing interest as substitutes of "traditional", non-biodegradable plastics. Polyesters are the favorites, thanks to the economic process technology and easy production of the starting monomers. Their behavior in the degradation process depends on their structure, their hydrophobic character, which limits the enzyme activity together with other factors like low surface area, high molecular weight and crystallinity. Several microorganisms are already known to be promising biopolymer degraders, fungi included, but rarely at low temperatures and under uncontrolled conditions, as in the case of littering. This study investigated the biodegradation by filamentous fungi, preserved at Mycotheca Universitatis Taurinensis of the University of Torino, of biodegradable aliphatic and aliphatic-aromatic polyesters, such as polybutylene succinate (PBS). The tested polymers were subjected to alkaline hydrolytic degradation concurrently to a primary solid screening, carried out to select fungal strains capable of growing in the presence of the polymers as sole carbon source, in form of films of 40 µm thickness at 15 °C and 24 °C. A good percentage of the tested fungal strains were able to grow on the different polyesters at 24°C, a lower ability was observed at 15°C. The materials have similar molecular weight but exhibit a very different hydrolytic behavior which corresponds to the trend observed in the solid screening, due to their difference in hydrophobicity, crystalline grade and chemical structure. These aspects mostly influence the biodeterioration, in particular the biofilm formation, and the bioassimilation steps. For these reasons, the degradation and bioassimilation ability of the best performing fungus in the preliminary solid screening were investigated on polymers and monomers in two different aqueous media at 24 °C. During the degradation in both liquid media, a significant growth of the fungal biomass has been observed. From the HPLC-RI analyses of the media, the depolymerization ability of the microorganism was confirmed. The degradation products in the chromatograms completely matched the monomer components of the tested polyesters, no unknown peaks were detected. However, some monomers were detected only in trace and their concentration fell below the detection limit after 20 days of degradation. The trials with monomers at different concentrations highlighted a concentration effect and a different assimilation rate in enriched solution.

Bioexploration Towards Novel Plastic-Degrading Microorganisms: Rumen Metagenomic Study For Synthetic Polyester Decomposition

Felice Quartinello

Institute of Environmental Biotechnology, Department of Agrobiotechnology, University of Natural Resources and Life Sciences Vienna – Konrad Lorenz Straße 20, 3430 Tulln, Austria 2Austrian Centre of Industrial Biotechnology, Konrad Lorenz Strasse 20, 3

The bio-economy concept is motivating the scientific community to produce bio- based and/or biodegradable polyesters and in parallel improve the microbial and/or enzymatic recycling of these materials (1). The application of highly specific biocatalysts allows depolymerization of synthetic polyesters as well as a stepwise recovery of the polymer building blocks from multilayer plastics and mixed waste. Since various microorganisms are not possible to cultivate in laboratory conditions, metagenomic approaches allows the assessment of such microorganisms and their relative enzymes living almost in any niche in the biosphere with distinct roles in the ecosystem. The rumen ecosystem is a natural “chemostat” where various heterogenous biochemical reactions are occurring. Among these, enzymatic hydrolysis of (hemi)cellulose and the responsible enzymes have been studied intensively, while other polymer-degrading enzymes potentially present in rumen remained under-explored (2).

In this work, the rumen content from Bos taurus was studied towards the hydrolysis of three synthetic polyesters. Specifically, from poly(butylene adipate-co-terephthalate) (PBAT) were released 0.75 and 0.5 mM for polymer powder and film, respectively, and thus exceeded when compared to the hydrolysis of the second terephthalic acid-based polymer—poly(ethylene terephthalate) (PET) (0.6 and 0.15 mM, for powder and film, reciprocally). On the other hand, the biobased polyester poly(ethylene furanoate) (PEF) demonstrated a higher degradation profile, according to HPLC and SEM analysis. Shotgun metagenome analysis (Nanopore MinION technology) of the rumen microbiome revealed the real proportion of all domains of life, showing the dominance of bacteria (98%), followed by Eukaryota (1%) and finally Archaea. In conclusion, the rumen might be considered a cheap source of plastic-degrading microorganisms and/or enzymes, which synergistically contribute for the decomposition of the synthetic polyesters (3).

Co-Crystalline and Nanoporous-Crystalline Polymers

Gaetano Guerra[1], Antonietta Cozzolino[2], Cristophe Daniel[2], Baku Nagendra[1], Paola Rizzo[1]

1 Dipartimento di Chimica e Biologia and INSTM Research Unit, Università degli Studi di Salerno, Via Ponte don Melillo, 84084, Fisciano, Italy,
2 Dipartimento di Chimica e Biologia and INSTM Research Unit, Università degli Studi di Salerno, Via Ponte don Melillo, 84084, Fisciano, Italy

The conference deals with crystallization of two commercially available polymers (syndiotactic polystyrene, sPS [1,2] and poly(2,6-dimethyl-1,4-phenylene) oxide (PPO), [3,4]) leading to co-crystalline (CC) forms with low-molecular-mass guest molecules and to derived nanoporous-crystalline (NC) forms.
Particular attention is given to the impressive solubility and diffusivity of organic guests, which can be achieved for NC PPO samples.[5] X-ray diffraction patterns and infrared linear dichroism, as collected for axially oriented NC PPO films, indicate the presence of large diameter crystalline helices with intrahelical location of the guest molecules.
Emphasis will be given to NC PPO films with orientation of the crystalline empty channels perpendicular to the film plane (c⃗ orientation), which exhibit very fast guest sorption [5] and good optical transparency.[6]
The final part of the conference is mainly devoted to perspectives of basic and industrial research that are expected in the near future for CC and NC PPO samples.

References

[1] - Petraccone, V.; Ruiz de Ballesteros, O.; Tarallo, O.; Rizzo, P.; Guerra, G. Chem. Mater. 20, 3663 (2008).
[2] - Tarallo, O.; Petraccone, V.; Albunia, A.R.; Daniel, C.; Guerra, G. Macromolecules 43, 8549 (2010).
[3] - Daniel, C.; Longo, S.; Fasano, G.; Vitillo, J. G.; Guerra, G. Chem. Mater., 23, 3195 (2011).
[4] -Nagendra, B.; Cozzolino, A.; Daniel, C.; Rizzo, P.; Guerra, G.; Auriemma, F.; De Rosa, C.; D'Alterio, M.C.; Tarallo, O.; Nuzzo, A. Macromolecules 52, 9646 (2019).
[5] -Daniel, C.; Rizzo, P.; Nagendra, B.; Cozzolino, A.; Guerra, G. Polymer 229, 124005 (2021).
[6] - Nagendra, B.; Rizzo, P.; Daniel, C.; Guerra, G. Macromolecules 54, 6605 (2021).

Conjugated Ladder Polymers and Polymer Networks: New Functions Imparted by Fused-Ring Constitution

Lei Fang (YIA Winner 2018)

Texas A&M University

Backbone conformation and rigidity are essential factors in determining the properties of macromolecules, as well as the associated supramolecular assemblies and bulk materials. Pursuing a rigid and coplanar molecular conformation often represents one of the primary objectives when designing and synthesizing conjugated polymers for electronic and optical applications. This goal can be achieved by imparting a ladder type constitution in the polymer backbone. This talk includes our efforts on the synthesis of ladder type π-systems fused by various types of bonds, including kinetically formed covalent bonds, thermodynamically formed covalent bonds, coordinate bonds, and hydrogen bonds. The characteristic properties of selected examples of these ladder type π-systems are discussed in comparison with control compounds that are not rigid and coplanar. The fundamental chain rigidity of these polymers are investigated by using advanced neutron scattering techniques. The unique optical, electronic, electrochemical, and mechanical properties of these materials are achieved and tailored in the context of a wide range of applications such as electronics, energy storage, artificial muscles, and stimuli responsive materials.

Double Hydrophilic Block Copolymers As An Avenue To Self-Assembly And Multi-Phase Systems

Bernhard V.K.J. Schmidt (YIA Winner 2020)

University of Glasgow

Water-soluble polymers play a crucial role in contemporary polymer science.1 There are several promising applications proposed for these materials, especially in the biomedical field. Thus, applications like drug-delivery, sensing or tissue engineering are in the focus of research. Another significant feature of hydrophilic polymers is their phase separation behaviour in aqueous environment, which enables molecular partitioning and structure formation. In the present talk, recent developments regarding double hydrophilic block copolymers in aqueous environment will be highlighted. A particular focus will be given to aqueous multi-phase systems, water-in-water emulsions and block copolymer particle formation.

The formation of completely water-based multi-phase systems is strongly related to the choice of the polymer component. Thus, we use polymer chemistry approaches to obtain new components for these aqueous systems.2 Furthermore, aqueous multi-phase systems can be emulsified in a Pickering emulsion approach and several routes to water-in-water emulsions will be presented, e.g. stimuli-responsive emulsification.3 As such, well-defined aqueous environments can be generated that will be of interest for various applications in the future. Finally, double hydrophilic block copolymers will be presented as precursors for nano particle formation.4

In summary, the concept of aqueous multi-phase systems and the utilization of double hydrophilic block copolymers to obtain new features for these systems will be presented.

1) V. G. Kadajji, G. V. Betageri, Polymers 2011, 3(4), 1972.
2) R. Lira, J. Willersinn, B. V. K. J. Schmidt, R. Dimova, Macromolecules 2020, 53 (22), 10179-10188.
3) M. Pavlovic, A. Plucinski, L. Zeininger, B.V. K. J. Schmidt, Chem. Commun. 2020, 56, 6814.
4) A. Plucinski, J. Willersinn, R. Lira, R. Dimova, B V. K. J. Schmidt, Macromol. Chem. Phys. 2020, 221 (13), 2000053.

Concurrent Control Over Sequence And Dispersity In Multiblock Copolymers

Athina Anastasaki

ETH Zurich

Controlling monomer sequence in synthetic macromolecules is a major challenge in polymer science and the order of building blocks has already been demonstrated to determine macromolecular folding, self-assembly and fundamental polymer properties. Dispersity is another key parameter in material design, with both low and high dispersity polymers displaying unique properties and functions. However, synthetic approaches that can simultaneously control both sequence and dispersity remain experimentally unattainable. In this talk I will present a simple, one pot, and rapid synthesis of sequence-controlled multiblocks with on demand control over dispersity while maintaining high livingness, good agreement between theoretical and experimental molecular weights and quantitative yields. Key to our approach is the regulation in chain transfer agent activity during controlled radical polymerization that enables the preparation of multiblocks with gradually ascending (Đ=1.16 →1.60), descending (Đ=1.66 →1.22), alternating low and high dispersity values (Đ=1.17 →1.61 →1.24 →1.70 →1.26) or any combination thereof.[2] The enormous potential of our methodology was further demonstrated through the impressive synthesis of highly ordered pentablock, octablock and decablock copolymers yielding the first generation of multiblocks with concurrent control over both sequence and dispersity.

Bio-Based Thermoset Polymer As Viable Alternative For Rigid Polyurethane Foams

Mikelis Kirpluks, Ralfs Pomilovskis

Polymer Laboratory, Latvian State Institute of Wood Chemistry, Riga, Latvia

The main challenge of the polyurethane (PU) material industry is associated with the production and handling of isocyanates. It is unlikely that urethane chemistry will be displaced as it exhibits very high effectiveness and its highly advantageous economies of scale. However, for instances where PU chemistry is undesired, it is very beneficial to have a useful alternative such as polymers obtained via carbon-Michael addition. A possibility to produce bio-based polymers from sustainable feedstock is further incentivised by new market demands as well as regulatory mechanisms. Furthermore, a cost-effective solution has to be designed because the majority of the polymer materials are used in bulk applications, thus the price is important for technology to be adopted by the industry.

The renewable materials have been proven as a viable alternative for petrochemical products in polymer production. Tall oil-based materials have a further advantage as they are produced from second-generation bio-based feedstock as the tall oil is a side-stream product of cellulose manufacture. In present study tall oil fatty acids have been valorised for Michael addition monomer synthesis and synthesised monomers have been used for different elastomer and rigid foam production.

For this study tall oil fatty acids were used to synthesize a two-component system that cures at room temperature after mixing, forming mechanically rigid, non-biodegradable and highly cross-linked polymer. Two types of bio-based monomers were synthesised, Michael donor – monomer containing acetoacetate groups and Michael acceptor – monomer containing acrylic acid moieties. The polymerization through the nucleophilic carbon-Michael addition was used to develop a bio-based thermoset polymer matrix, the physical and thermal properties were studied. The proposed technology has the potential in the production of two-component polymer foams, resins and coatings and it is a direct alternative to the two-component PU material production methods.

Bio-Based Polymers Endow Environmentally Sustainable Energy Storage Systems With Long Lifespan

Erlantz Lizundia[1,2]

1 Life Cycle Thinking Group, Department of Graphic Design and Engineering Projects. University of the Basque Country (UPV/EHU), Plaza Ingeniero Torres Quevedo 1, 48013 Bilbao, Biscay, Spain.
2 BCMaterials, Basque Center for Materials, Applications and Nanostructures, Edif. Martina Casiano, Pl. 3 Parque Científico UPV/EHU Barrio Sarriena, 48940 Leioa, Biscay, Spain.

The development of efficient, environmentally sustainable and cost-effective energy storage technologies is essential to counteract natural resource depletion, environmental pollution and global warming. As the majority of current batteries rely on critical raw materials and petroleum-derived polymers, their implementation bears serious environmental burdens originating from toxic chemistries or non-renewable/non-degradable components.
Accordingly, bio-based polymers can improve the environmental sustainability of batteries. Importantly, polysaccharides are perfect candidates as they offer the often self-excluding requisites of good electrochemical performance, renewability, and degradability. The potential of cellulose, chitin, or agarose to replace the toxic, non-renewable and non-degradable battery components is explored. Alike, alternatives to upgrade the electrochemical performance of lithium-ion batteries, and less technologically mature sodium-ion batteries and zinc-ion batteries are showed. Self-assembly and sol-gel synthesis approaches are used to fabricate biopolymer electrolytes. A special attention to nanocellulose is paid given its controllable porosity, suitable mechanical/thermal properties, and large electrolyte affinity. Overall, biopolymer-electrolytes show high ionic conductivities, large transference numbers and allow strikingly homogeneous ion plating/stripping. This is translated into efficient ion electrodeposition, good rate capability and remarkable operation lifespan.
New battery concepts aimed to reduce the accumulation of battery-waste are also explored as a part of a circular strategy. The replacement of the conventional battery components by biopolymers based on renewable and degradable materials renders transient batteries. In other words, we develop high-performance batteries capable of undergoing controlled degradation processes after a stable operation period, leaving behind harmless residues. To unequivocally determine the environmental advantages of different battery chemistries, we couple these works with life cycle assessment (LCA) studies. Obtained quantitative environmental impact results enable making informed choices on the sustainability of different battery configurations and available recycling methods.
Overall, these approaches highlight the great potential of biopolymers in the uptake of circular economy concepts applied to the sustainable energy storage field.

Polyurethanes As Low Cost And Sustainable Moisture And Oxygen Barriers For Flexible Perovskite Solar Cells

Matteo Bonomo[1], Francesca De Rossi[2], Davide Gallo1, Ana Yancy Segura Zarate[1], Babak Taheri[2], Gabriele Viada[1], Simone Galliano[1], Thomas Meredith Brown[2], Alberto Menozzi[3], Francesca Brunetti[2], Claudia Barolo[1]

1 University of Turin
2 University of Rome Tor Vergata
3 Demak Polymers

Long-term stability of Perovskite Solar Cells (PSCs) is the main issue to be solved for a forthcoming commercialization of this technology. The stability of PSCs mainly suffers for water and oxygen infiltration as well as prolonged exposition to UV radiation, therefore, encapsulation of devices is mandatory to achieve good long-term stability [1]. Polyurethanes (PU) are cost-effective and environmental-friendly (partially bio-based and waste-derived) materials whose mechanical, chemical and physical properties could be easily tuned by thoughtful choice of their precursor.
In this work we proposed to use this class of materials as encapsulant for (flexible) perovskite solar cells [2]. We focused our attention on the barrier properties of PU, especially in the prevention of degradation caused by both moisture and oxygen.
To test their UV and thermal stability, polyurethanes were stressed by means of various approached: They were soaked with UV radiation for different times (i.e. 2, 4 and 8 hours under continuous irradiation) and thermally stressed (i.e. 100 °C up to one week and -50 °C for 2 weeks). Remarkably, both UV-vis and ATR analyses of polymers did not show any significant modification as a consequence of the stressing.
The polymers were then deposited on perovskite solar cells, the photoelectrochemical properties of encapsulated device remain constant up to three months. Notably, the incapsulated cells showed higher stability stored under ambient light with 50% RH and temperature ranging from 18 to 32 °C by retaining 94% of the initial power conversion efficiency after more than 2500 hours whereas unprotected device lost more than 90% of their performance during the same period.
This result is remarkable as it allowed to demonstrate for the first time the use of polyurethane based resins promising encapsulant materials for PSCs.

Sustainability Of Dynamic Covalent Polymer Networks

Joost Brancart[1], Seppe Terryn[2], Ellen Roels[2], Ali Safaei[1], Guy Van Assche[1]

1 Physical Chemistry and Polymer Science (FYSC), Vrije Universiteit Brussel
2 Brubotics & Imec, Vrije Universiteit Brussel

Dynamic covalent chemistries have been widely used to create reversibly crosslinked polymer networks that show improved (re)processability compared to permanently crosslinked networks. In dissociative networks, the crosslink density of the polymer network decreases with increasing time and intensity of the application of the adequate stimulus, such as heat or light, resulting in a dramatic change in the viscoelastic behaviour. The thermoreversible Diels-Alder reaction between furan and maleimide is the most widely studied dynamic covalent chemistry. Heating the thermally reversible polymer networks shifts the reaction equilibrium towards the gradual breaking of the cycloadduct crosslinks, eventually leading to degelation of the network structure. This reversible gel transition was employed to create complex objects using many industrially relevant manufacturing techniques such as casting, moulding and additive manufacturing [1]. In contrast, associative networks do not show a net change in network connectivity. The rate at which a certain functional group exchanges with existing covalent bonds changes upon the increase of the stimulus intensity, allowing reprocessing.
Dynamic covalent chemistries have also become very popular to create self-healing materials that are able to reform broken covalent bonds to recover their functional properties. These materials extend the service lifetime of structures and systems, thus increasing the durability and sustainability of the derived objects. The self-healing property has been demonstrated and validated in applications such as coatings, composites and robotics [2]. The thermomechanical and viscoelastic behaviour and the healing performance of the materials can be tuned to the application's requirements using accurate knowledge of the reaction kinetics and thermodynamics [3] and structure-property relations [4].

[1] Roels E., et al. (2022) Advanced Materials, 34(1), 2104798. DOI: 10.1002/adma.202104798
[2] Terryn S., et al. (2021) Materials Today, 47, 187-205. DOI: 10.1016/j.mattod.2021.01.009
[3] Cuvellier A., et al. (2019) Polymer Chemistry, 10, 473-485. DOI: 10.1039/c8py01216d
[4] Safaei A., et al. (2021) Polymers, 13, 2522. DOI: 10.3390/polym13152522

Advanced Nano-Composites Based On Poly(Vinylidene Fluoride) Block Copolymers

Katja Loos

University of Groningen

The development of light and flexible capacitive energy storage devices with high electrical energy densities is of crucial significance to respond to the ever-rising demands in advanced applications and electricity needs and to achieve current and future sustainability goals. Incorporation of high dielectric constant ceramic fillers inside the ferroelectric polymer matrix offers great potential to improve the energy density of dielectric materials. However, this approach often suffers from highly reduced breakdown strength caused by the large difference of the matrix and filler dielectric constants together with often poor dispersion of the ceramic additives inside the polymer.

Besides commonly used ceramic composites, polymer-based multiferroic materials, which combine piezoelectric polymers and inorganic phases, have been attracting a growing research interest since they can be readily fabricated by cheap low temperature processing methods resulting in flexible materials with lower leakage currents and dielectric losses. In particular, semicrystalline polymers such as poly(vinylidene fluoride) (PVDF) have strong piezo-, pyro- and ferroelectric properties. PVDF has superior piezoelectric properties as compared with other types of polymeric materials due to its polar crystalline structure.

Preparing well-defined nanocomposites based on fluorinated polymers is not straight forward. The dense packing of fluorine atoms causes a low surface energy of PVDF, which results in strong demixing of this polymer with most inorganic fillers. A very elegant way to freely tune all size parameters and aspect ratios of a multiferroic nanocomposite is the use of morphologies that arise from the self-assembly of block copolymers as a template. PVDF-based block copolymers, with their ability to self-assemble into well-ordered morphologies, deserve particular interest, as precursors for novel functional nanostructured materials with extraordinary properties. With this it becomes possible to tailor well-defined nanocomposites with excellent properties.

Expanding The Range Of Processable Polymers By Melt Electrowriting For Medical Applications

Sarah Burkhardt, Christina Kwade, Kilian Maria Arthur Mueller, Petra Mela

Chair of Medical Materials and Implants, Technical University of Munich

Introduction

Melt Electrowriting (MEW) is an electric field-assisted additive manufacturing technique for the fabrication of fibrous constructs. A high-voltage is applied between a moving collector and a syringe containing a molten polymer so that a Taylor cone is formed and micron-sized fibers are deposited on the collector according to a predefined pattern thus obtaining controlled complex 3D architecture. MEW has already demonstrated great potential in bio medical applications like tissue engineering. However, the library of materials processable by MEW is still limited.

Methodology

In this study we developed a system that allows us to easily adapt the process of MEW to the specific requirements of the selected polymers. We chose polymers with different mechanical properties, degradation behavior, and melting temperatures to evaluate the process. Beside polycaprolactone (PCL) as gold standard material for MEW, we investigated the fast degrading poly-p-dioxanone (PPDO), and the thermal sensitive polylactic acid (PLA). SEM images were taken to evaluate the quality of the produced samples. In addition, cell tests were conducted to verify the suitability of our process for tissue engineering applications.

Results

With the developed method, we successfully produced MEW samples from different materials with different requirements on the MEW machine and process and could therefore overcome current limits of MEW. SEM analysis of the produced scaffolds showed we were able to achieve fibers with the same diameter range and 3D microarchitecture typical of MEW. Cell experiments showed promising results in terms of cell adhesion and proliferation and therefore confirmed the suitability of the method for tissue engineering applications.

Conclusion(s)

This work widens the range of materials that can be applied for scaffold production for tissue engineering and potentially expands the field of application of Melt Electrowriting.

Flexoelectric Response Of PVDF-Based Materials Prepared By Solution Blow Spinning

Javier González-Benito, Victor M. Ruiz, Dania Olmos

University Carlos III of Madrid

Although the most well-known electromechanic response is piezoelectricity, the little studied flexoelectricity has high potentiality for many purposes. Flexoelectricity is based on the electrical polarization of a material due to the presence of a non-uniform strain field or strain gradient. All dielectrics are flexoelectric but only certain materials or materials under certain circumstances may have significant flexoelectric response. For instance, PVDF presents high flexoelectric coefficient in comparison to other polymers because of the presence of highly polar functional groups. In the present work, the mechanical response and flexoelectric behavior of materials based on PVDF prepared by SBS are considered, studying the effect of porosity and the addition of multiwalled carbon nanotubes. In particular, the strength of the composite materials under cyclic deformation was studied. This strength depends on mainly three factors, the material macroscopic design, the composition of the composite and dispersion of the filler. On the other hand, flexoelectric response depends on the morphology and, the nature and the composition of the materials. Porous materials, apart from leading to more intense flexoelectric responses are more efficient in terms of dissipation of energy. All PVDF-based materials under study yielded measurable flexoelectric response, indicating that any of them might be used for sensors of pressure and even energy-harvesters with potential applications in wearable electronics.

Epoxy Sustainable Nanocomposites Reinforced With Functionalized Nanocellulose For Electronic Coatings

Madalina Ioana Necolau[1], Celina Maria Damian[1], Brindusa Balanuca[1, 2], Adriana Nicoleta Frone[3], Horia Iovu[1, 4]

1 Advanced Polymer Materials Group, University Politehnica of Bucharest
2 Department of Organic Chemistry "C. Nenitescu", University Politehnica of Bucharest, Bucharest, Romania
3 National Institute for Research & Development in Chemistry and Petrochemistry, Bucharest, Romania
4 Academy of Romanian Scientist, Bucharest, Romania

Epoxidized linseed oil (ELO) is widely studied in the coatings industry due to its high versatility, applicability, and the high content of oxirane rings. Carboxylic acids like citric acid (CA) can generate β-hydroxyester bonds when they react with the oxirane rings [1]. For this reason, recent studies have focused on this class of crosslinking agents to obtain sustainable ELO-based networks for different applications. By adding nanocellulose to the epoxy systems, improved thermal and mechanical properties can be achieved [2]. The research studies the influence of different functionalization agents for the surface of nanocellulose, on the compatibility, thus the efficient transfer within the ELO based nanocomposites.
The carboxyl acid solutions were prepared by adding H2O or THF as activator for appropriate volume of ELO, then different amount of NC and functionalized NC were added. Ultrasonication was used to disperse NC within matrix. Differential scanning calorimetry (DSC) and Fourier transform infrared spectrometry (FTIR) were used to monitor the thermal curing reactions, both techniques being employed to confirm the network formation mechanism and to define the curing kinetics. The effect of different NC concentration on the polymeric matrix derived from ELO was studied, considering thermal and mechanical behavior, water affinity and biodegradability.

Acknowledgments
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References
[1] F.I. Altuna, V. Pettarin,R.J.J. Williams, Self-healable polymer networks based on the crosslinking of epoxidised soybean oil by an aqueous citric acid solution. Green Chem. 2013, 15, 3360
[2] N.H. Hamid, M. Jawaid, W.S.I.W. B. Hisan, S.N. Sarmin, Effect of tetraethoxysilane on the dimensional stability and static bending properties of nanocellulose, tannin, and activated carbon mixed with epoxy resin, Journal of Materials Research and Technology 2021, 15, 416-426

Polymer And Solvent Mediated Nano-Cellulose Chiral Nematic Phases

Rachel Yerushalmi-Rozen

Ben-Gurion University of the Negev

Colloidal suspensions of cellulose nanocrystals (CNCs) that self-assemble into chiral nematic phases are sensitive to the suspending solvent, composition of the solution, and the presence of polymeric molecules. Each of these components shifts the phase diagram of the assembling CNC and the properties of the chiral nematic (N*) phase. Though entropic interactions such as depletion and excluded volume are expected to dominate these systems, our studies indicate that they are dominated by the detailed chemical composition and structure of the solvent and the additives [1]. Three different systems will be presented. A binary liquid mixture of water and ethylene glycol where the effect of the solvent-mixture composition on the properties of the CNCs mesophases is found to be scale-dependent [2]: The micron-size pitch of the N* phase decreases as the dielectric constant of the solvent mixture is reduced (higher EG content). Yet the nanometric inter-particle spacing of the CNCs rods (measured using SAXS and cryo-TEM) is almost independent on the EG content, nor is the transition to the biphasic regime. In addition, the effect of fully soluble hydrophilic polymers and core-shell polymeric micelles on the assembly of the CNCs and the phase behavior as revealed via . scattering methods and in-situ transmission electron microscopy (cryo-TEM) will be described.

It is suggested that understanding of polymer-CNCs interactions in suspensions may enable the engineering of CNCs assembly into optically active hybrids and composites.

References

[1] Polymer Induced modification of Cellulose Nanocrystal Assemblies in Aqueous Suspensions N. Cohen. et.al ACS Appl. Poly. Mater. 2020, 2,2,732-740

[2] Nano-to-meso structure of cellulose nanocrystal phases in ethylene–glycol–water mixture Attia et.al Soft Matter, 2020,16, 8444.

Influence Of Biofillers On The Crosslinking Of Natural Rubber Compounds And The Performance Of Vulcanizates

Anna Sowińska-Baranowska, Magdalena Maciejewska

Department of Chemistry, Institute of Polymer and Dye Technology, Lodz University of Technology

Biocomposites are increasingly used in various sectors of the economy, especially in the tire industry. Due to high consumer demand as well as the continuous development of this sector, the global market for the production and industrial application of biopolymers is constantly developing. The use of biodegradable and / or environmentally friendly materials has a positive effect on the right balance of waste management. In Poland, the development and production of biomaterials is not sufficient, but it has enormous potential. The idea of this research work is in line with the global trend of a biocomposites production, which will not only be environmentally friendly and recyclable, but much importantly, they will be distinguished by good mechanical strength and thermal stability, which will consequently expand the area of their potential practical application. Composites filled with biofillers based on cellulose, chitin or starch have been of interest in recent decades due to their environmental friendliness, low cost and good thermomechanical properties.

Two types of biofillers were used in this study, i.e. starch and ground walnut shells in various amounts by weight. Additionally, aminosilane and ionic liquid 1-butyl-3-methylimidazolium chloride were used in order to increase the activity of biofillers. The aim of the work was to investigate the effect of the amount of added biofillers, as well as their modification with aminosilane and ionic liquid, on the characteristics of the cross-linking process of natural rubber (NR) composites and their functional properties, including crosslink density, mechanical properties in static and dynamic conditions, hardness, thermal stability and resistance to thermo-oxidative aging.

Electrical Conductivity And Crystallization Dynamics Of EVA Nanocomposites In The Melt State

Antonis Gitsas[1], Gudrun Stalmann[2], Aleksandar Matic[2], Davide Tranchida[3], Thomas Gkourmpis[4]

1 Innovation & Technology, Borealis Polyolefine GmbH, Linz, Austria
2 Department of Applied Physics, Chalmers University of Technology, Göteborg, Sweden
3 Advanced Analytical Labs, Borealis Polyolefine GmbH, Linz, Austria
4 Innovation & Technology, Borealis AB, Stenungsund, Sweden

For a number of industrially relevant applications, good mechanical performance of flexible components needs to be combined with excellent dielectric properties. The addition of high aspect ratio fillers offers novel design options but simultaneously their dispersion adds an additional level of complexity to the system, in particular through the complex interaction between filler, matrix and the polymer amorphous and crystalline phases. [1-2] In this work, nanocomposite systems comprised of poly(ethylene vinyl acetate) (EVA) matrix and carbon black (CB) or graphene nanoplatelets (GNP) obtained using a melt state mixing process, were used to investigate the conductivity and crystallization dynamics by DSC, SEM and dielectric spectroscopy. The performance turns out to be dependent on the interplay between i) the interphase interactions between matrix and filler, and ii) the degree of filler agglomeration. The interphase between the polymer matrix and the conductive filler is rather sharp, as the dielectric relaxation of EVA is not affected by the presence of the fillers. On the other hand, the signal intensities have increased in the composites. This could be attributed to phenomena such as increased ionic mobility close to the matrix-filler interphase. As a result, the conductive pathway is solely consisting of units of the conductive filler, leaving the polymer matrix unaffected and thus retaining the desirable thermomechanical properties. Electrical hysteresis as a function of temperature and filler loading was measured with the use of positive and negative temperature coefficients. In contrast to CB-based systems, GNP nanocomposites exhibit an almost negligible amount of electrical hysteresis upon cooling both above and below the percolation threshold. This behaviour has been attributed to the filler capability of maintaining the integrity of the conductive network, by restricting the onset of crystallisation to regions where no filler is present. Thus the polymer dynamics remain largely unaffected, and following the Dyre model which assumes charge transport occurring by hopping of charge carriers in the spatially varying random energy landscape.

[1] Oxfall, H.; Ariu, G.; Gkourmpis, T.; Rychwalski, R. W.; Rigdhal, M. Effect of carbon black on electrical and rheological properties of graphite nanoplatelets/poly(ethylene-butyl acrylate) composites eXPRESS Polym. Lett. 2015, 9, 66.
[2] Gkourmpis, T. in Controlling the morphology of polymers: Multiple scales of structure and processing Chapter: 8 Eds. G. R. Mitchell and A. Tojeira, Springer, Switzerland, 2016.

Enhancement Of The Electrical Conductivity And Mechanical Properties Of PLA/MWCNT Composite Thanks To A Natural Biopolymer: The Lignin

Silvia Lage-Rivera[1], Ana I. Ares-Pernas[1], Goretti Arias-Ferreiro[1], Aurora Lasagabáster-Latorre[2], Pablo Ligero[3], María Victoria González-Rodríguez[1], María-José Abad[1]

1 Universidade da Coruña, Campus Industrial de Ferrol, Grupo de Polímeros-CIT, 15403 Ferrol, A coruña, Spain
2 Dpto Química Orgánica I, Escuela de Óptica, Universidad Complutense de Madrid, Madrid, Spain
3 Enxeñería Química Ambiental Group, Centro de Investigacións Científicas Avanzadas (CICA), Universidade da Coruña, 15071, A Coruña, Spain

The 3D industry has shown great potential developing customized products in several areas such as toys, medicine, or electronic devices. However, its growth is being restricted by the lack of functional material like conductive polymers. One attractive solution are the conducting polymer composites (CPC), composed by a polymer matrix and a conductive nanofiller.
The polylactic acid (PLA) is a biopolymer obtained from natural sources and biodegradable under certain condition. It is electrically insulating but combined with a conducting nanofiller as MWCNT (multi-walled carbon nanotubes), it is possible to obtain materials with certain levels of conductivity. The new materials require additives such as TEC (Triethyl Citrate) or PEG (Polyethylene glycol), to improve the nanofiller dispersion throughout the matrix and maximize the electrical properties.
In this work, we have compared the efficiency of two plasticizers, the PEG and the lignin, a natural biopolymer. Both plasticizers improved the electrical conductivity and the mechanical properties of the samples. Furthermore, the sample with 1% of lignin displays the highest conductivity, related with the conductive paths formed inside the polymer composite. As a conclusion, we have obtained a more sustainable composite with high conductivity using lignin as natural plasticizer.

PLA-Lignin Films For Sustainable Packaging

Alice Boarino, Harm-Anton Klok

Institut des Matériaux and Institut des Sciences et Ingénierie Chimiques, Laboratoire des Polymères, École Polytechnique Fédérale de Lausanne (EPFL), Bâtiment MXD, Station 12, CH-1015 Lausanne, Switzerland

Lignin is the most abundant aromatic biopolymer on our planet, and is currently discarded in large quantity as a byproduct of paper industry.1 The complex structure of lignin, composed of aromatic rings with hydroxy and methoxy functional groups, gives to this plant-derived polymer the potential to act as an antioxidant and inhibit radical oxidation reactions. Moreover, lignin possesses chromophoric groups, which can absorb UV-light. 2,3 These properties render lignin a promising material for the application in food packaging, helping to extend the shelf life of food by protecting it from oxidation and UV-degradation processes.

In this research work, lignin was incorporated into another sustainable polymer, poly(lactic acid) (PLA). PLA represents an excellent alternative to conventionally used petroleum-based plastics, but the lack of antioxidant and UV-barrier activities limits the PLA application in food packaging.4 By incorporating lignin into PLA films, these limitations were overcame without significantly compromising the polymer mechanical properties. Lignin nanoparticles with high surface-to-volume ratio were prepared and efficiently dispersed in a PLA matrix by grafting some PLA chains from their surface. The achieved films displayed outstanding antioxidant and UV-barrier activity, pointing out their potential for the application in sustainable food packaging.

1) M. Upton, A. M. Kasko, Chem. Rev., 2016, 116, 2275.
2) S. Domenek, A. Louaifi, A. Guinault, S. Baumberger, J. Polym. Environ., 2013, 21, 692–701.
3) H. Zhang, X. Liu, S. Fu, Y. Chen, Int. J. Biolog. Macromol., 2019, 133, 86–92.
4) E. Drumright, P. R. Gruber, D. E. Henton, Adv. Mater., 2000, 12, 1841–1846.

Point of Care 3D Printing of PEEK for Orthopaedic Applications

Steven Kurtz[1,2], Hannah Spece[1]

1 Drexel University, Philadelphia, PA
2 Exponent Inc., Philadelphia, PA

Introduction

The ability to manufacture orthopaedic implants and bone defect scaffolds at the point-of-care has become a desire for clinicians wanting to provide efficient patient-specific treatment, especially in an ambulatory surgical environment. As an alternative to costly 3D printed metal, some hospitals have adopted more economical, extrusion-based 3D printing (fused filament fabrication; FFF) for creating non-implantable instruments with low-temperature plastics. Recent innovations have allowed for the printing of high-temperature engineering polymers such as polyetheretherketone (PEEK). Due to its low modulus of elasticity, high yield strength, and radiolucency, PEEK is an attractive biomaterial for implantable devices, and has decades of clinical history in spinal fusion applications. Though concerns exist regarding PEEK for orthopaedic implants due to its bioinertness, the creation of porous networks has shown promising results for bone ingrowth.

In this study, we manufactured porous PEEK constructs via clinically-used FFF using a commercially available, 3D printer. We assessed the effect of porous geometry on cell response and hypothesized that 3D printed, porous PEEK will exhibit greater preosteoblast viability and activity compared to solid PEEK. The work represents an innovative approach to advancing point-of-care 3D printing, cementless fixation for total joint arthroplasty, and additional bone defect salvage applications typically reserved for porous metal.

Methods

Three porous constructs – a rectilinear pattern and two triply period minimal surface designs (TPMSs) - were designed to mimic the morphology of trabecular bone. The structures, along with solid PEEK samples for use as a control, were manufactured via FFF using an Apium P220 printer and 450G PEEK filament. The samples were mCT scanned to determine the resulting pore size and porosity. The PEEK constructs were then seeded with pre-osteoblast cells for 7 and 14 days. Cell proliferation and alkaline phosphatase activity (ALP) were evaluated at each time point, and the samples were imaged via SEM.

Results

mCT imaging showed the pores in the PEEK constructs to be open and interconnected. The average pore size was 535 ± 92 μm for the rectilinear, 484 ± 237 μm for the diamond, and 669 ± 216 μm for the gyroid. Porosity was 71%

for the rectilinear, 76% for the diamond, and 68% for the gyroid. The average error between the theoretical and actual values was -37.3 µm for pore size and -2.3 % for porosity.

Normalized ALP activity of the three porous PEEK samples at 7 days were found to be significantly greater than the solid sample ($p < 0.05$ rectilinear, $p < 0.005$ gyroid, $p < 0.001$ diamond). At 14 days, the same relationships were observed ($p < 0.001$ for all three designs). No difference between the three porous geometries was found.
SEM imaging revealed cells with flat, elongated morphology attached to the surface of the PEEK. The 14-day samples appeared to have proliferated well and spread along the PEEK pores. Extensions of filopodia and lamellipodia were observed along with large blankets of cells covering the PEEK surface.

Discussion
We demonstrated the ability of FFF-printed, porous PEEK surfaces to promote cellular processes necessary for bone-implant fixation. While all porous structures showed promising results, more investigation into their material characteristics and osteogenic potential are necessary to determine which geometry may be suitable for orthopaedic use. Our pilot research offers an innovative approach to advancing point-of-care 3D printing, cementless implant fixation, and additional applications typically reserved for porous metal.

Single-Chain Folded Unimer Micelles For The Encapsulation And Release Of The Anticancer Combretastatin A-4 Drug

Elisa Guazzelli, Matteo Calosi, Simona Braccini, Marco Lessi, Fabio Bellina, Giancarlo Galli, Elisa Martinelli

Department of Chemistry and Industrial Chemistry - University of Pisa

In recent years the use of solvophobic interactions, among many others, attracted notable attention owing to the formation of unimer micelles in a selective solvent, typically water, through single-chain folding. These nanoobjects differ from the random coil state and generally consist of a hydrophobic compartment, shielded by a hydrophilic shell. These unimer micelles fall in the larger category of the so-called single-chain nanoparticles (SCNPs) and are in the size regime of many proteins and viruses (1–20 nm). A tailored synthesis and in-depth characterisation of size, shape, and conformation of these materials might drive their future exploitation in environmental chemistry, industrial catalysis, biomedicine and drug delivery.[1–3]

In our previous works, the self-assembling behaviour of amphiphilic (meth)acrylic random copolymers with perfluorohexyl and oligo(oxyethylene) side chains was investigated through a number of different and complementary methodologies. Dynamic Light Scattering (DLS) measurements on water solutions of the copolymers at room temperature showed the presence of such unimer micelles with hydrodynamic diameter Dh ≤ 8 nm. These single-chain nanoparticles were thermoresponsive and reversibly collapsed into much larger, multi-chain aggregates with Dh = 500-1600 nm at a cloud point temperature (Tcp) easily modulated by the copolymer structure in terms of composition and side-chain length of the hydrophilic component. Small angle neutron scattering (SANS) results allow to clarify the effect of temperature on the self-assembling features and the structural morphology of both unimer single-chain entities and larger multi-chain aggregates. The existence of three distinct phases of self-assembled structures was pointed out as a function of increasing temperature: 1) globular unimers; 2) coexistence of extended unimers and aggregates; and 3) aggregates, which overall showed full reversibility in a wide range of copolymer concentrations.[4,5] Molecular dynamics (MD) simulations were carried out to evaluate folding trajectories of the amphiphilic copolymers and supported the formation of globular, unimer micelles with a structural variability in water.[6] Self-folding appeared to result from the interplay between hydrophobic interactions and structural constraints within the random copolymer.

On the basis of this rationale, in the present work water-soluble amphiphilic random copolymers composed of tri(ethylene glycol) methacrylate (TEGMA) or poly(ethylene glycol) methyl ether methacrylate (PEGMA) and perfluorohexylethyl acrylate (FA) were synthesized by ARGET-ATRP and their self-assembling ability in water was exploited to encapsulate Combretastatin A-4 (CA-4), a very active, but poorly water-soluble, anticancer drug. Both amphiphilic copolymers were

confirmed to predominantly self-fold in unimer micelles in aqueous solution with small hydrodynamic diameters (≤ 8 nm) that thermoreversibly self-associated in larger concentration-dependent size multi-chain aggregates. The more hydrophilic PEGMA-co-FA copolymer presented higher Tcps at the given concentrations. Encapsulation of drug occurred with a high efficiency (≥ 81%), although it was based on different mechanisms for the two copolymers. In particular, the drug was found to be incorporated in the unimer micelles of TEGMA-co-FA, whereas it was preferentially encapsulated into multi-chain aggregates of PEGMA-co-FA, whose formation was induced by the hydrophobic drug itself. The addition of CA-4 affected the thermoresponsiveness of copolymers causing a significant reduction in the Tcp which linearly decreased by increasing the amount of drug with respect to the copolymer alone. Release of drug was noticeably faster for PEGMA-co-FA but for both copolymers was significantly slowed down with respect to the free, i.e. not encapsulated, drug. Release occurred at temperature below Tcp, indicating that thermoresponsiveness was not necessary to trigger the process, even though it appeared to moderately increase the release rate in the linear region. Cytotoxicity tests carried out on PEGMA-co-FA at 37 °C using Balb/3T3 clone A31 cells showed that cells presented both viability and morphology comparable to those of the control at any given concentration.

These findings show that the self-assembling amphiphilic random copolymers of this work are potential candidates as nanocarriers for the effective encapsulation and release of highly hydrophobic drugs whose release rate can be tuned by varying their degree of amphiphilicity, e.g. the length of the oxyethylenic side chain, and/or thermoresponsive behaviour, i.e the cloud point temperature. The work presented here encourage the further investigation of the cutting-edge topic of self-folding SCNPs in the field of biomedical applications in general and controlled drug delivery, in particular. Depending deeply on polymer design, initial toxicity evaluations attribute high biocompatibility to SCNPs and, in virtue of their size, extraordinary distribution behavior is expected. Further systematic investigations into in vitro and in vivo properties are, however, required in order to understand and predict biodistribution behavior, biocompatibility and drug release of SCNPs under realistic conditions, and to take full advantage of their potential as a new class of biomaterials.

References

Single-Chain Polymer Nanoparticles; Pomposo, J.A., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2017; ISBN 9783527806386.

Terashima, T. Controlled Self-Assembly of Amphiphilic Random Copolymers into Folded Micelles and Nanostructure Materials. J. Oleo Sci. 2020, 2020, 1–10.

Kröger, A.P.P.; Paulusse, J.M.J. Single-chain polymer nanoparticles in controlled drug delivery and targeted imaging. J. Control. Release 2018, 286, 326–347.

Martinelli, E.; Guazzelli, E.; Galli, G.; Telling, M.T.F.; Poggetto, G.D.; Immirzi, B.; Domenici, F.; Paradossi, G. Prolate and Temperature-Responsive Self-Assemblies of Amphiphilic Random Copolymers with Perfluoroalkyl and Polyoxyethylene Side Chains in Solution. Macromol. Chem. Phys. 2018, 219, 1800210.

Domenici, F.; Guazzelli, E.; Masotti, E.; Mahmoudi, N.; Gabrielli, S.; Telling, M.T.F.; Martinelli, E.; Galli, G.; Paradossi, G. Understanding the Temperature-Responsive Self-Assemblies of Amphiphilic Random Copolymers by SANS in Dinf>2/inf>O Solution. Macromol. Chem. Phys. 2021.

Guazzelli, E.; Martinelli, E.; Galli, G.; Cupellini, L.; Jurinovich, S.; Mennucci, B. Single-chain self-folding in an amphiphilic copolymer: An integrated experimental and computational study. Polymer 2019, 161, 33–40.

Well-Controlled Drug Delivery Systems Based On Polycaprolactone Hollow Fibers

Daniel Cuadra Rodriguez[1], Suset Barroso Solares[1, 2, 3], M. Luz Rodriguez Mendez[2, 3], Miguel Angel Rodriguez Perez[1, 2], Javier Pinto[1, 2]

1 Cellular Materials Laboratory (CellMat), Condensed Matter Physics Department, University of Valladolid, 47011, Spain
2 BioecoUVA Research Institute, University of Valladolid, 47011, Valladolid, Spain
3 Group UVASENS, Escuela de Ingenierías Industriales, University of Valladolid, Paseo del Cauce, 59, Valladolid, 47011, Spain

Currently, polymers are present in many applications in our society due to their versatility and low cost. They are widely used in the aeronautic and automotive industry, packaging, or even biomedical applications, among others. Focusing on the last sector, polymer-based matrices are employed in several systems in the biomedical field, such as drug delivery.

The control of the drug dosage is a key parameter to ensure the efficiency of medical treatment, as well as to avoid undesired toxicity. However, conventional drug delivery systems usually present a non-constant or well-controlled drug release capability. Accordingly, the development of new drug delivery systems with a controlled release has attracted great attention in the last years. Among diverse approaches, polymer-based devices have shown to be able to provide a constant release rate, being of particular interest when they are based on biocompatible and biodegradable polymers.

In this work, we have developed a new generation of polymer-based hollow fibers that could be employed as drug delivery systems. In a first step, polycaprolactone, a well-known biodegradable and biocompatible polymer, was used to fabricate solid microfibers by using a conventional electrospinning process. Then, the hollow fibers were obtained for the first time by foaming the solid fibers, overcoming the limitations of the gas dissolution foaming when applied to micrometric materials. Moreover, by tuning the parameters of the gas dissolution process, two different kinds of fibers were obtained: hollow fibers with smooth surface and hollow fibers with porosity on the surface.

Finally, Ibuprofen was successfully introduced in all the fibers by CO2 dissolution process, achieving large amounts of drug up to 15 wt.%. Release tests were performed in distilled water, and several differences in the release rate, related to the morphology of the fibers, were found. Solid fibers and hollow fibers with smooth surface offer a non-constant release in 7 and almost 24 hours, respectively. However, hollow fibers with surface porosity provide a constant release in one and a half day. Therefore, they could be employed as drug delivery systems with well-controlled release and local application.

Polymerization Induced Self-Assembly (PISA): A Powerful Approach Toward Formulation Of Advanced Nano-Objects Of Polysaccharides-Based Copolymers

Djallal Ikkene, Wan Nurhidayah Wan Hanaffi, Jihad Oumerri, Jean-Luc Six, Khalid Ferji

Laboratoire de chimie physique macromoléculaire - LCPM- Nancy 54001, France

Polysaccharides-based nano-objects are promising candidates for biomedical technologies, such as nanocarriers for drug delivery or as biomembrane mimics, because of their biocompatibility, biodegradability, low immunogenicity, and specific bioactivity. However, investigations focused on the self-assembly of polysaccharide-based amphiphilic copolymers described mostly primitive morphologies (spherical micelles or core–shell nanoparticles), while advanced ones (worms and vesicles) are very scarce. This is because of the insolubility of polysaccharides in most common organic solvents that overcome the use of traditional self-assembly process (nanoprecipitation for instance). Herein, we demonstrate how the PISA, which is a one pot self-assembly process, is the most adequate methodology to study the self-assembly of such specific amphiphilic copolymers in water. On the one hand a model system based on dextran as hydrophilic polysaccharide was used. On the other hand, as proof of concept, smart polysaccharide based-nanocarriers were prepared by PISA using sensitive polymers to external stimuli, to demonstrate the versality of this methodology to prepare functional nanocarriers for nanomedicine. Nano-objects formulated were deeply characterized using Dynamic/static light scattering measurements, (cryo)transmission electron microscopy, and atomic force microscopy.

[1] K. Ferji, P. Venturini, F. Cleymand, C. Chassenieux and J.-L. Six, Polymer Chemistry. 2018, 9, 2868-2872.
[2] J-L. Six And K. Ferji, Polymer Chemistry, 2019,10, 45-53.
[3] D. Ikkene, A.A. Arteni, H. Song, H. Laroui, J-L. Six and K. Ferji, Carbohydrate Polymers, 2020, 234, 115943.
[4] D. Ikkene, A.A. Arteni, M. Ouldali, J-L. Six and K. Ferji, Polymer Chemistry, 2020, 11, 4729-4740.
[5] D. Ikkene, A.A. Arteni, M. Ouldali, G. Francius, A. Brûlet, J-L. Six and K. Ferji, Biomacromolecules, 2021, in press.
[6] V. Castro, B. Nomeir, A.A. Arteni, M. Ouldali, J.-L. Six and K. Ferji, Polymers 2021, 13, 4064.

Sustainable Approach To Combine Tio2 With Various Polysiloxane Matrices To Produce Self-Sterilising, UV-Protecting, Self-Cleaning, And Flame-Retardant Cotton Textiles For Technical Applications

Mohammad Mamunur Rashid[1], Brigita Tomšič[1], Barbara Simončič[1], Ivan Jerman[2], Danaja Štular[2], Matija Zorc[1]

1 University of Ljubljana, Faculty of Natural Sciences and Engineering, Slovenia
2 National Institute of Chemistry, Slovenia

Current approaches and technologies in the processes of the chemical modification of textile fibres to produce multifunctional textiles are not strictly aligned with the environmental and economic concept of sustainability when investing in the production of high value-added textile products. Sol–gel technology is known to be an environmentally friendly process enabling the synthesis of nanomaterials of different morphologies and chemical structures. Among such nanomaterials TiO2 is well established photocatalyst, granting self-cleaning, antimicrobial and UV-protective properties to the textile fibres. Its main drawback is poor adhesion to the textile fibres. Accordingly, establishing a strong cooperative bond between TiO2 and the textile surface while enhancing the photocatalytic activity remains an important challenge in the production of multifunctional technical textiles.
In this study, TiO2 and the antimicrobial bio-barrier-forming dimethyloctadecyl [3-(trimethoxysilyl) propyl] ammonium chloride (SiQAC) or the flame retardant precursor 3-(trihydroxysilyl) propyl methyl phosphonate (TPMP) were combined in a 1:1 molar ratio. Both nanosols were applied to cotton fabrics by a pad-dry hydrothermal technique, while 2.0 mM AgNO3 was added in a hydrothermal bath to produce TiO2/SiQAC/Ag or TiO2/TPMP/Ag coated textiles. The treated textile samples were dried and cured at 150°C for 3 min. Antibacterial activity against E. coli and S. aureus, UV protection, self-cleaning and flame retardant properties were evaluated according to established standard methods.

The research results confirmed the successful development of TiO2/SiQAC/Ag and TiO2/TPMP/Ag textile surfaces in a sustainable manner. Cooperative activity between all components of TiO2/SiQAC/Ag and TiO2/TPMP/Ag nanocomposites on the textile surface was achieved, providing wide-ranging functionalities such as self-cleaning, self-sterilisation, UV protection and flame retardancy, while the incorporation of Ag into the nanocomposite matrix, significantly enhanced the photocatalytic activity of TiO2.

Alginate And Alginate-Chitosan Hydrogels For Wastewater Remediation: Effect Of Composted Biowaste-Derivative Addition

Maria Laura Tummino[1, 2], Pierangiola Bracco[1]

1 Università degli studi di Torino
2 Current address: Consiglio Nazionale delle Ricerche - STIIMA Biella

The rising utilization of renewable and residual biomasses for environmental preservation and remediation are important objectives to be pursued to minimize the environmental impact of human activities [1]. In this perspective, biowaste-containing hydrogels are herein proposed as aqueous pollutant adsorbents. We prepared hydrogels by crosslinking sodium alginate (derived from brown algae) with Ca2+ or chitosan (derived from crustacean exoskeleton), by adding soluble biowaste-derived substances isolated from green compost (BBS-GC). Alginate, chitosan and BBS-GC (that bear similarities with humic-like substances) are sustainable, non-toxic and environmental-friendly reactants, bringing a multiplicity of different functional groups, able to act as sequestrating agents for the remediation of contaminated wastewaters [1,2]. Thanks to the multi-analytical approach adopted for the physicochemical characterization of the materials (i.e. scanning electron microscopy, thermogravimetric analysis, water uptake/swelling measurements, Fourier transformed infrared spectroscopy, rheological measures), it was possible to define some relationships among structural, morphological and rheological features of the gels together with their adsorbing properties, evaluated in the removal of different dyes, which represent typical polluting substances discharged downstream of textile industries [3]. The enhanced performances registered for the BBS-GC-containing gels in comparison with reference ones, suggest their potential use as sustainable tools for wastewater treatments.

[1] Tummino M.L., Testa M.L., Malandrino M., Gamberini R., Bianco Prevot A., Magnacca G., Laurenti E., Nanomaterials, 2019, 9, 162
[2] Tummino M.L., Magnacca G., Cimino D., Laurenti E., Nisticò R., International Journal of Molecular Sciences, 2020, 21, 550
[3] Semeraro P., Fini P., D'Addabbo M., Rizzi V., Cosma P., Agriculture and Biotechnology, 2(4), 2017, 1835

The B-Cyclodextrin Polymer Cross-Linked Via 3,3′,4,4′-Biphenyltetracarboxylic Dianhydride For Removal Of Organic Dyes From Water

Jakub Łagiewka, Iwona Zawierucha, Tomasz Girek

Faculty of Science and Technology, Jan Dlugosz University in Czestochowa, Armii Krajowej 13/15, 42-200 Czestochowa, Poland

For several decades, the importance of chemical industry has been increasing in the daily life of humanity, it has led to the emission of many harmful pollutants for the environment and the human health. One of the most harmful groups are organic dyes, which are composed with polycyclic aromatic groups. Nowadays, prominent materials for dye removal are based on polysaccharides with efficient sorption properties, cheap and efficient synthesis. For instance, β-cyclodextrin (β-CD) is a macrocyclic oligosaccharides composed of 7 α-D-glucopyranose units and connected with α-1,4-glycosidic bonds. β-CD polymer are useful sorbent because of the ability to form inclusion complex with organic molecules inside hydrophobic cavity. The inclusion phenomena is the main driving force to bind organic molecules, but in some cases like cross-linking is possible to introduce other binding groups and apply additional forces like hydrogen bonds, electrostatic interactions, π-π interactions. Our goal was to design a novel sorbent, the β-CD was cross-linked via 3,3′,4,4′-biphenyltetracarboxylic dianhydride. Firstly, the β-CD was activated with NaH to produce oxyanions which opened anhydride ring in the nucleophilic substitution reaction. The cross-linking agent was connected with CD via ester bond, additionally free carboxyl groups was formed from anhydride rings. The structure was confirmed with infrared spectroscopy (FTIR), morphology was analyzed with scanning electron microscopy (SEM), thermal properties was studied with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Finally, the polymer was applied to remove an organic dye from aqueous solutions. The sorption studies were performed in batch conditions to determine optimal sorption parameters: pH, contact time. To conclude, we have obtained a novel polymer of CD with an ability to remove organic dyes from water.

Sub-Micrometric Cross-Linked Mats And Fibrous Carbons Produced From NADES-Derived Beta Cyclodextrin-Based Polymers

Claudio Cecone, Gjylije Hoti, Fabrizio Caldera, Marco Zanetti, Francesco Trotta, Pierangiola Bracco

University of Turin

Electrospinning is a facile, cost effective, and flexible technique which allows the production of fibres at micron, sub-micron and nano-scale, from an electrically charged jet of polymer solutions. The development of this technique has now consolidated its role in the processing of a rich variety of polymers mostly for filtration, biosensors, drug delivery, tissue engineering, and wound dressings applications.[1] In this frame, beta cyclodextrin-based polymers have attracted scientific and industrial attention thanks to their tuneable synthesis, good chemical stability, and biocompatibility. Also, with the aim to render their fabrication more sustainable and suitable for large-scale productions, the substitution of toxic compounds and organic solvents with eco-friendly alternatives, represents an active field of research. A sustainable alternative to organic solvents has recently been given by natural deep eutectic solvents (NADES). Citric acid/choline chloride NADES systems have been exploited as suitable solvent/reactive media for the synthesis of functional water-soluble beta cyclodextrin-based polymers.[2] In this work, the production of sub-micrometric fibres from the electrospinning of NADES-derived beta cyclodextrin-based polymer solutions was investigated, using water as unique solvent. Also, the possibility to cross-link the obtained fibres via facile thermal treatment, without altering the fibrous morphology was demonstrated; cured, insoluble micrometric fibrous mats were obtained. Eventually, the spun mats were screened as suitable bio-derived precursors to produce porous carbon nano-fibres, while the use of polyethylene oxide as pore initiation agent, allowed to observe carbon fibres characterized by nano-porosities.

References
[1] D. Li, Y. Xia, Advanced Materials, 2004, 16 1151–1170.
[2] C. Cecone, G. Hoti, I. Krabicova, S.L. Appleton, F. Caldera, P. Bracco, M. Zanetti, F. Trotta, Green Chemistry, 2020, 22, 5806–5814

The Efficiency Of Straw Modification Methods In Functionalization Of Elastomer Composites

Justyna Miedzianowska[1], Marcin Masłowski[2], Krzysztof Strzelec[2]

1 Institute of Polymer & Dye Technology, Lodz University of Technology
2 Institute of Polymer and Dye Technology

In recent years, more and more attention in polymer technology has been devoted to composites produced with the use of renewable natural resources. The growing ecological awareness of the society, the current legal regulations on environmental protection and the willingness to manage natural waste mean that the interest in polymer biocomposites is constantly increasing. For this reason, new environmentally-friendly solutions are sought for the production of polymeric materials. Straw as a by-product in agriculture and weeds are natural, cheap, renewable and available sources of lignocellulosic fibers that can be a valuable addition to the preparation of biocomposites.
The aim of the research was to gain knowledge on the effectiveness of various methods of cereal straw modification and to recognize their influence on the functional and processing properties of elastomer composites. The research investigated how the processes of mechanical grinding of lignocellulosic material and its chemical treatment (silanization) affect the characteristics of the properties of natural rubber compositions.
The presented research includes the characterization of additives in terms of thermal stability, surface morphology and flammability. On the other hand, the recognition of the properties of biocomposites concerned the rheometric characteristics of rubber mixtures during their processing, as well as the determination of the vulcanization parameters of elastomer composites and the assessment of the impact of the natural additives used on the cross-linking density of vulcanizates. The effectiveness of straw additives as modifiers of natural rubber composites in improving the strength properties and flammability of elastomeric materials was also presented.
Appropriate processing of the straw material allows increasing the interfacial adhesion in the composite, positively influencing the functional and processing properties of the material. In addition, the modification of straw improved its thermal stability and contributed to the reduction of flammability of natural rubber vulcanizates.

Pro-Ecological Hybrid Pigments Based On Natural Dyes And Mineral Supports As Multifunctional And Ph Sensing Colorants For Polymer Composites

Bolesław Szadkowski[1], Jacek Rogowski[2], Waldemar Maniukiewicz[2], Emmanuel Beyou[3], Anna Marzec[1]

1Institute of Polymer and Dye Technology, Lodz University of Technology, Lodz, Poland,
2Institute of General and Ecological Chemistry, Lodz University of Technology, Lodz, Poland,
3UMR CNRS5223, Ingénierie des Matériaux Polymères, Université Lyon 1, F-69622, Villeurbanne, France

Presenter Contact Details: boleslaw.szadkowski@p.lodz.pl, +48603932698

Natural dyes and pigments have been used as colorants for hundreds of thousands of years, and they are back in the spotlight now because of their diverse plant sources, high safety and environmental friendliness. Recently, hybrid pigments have become very popular due to the combination of the advantages of both an organic dye and an inorganic carrier, which increases their application potential.

This study entails the synthesis of a series of natural hybrid pigments using different anthraquinone dyes and mineral fillers. Based on the secondary ion mass spectrometry, 13C solid state nuclear magnetic resonance and X-Ray photoelectron spectroscopy, it was proved that organic chromophores interacted with metal ions (Mg2+, Ca2+ and Al3+) present in the mineral supports forming stable, multicolour organic-inorganic pigments. The as-prepared hybrid pigments were explored as a type of eco-friendly pigments with improved thermal stability, chemical resistance and reduced tendency to migration compared to corresponding natural dyes. Moreover, the natural pigments exhibited strong pH-sensing activity, changing their color upon exposure to HCl and/or NH3 vapors. The structure, stability and color response of hybrid pigments upon exposure to acidic or base vapors could be controlled by proper selection of mineral support. In the second step, the designed hybrid pigments were successfully applied to elastomer and thermoplastic elastomer. The incorporation of the hybrid pigments into polymer matrix led to obtain multicolor polymer composites with pH sensing activity and reduced flammability. Evaluation of the pH sensing activity of the polymer composites filled with hybrid pigments revealed that the changes in color were more rapid when elastomer matrix was employed for composite preparation.

The present study shows a facile and promising strategy for preparation of eco-friendly colorful pH sensors that can simultaneously act as colorants and functional additives for polymer composites.

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Abstracts II

Poster Exhibition

A.1 Poloxamer Gel as New Strategy for Adjuvant Therapy of Melanoma

Elisabetta Esposito[1], Maddalena Sguizzato[1], Alessandra Pecorelli[2], Nicolas Huang[3], Rita Cortesi[1], Giuseppe Valacchi[4, 5]

[1] Department of Chemical and Pharmaceutical Sciences, University of Ferrara, I-44121-Ferrara, Italy
[2] 2NC State University, Plants for Human Health Institute, Animal Science Dept. NC Research Campus, Kannapolis, NC 28081, USA
[3] Institut Galien Paris-Sud, CNRS UMR 8612, Univ Paris-Sud, Université Paris-Saclay, Faculté de Pharmacie, 92296 Châtenay-Malabry, France
[4] Department of Biomedical and Specialist Surgical Sciences, University of Ferrara, I-44121 Ferrara, Italy
[5] NC State University, Plants for Human Health Institute, Animal Science Dept. NC Research Campus, Kannapolis, NC 28081, USA

The investigation focuses on the production and characterization of poloxamer gels containing gallic acid, a natural antioxidant molecule. The gels have been designed to be applied on the skin in order to treat melanoma. Particularly, a rheological characterization and determination of gel transition temperature has been conducted to select the poloxamer concentration suitable for topical administration of the gel. Franz cells associated to different membranes have been employed to study the gallic acid diffusion. Namely, the diffusion has been firstly evaluated through single synthetic membranes, i.e. cellulose, nylon, polycarbonate, polytetrafluoroethylene, polyvinylidene fluoride and the commercial Strat-M membrane. As second approach, in order to reproduce the gallic acid diffusion through the skin, the membranes were employed in association and compared to stratum corneum epidermis membranes. Gallic acid diffusion from poloxamer gel has been evaluated through selected membranes. It was found that gallic acid diffusion was strongly influenced by the type of membrane, both in the case of the aqueous solution or poloxamer gel. Scratch wound healing and migration assays conducted on human keratinocytes and melanoma cells demonstrated the ability of gallic acid loaded in poloxamer gel to affect cellular migration. The encouraging results suggest that the gel could be possibly proposed as adjuvant for the treatment of cutaneous melanoma or other hyperproliferative diseases such as psoriasis.

A.2 Evaluation of Thermal Properties Of PCL-Based Linear and Star Shaped Copolymers Prepared by Ring-Opening Polymerization

Dimitrios Bikiaris[1], Evi Christodoulou[2], Panagiotis Klonos[2], Evangelos Karavas[3]

[1] *Aristorle University of Thessaloniki*
[2] *Aristotle University of Thessaloniki*
[3] *Pharmathen S.A., Pharmaceutical Industry*

Polycaprolactone (PCL) is a semi-crystalline biodegradable polymer with low melting temperature (~60 °C), appropriate mechanical properties, and good solubility in several solvents. It has attracted much attention as an ideal material for drug delivery, tissue engineering and other applications. However, due to its high degree of crystallinity and hydrophobicity, PCL degrades rather slowly. Producing new PCL-based copolymers can help accelerate the biodegradation rate, and tailor its mechanical and thermal properties.
In the present study, a series of PCL-based random copolymers were synthesized by ring-opening polymerization of ε-caprolactone (ε-CL) with three different alcohols -methoxy poly(ethylene glycol) (mPEG), glycerol, and pentaerythritol. Their successful synthesis was confirmed by FTIR and NMR spectroscopy. Crystallinity was studied by XRD and their thermal transitions were investigated by TGA and DSC.
Crystalline peaks of PCL were recorded in all XRD patterns, but the slightly lower peak intensities indicated a decreased degree of crystallinity. The thermal degradation of all random copolymers was similar to that of the PCL homopolymers as it can be observed for the TGA thermograms. All samples were as thermally stable as PCL, except for PCL-mPEG copolymer which showed slightly lower stability. Several values of interest were determined by DSC measurements such as crystallization and melting temperatures (T_c and T_m) as well as glass transition temperature (T_g). It was found that branched copolymers have similar T_m and T_g values with neat PCL, while this with mPEG has slightly lower values. This is due to plasticized effect of mPEG in PCL. These materials will be evaluated as appropriate matrices for drug nanoencapsulation.

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A.3 Synthesis of mPEG-PCL Random Copolymers and Study of Their Rheological Behavior

Evi Christodoulou[1], Kostas Tsachouridis[1], Thanasis Athanasiou[2], Dimitrios N. Bikiaris[1], Evangelos Karavas[3]

[1] Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece;
[2] Polymer & Colloid Science Group, IESL-FORTH, 71110 Heraklion, Greece
[3] Pharmathen S.A., Pharmaceutical Industry, Dervenakion Str 6, Pallini Attikis, 15351 Attiki, Greece

PCL is a semi-crystalline aliphatic polyester produced by ring-opening polymerization of the cyclic ester monomer ε-caprolactone. PCL is of great significance due to its biodegradability, biocompatibility, high flexibility, and low glass transition temperature/melting point. It has found several applications, in pharmaceutical technology (as a drug carrier or coating material), tissue engineering etc. Poly(ethylene glycol) (PEG) and its end-group products (such as methoxy polyethylene glycol, mPEG), known for their hydrophilicity, non-toxicity, and absence of immunogenicity, can be selected to be attached to PCL, forming copolymers with improved properties. mPEG-PCL copolymers are important synthetic biomedical materials with amphiphilicity and controlled biodegradability, ideally suitable for long-term delivery.

In the present study, a series of random mPEG-PCL copolymers has been prepared via ring-opening polymerization of ε-caprolactone with methoxy-poly(ethylene glycol), by changing two reaction parameters: (a) mPEG:PCL molar ratio (1:1 or 1:3) and (b) mPEG's molecular weight (750, 2000, 5000 and 10000). Their synthesis was confirmed by NMR and FTIR spectroscopy, and rheological characterization has been performed afterwards. It was found that all samples exhibited Newtonian behavior above T_m. Increasing the PCL content seemed to enhance the mechanical properties and increase dissipation. It is difficult to predict whether the increase of mPEG's MW will enhance the flow properties of the copolymer, since the higher MW (mPEG1000) dynamic viscosity was found unexpectedly low.

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A.4 Analysis of Plate-Like Medical Implant Structures Using Higher-order Theory with C^1 Continuity and Efficient p-Finite Elements

Mohamad Hasan Bin Tasneem, Farooq Al Jahwari

Department of Mechanical & Industrial Engineering, Sultan Qaboos University

Structural elements in the form of plates and shells have significant applications in a wide range of industries such as medical implants which grew rapidly for the past few years. Medical implants require high accuracy in predicting deformation and stresses to minimize the sufferings on human body while using the implants temporarily or permanently. These implants for trauma patients typically appear in the form of flat or curved plates or shells. Considerable progress has been made in the analysis of plates/shells and many theories were developed to determine deformation and stresses as accurately as possible. However, many of these theories suffer from lesser accuracy in predicting the transverse shear stresses compared to the other stress components. This could be attributed to the predefined assumption of thickness inextensibility and discontinuity of stresses and strains across elements for plates under bending as posed by these theories. This research work presents a numerical approach based on a modified theory which removes the above assumptions and enforce continuity of strains and stresses across elements. Finite element method is adopted to solve the equilibrium equations which necessitates the derivatives continuity across elements. Two specific types of finite elements i.e. the bi-linear quadrilateral (9-node) and bi-cubic quadrilateral (16-node), are used along with continuity enforcement using a penalty function. The obtained results are very accurate for implants made from soft natural biopolymers like Chitosan and synthetics like PEEK. After applying various loading and boundary conditions, the maximum error in central deformation is less than 1%, while the error for stresses ranges in between 3 to 6%. Also, when comparing the two finite elements, the 16-node element performed better in predicting both the deformation and stresses with smaller mesh size.

A.5 Polyhydroxybutyrate (PHB) Composites for Fishing Purposes: A Reduction of Marine Waste Environmental Impacts

Laura Alonso, Julen Ibarretxe, Pello Jimbert, Roberto Fernandez-Martinez, Rikardo Minguez, Maider Iturrondobeitia

University of the Basque Country

Over the years, our oceans have witnessed an enormous accumulation of marine plastic waste resulting from ocean-related economic activities. As plastic pollution adversely affects marine wildlife and habitat, our society requires urgent solutions to address this increasingly alarming dilemma. Here we turn our attention into Circular Economy principles to reduce the amount of non-biodegradable petroleum-based marine litter. We consider polyhydroxybutyrate (PHB) as a potential biobased polymer to replace petroleum based single use products in commercial fishing purposes. PHB is selected due to its extraordinary rapid biodegradation in aquatic environments. PHB based composites (inorganic and biobased) are obtained and characterized as well as their end-of-life in sea water conditions. Melt blending and solvent casting processing techniques are used for the pruposes Results reveal that regarding the end-of-life options with a biodegradation scenario, PHB is preferred compared to petroleum based polymers due to its biodegradation, the yield biogenic CO_2, which can be used as a renewable energy source.

A.6 Development of Eco-Friendly Nanomembranes of Aloe Vera/PVA/ZnO for Potential Applications in PPEs

Muhammad Usman Munir, Daiva Mikučionienė

Kaunas University of Technology

Due to current Covid-19 pandemic, there is crucial need of development of antimicrobial and antiviral personal protective equipment such as facemasks and gowns. Therefore, in this research we fabricated electrospun nanofibers composite with Polyvinyl alcohol, Aloe Vera, and Zinc oxide nanoparticles for development of facemask inner layer. Electrospun nanofibers were made with varying concentration of Aloe Vera (1%, 2%, 3%, 4%) with constant concentration of ZnO (0.5%) and with varying concentration of ZnO nanoparticles (1%, 2%, 3%, 4%) with constant concentration of Aloe Vera (0.5%). To check the morphology and composition, all prepared nanofibers were subjected to different characterization techniques such as SEM, EDX and FTIR. Also, their antimicrobial activity was checked both with qualitative and quantitative approach against Gram-positive (Staphylococcus aureus) bacteria and Gram-negative (Escherichia coli) bacteria. The results suggested that increasing ZnO concentration kills and inhibits bacterial growth more proficiently as compared to increasing Aloe vera concentration in electrospun nanofibers, the highest antimicrobial was found with 4% ZnO killing almost 100% of Gram-positive (Staphylococcus aureus) bacteria and 99.2% of Gram-negative (Escherichia coli) bacteria. These fabricated nanofibers have potential application in facemasks and would help control the spread of many diseases.

A.7 Application of Natural Polymers for the Design of the New B-Carotene Complexes

Antanas Straksys, Ruta Gruskiene, Jolanta Sereikaite

β-Carotene (CAR) is a natural pigment composed of a polyene system with eleven conjugated double bonds and a β-ring at each end of the chain. It has various biological activities that contribute to human health. However, the application of β-carotene is limited due to its low water solubility and chemical instability. Those drawbacks can be overcome by designing new delivery systems for β-carotene. The study is aimed to develop the new β-carotene complexes using xylan (XYL) and chitosan and fucoidan. The materials used for encapsulation have beneficial effects for human health, e.g. antimicrobial and antioxidant activities or serve as a prebiotic fiber [1-3].

The encapsulation of β-carotene was performed by a layer-by-layer method and subsequent freeze-drying. First, the complex of β-carotene and xylan was prepared using three different CAR/XYL mass ratios from 1/1 to 1/3. Further, the complexes were coated with chitosan and finally by fucoidan. The interaction of components was shown by Raman and FT-IR spectroscopies. The size and zeta-potential of particles were determined by the DLS method. The morphology of the complexes was analysed by SEM. The antioxidant activity was measured using DPPH and FRAP assays and expressed in Trolox units (mgTE/g).

The prepared new β-carotene complexes have the potential for applications in food and cosmetics.

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References

[1] Zeybek, N. et al., Carbohydrate Polymers 236 (2020).
[2] Inanli, A.G. et al., Trends in Food Science & Technology 97 (2020).
[3] Luthuli, S. et al., Marine Drugs 17(2019).

A.8 Using Iron Catalyst to Prepare Biocompatible Oligomers

Cordula Hege[1], Amy Stimpson[1], Chris Fox[2], Derek Irvine[1]

[1] *University of Nottingham*
[2] *IDRI*

Oligomers can be useful for medical application like vaccine adjuvants or also for printing. Oligomers are especially favourable for printing formulations. As one gets materials in the needed viscosity range. Methacrylic polymers are known to be widely tolerated in vivo, so they are widely used in biology and medicine. So, to prepare the oligomers mainly methacrylic monomers were used.
Catalysed-chain transfer polymerisation (CCTP) an effective method to prepare oligomers. However, mainly cobalt catalysts are used for that. As cobalt is toxic, this disadvantageous for medical applications. Iron is abundant in nature, like that it is more sustainable and has a higher biocompatibility. The catalyst was prepared *in situ.* For that iron bromide and dimethyl glyoxime or diphenyl glyoxime were added as ligands. Different catalyst concentrations were used. The reactions were made in bulk and with toluene as solvent.
The level of control is influenced by the reaction conditions, as well as the used monomers. One needs a higher amount of iron to control the reaction, than one would need for cobalt-catalysed reactions.
Still, iron catalysts were found to be a possible replacement for cobalt catalysts to perform CCTP. They allow to prepare reproducible, biocompatible oligomers. Further work will be done to optimise the conditions.

A.9 Poly(2-isopropenyl-2-oxazoline) as Drug Carrier for Controlled Drug Release

Monika Majerčíková[1], Monika Faktorová[1], Ema Paulovičová[2], Ján Markus[3], Silvia Letasiová[3], Juraj Kronek[1], Zuzana Kroneková[1]

[1] Department for Biomaterials Research, Polymer Institute, Slovak Academy of Sciences, Slovakia
[2] Department of Immunochemistry of Glycoconjugates, Immunol & Cell Culture Labs, Institute of Chemistry, Center for Glycomics, Slovak Academy of Sciences, Slovakia
[3] MatTek In Vitro Life Science Laboratories, s. r. o., Slovakia

Research in the field of 2-oxazolines has focused on biomedical applications. They represent biocompatible polymers capable to incorporate hydrophobic drugs, such as anti-inflammatory and chemotherapeutic drugs. Poly(2-isopropenyl-2-oxazoline) (PIPOx) has been prepared by the atom transfer radical polymerization (ATRP) through vinyl group of bifunctional monomer. Drugs can be attached to the side chain of PIPOx by the addition reaction with the 2-oxazoline ring. The cytotoxicity of PIPOx is dependent on the molar mass, concentration and cell type. The immunomodulatory properties of PIPOx were shown on mouse spleen cells.

This work focuses on the modification of PIPOx with molar mass in the range of 3000-44000 $g.mol^{-1}$ with Ibuprofen in the range of 1-10% as verified by FTIR. The drug release from the conjugate was monitored by HPLC for 60 days at different pH at 37 °C. Non-toxic and anti-inflammatory properties of PIPOx and conjugates were proved *in vitro* by both, MTT and ELISA assays using 3D reconstructed human epidermis model, EpiDerm™. We demonstrated that we can control the molar ratio of a conjugated drug and the rate of release is dependent on pH.

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A.10 3D-Bioprinted Models: A Potential Tool for Estimating Safety of Plastic Food Packaging

Mariangela Rea[1], Giorgia Pagnotta[1], Luana Di Lisa[1], Gianandrea Pasquinelli[2], Sabrina Valente[2], Maria Letizia Focarete[1]

[1] Department of Chemistry "G. Ciamician", University of Bologna, Bologna, Italy
[2] Clinical Pathology Lab, Department of Experimental, Diagnostic and Specialty Medicine, DIMES, University of Bologna, Bologna, Italy

Nowadays, it is impossible to think of foods that are sold in an unpackaged state, indeed, food packaging is pervasive and essential. On the other hand, attention must be paid to the impact that the use of Food Contact Materials can have on people health. More specifically, toxic chemicals employed in food packaging can migrate into foodstuffs and thus, be ingested by humans[1]. Hence, there is the need to assess the safety of these substances. Actual methods employed for the evaluation of the safety of packaging include 2D-*in vitro* assays and animal testing, that are both characterized by some limitations, including poor correlation with the *in vivo* human situation[2].
The need to improve models to detect toxicity can be accomplished by the realization of 3D-cell culture and innovative organotypic *in vitro* models. Due to the central role of the liver in the biotransformation of foreign compounds, such as the chemicals contained in food packaging materials, the hepatotoxicity assessment is essential. 3D-Bioprinting technique, which involves the use of bioinks, i.e. the combination of cells and hydrogels, can be exploited for developing hepatic constructs, characterized by a high liver-specific function of the tissue. In this work, GelMa hydrogel is synthesized and characterized from a rheological point of view, for the realization of liver models. This material can be photo-crosslinked, to obtain the desired mechanical properties, matching those of natural human liver, and on the other hand it ensures cellular adhesion. Once the bioink formulation is optimized, the bioprinting process is carried out and cell viability and proliferation is evaluated. The obtained 3D liver model might be used, in combination with a microfluidic device, to evaluate the toxicity levels of plastic food packaging additives.

A.11 Novel PHBV/PVA-Based Semi-IPN Hydrogels with Conductive Nanoparticles: Synthesis and Physicochemical Characterisation

José Luis Aparicio-Collado[1], Juan José Novoa[2], José Molina-Mateo[1], Constantino Torregrosa Cabanilles[1], Ángel Serrano-Aroca[3], Roser Sabater i Serra[1, 4]

[1] Centre for Biomaterials and Tissue Engineering, Universitat Politècnica de València, 46022 València, Spain
[2] University of Applied Sciences Technikum Wien, Vienna, Austria
[3] Biomaterials and Bioengineering Lab, Centro de Investigación Traslacional San Alberto Magno, Universidad Católica de Valencia San Vicente Mártir, 46001 Valencia, Spain
[4] CIBER-BBN, Biomedical Research Networking Centre in Bioengineering, Biomaterials and Nanomedicine, València, Spain

Polyhydroxybutyrate-co-hydroxyvalerate (PHBV) is a promising material that has shown great potential in tissue engineering due to its biodegradability, low cytotoxicity, bioactivity and piezoelectric properties. However, it presents some drawbacks, such as considerable hydrophobicity and poor thermal stability. These handicaps can be overcome by blending with flexible and thermally stable polymers such as poly (vinyl alcohol) (PVA), a hydrophilic and biodegradable synthetic polymer. In addition, conducting polymers, such as polypyrrole (PPy), have emerged as a research source in the biomedical field due to their ability to enhance cell response. Therefore, PHBV/PVA semi-interpenetrating networks (semi-IPN) with electroactive properties can be an interesting approach in tissue engineering research.

Novel PHBV/PVA semi-IPN (PHBV/PVA 30/70 ratio) with PPy conductive nanoparticles (up to 15%) was prepared with the aim to generate electroactive hybrid hydrophilic networks with potential applications in tissue engineering. Physicochemical properties were analysed by Fourier transform infrared, differential scanning calorimetry, thermogravimetric analysis, contact angle, swelling and dielectric spectroscopy. Structural analysis was carried out by electron microscopy.

The conductivity of these advanced networks rose significantly at higher PPy nanoparticles content. The semi-IPN nanocomposites present good miscibility and compatibility between all the constituents, with no phase separation and strong interactions between phases. Incorporating PPy nanoparticles significantly reduced the hydrogel swelling, even at low concentrations, indicating molecular interactions between the PPy nanoparticles and the hydrogel matrix. PPy nanoparticles also act as nucleating agents, increasing crystallisation. Moreover, the network showed better thermal stability than the neat polymers, remaining in the tertiary system. These features make this hybrid semi-IPN a promising biodegradable biomaterial for tissue engineering applications.

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A.12 Bio-Nanocomposite Hydrogels Based on Zinc Alginate/Graphene Oxide for Tissue Engineering

Roser Sabater i Serra[1, 2], José Luis Aparicio-Collado[1], José Molina-Mateo[1], Constantino Torregrosa Cabanilles[1], José María Meseguer Dueñas[1, 2], Ángel Serrano-Aroca[3]

[1] Centre for Biomaterials and Tissue Engineering, Universitat Politècnica de València, 46022 València, Spain
[2] CIBER-BBN, Biomedical Research Networking Centre in Bioengineering, Biomaterials and Nanomedicine, València, Spain
[3] Biomaterials and Bioengineering Lab, Centro de Investigación Traslacional San Alberto Magno, Universidad Católica de Valencia San Vicente Mártir, 46001 Valencia, Spain

Bio-nanocomposites hydrogels based on sodium alginate (SA) as polymer matrix and graphene oxide (GO) nanosheets with zinc as the crosslinking agent were synthesised with the aim of incorporating their bioactive and biocidal effects as intrinsic characteristics of the composite for potential application in the field of biomedicine, particularly skeletal-muscle and bone tissue engineering. The zinc concentration was restricted to the minimum amount required to achieve alginate gelation while providing bioactivity to the hydrogel. Although low (3% w/w), the quantity of GO nanosheet was enough to strengthen the alginate matrix and provide the nanocomposite hydrogel with bioactive and biocidal properties.

The swelling, thermal behaviour/degradation and dielectric properties of zinc-alginate/GO nanocomposites were determined and their properties compared with those of sodium alginate/GO and zinc-alginate to obtain detailed information on its structure. Also, molecular interactions and morphology aspects of the synthesised nanocomposites, were analysed by FT-infrared spectroscopy and transmission electron microscopy, respectively.

The dispersed GO nanosheets were successfully incorporated into the alginate matrix in the form of a complex nano-network involving different interactions: bonds between alginate chains induced by Zn ions, interactions between GO nanosheets through Zn ions and hydrogen bonds between alginate chains and GO nanosheets. The glass transition temperature shifted to a higher temperature due to the reduced mobility induced by additional crosslinking bonds after incorporating the GO nanosheets and Zn into the polymer matrix. The composite's structural organisation showed enhanced thermal stability. Dielectric spectroscopy revealed that charge carrier mobility was hampered by the compact structure of the nanonetwork, which reduced conductivity and required higher activation energy to trigger the process.

Our study indicates that stable and highly interconnected nanocomposite networks can be obtained from GO nanosheets dispersed in SA matrices through interactions with low amounts of zinc.

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A.13 Synthesis, Optimization, Characterization, and Interaction Studies of Plant-Oil Based Epoxidized Monoesters for Polar Polymeric Materials?

Irfan Shahzad

Hochschule Merseburg

In the present work, epoxidized monoester of glycerol formal from soybean oil (Bio-oil 1) was investigated as a plasticizer in acrylonitrile—butadiene rubber (NBR). The migration of the plasticizer from plasticized NBR sample to unplasticized NBR sample during short-term thermal aging was investigated using infrared spectroscopy (IR). [1] To further reduce the migration, Bio-oil 1 was synthetically modified to carbonated monoester of glycerol formal in the presence of tetrabutylammonium bromide catalyst (TBAB) and constant supply of CO_2 gas, so that the polarity of the plasticizer is enhanced, and its migration is curtailed. Corresponding migration analysis demonstrated reduction in migration with this modification step. [2] Although this cycloaddition reaction needed optimization, as tedious reaction time of 70 hours under atmospheric pressure conditions was required due to the steric hindrance offered by the internal epoxy groups and mass transfer limitations due to the two phases (gas-liquid) involved. Different approaches were evaluated to optimize reaction output and the time required to complete the cycloaddition of CO_2 in Bio-oil 1. Deep eutectic solvents (DES) along with the conventionally used TBAB catalyst demonstrated best results under high-pressure conditions of 40 bars while the catalyst system comprising Potassium iodide (KI) and 18-crown-6 ether as phase transfer catalysts provided satisfactory conversion results. [3]

1. Shahzad et al. “In situ migration analysis and diffusion coefficient determination of bio-based plasticizer from NBR using FTIR-ATR and estimation of migrated plasticizer contents by TGA analysis” Macromolecular symposia 2019
2. Shahzad et. Al “Synthetical modification of plant oil-based plasticizer with CO2 leads to reduced migration from NBR rubber” Journal of Applied polymer science 2021
3. Shahzad et. Al “CO2 cycloaddition to plant oil-based epoxidized monoester: Optimization and catalyst screening” Macromolecular symposia 2022 (under review)

A.14 Study of new poly(lactic acid) block copolymers with poly(hexylene succinate) as appropriate microparticles for long-acting injectables of risperidone drug.

Iouliana Chrysafi[1], Stavroula Nanaki[2], Pavlidou Eleni[3], Dimitrios Bikiaris[2]

[1] Laboratory of Advanced Materials and Devices, Department of Physics, Faculty of Sciences, Aristotle Univer-sity of Thessaloniki, Thessaloniki, GR-54124, Macedonia, Greece; iochrysa@physics.auth.gr
[2] Laboratory of Polymers Chemistry and Technology, Department of Chemistry, Faculty of Sciences, Aristotle University of Thessaloniki, GR-54124, Macedonia, Greece
[3] Laboratory of Advanced Materials and Devices, Department of Physics, Faculty of Sciences, Aristotle University of Thessaloniki, Thessaloniki, GR-54124, Macedonia, Greece

In the present work, risperidone microparticles using new poly(lactic acid)-poly(hexylene succinate) (PLA-b-PHSu) block copolymers in different ratios, 95/05, 90/10 and 80/20 w/w were synthesized and examined for long-acting injectable formulations. The spray-drying method was used in order to obtain microparticles and to encapsulate risperidone. Neat risperidone and the prepared microparticles were studied by Scanning Electron Microscopy, X-ray Diffraction (XRD), and Differential Scanning Calorimetry (DSC). Among the results, the spherical shape of the microparticles was confirmed, while from XRD and DSC it was found that risperidone is encapsulated in microparticles in amorphous form. The drug loading and the entrapment efficiency of risperidone were studied as well as the in-vitro drug release from the prepared microparticles. The drug loading and the entrapment efficiency of risperidone as well as the in-vitro drug release from the prepared microparticles were studied. It came up that as the content of PHSu increased, a higher percentage of risperidone was released, with PLA-b-PHSu 80/20 w/w succeeding to release 100% of risperidone after 12 days. Moreover, as the content of PHSu in the copolymers increased, the drug loading and the entrapment efficiency decreased.

A.15 Surrogate-Imprinted Polymers for the Detection of Viruses

Beatriz María Fresco-Cala[1, 2], Ana Gálvez-Vergara[2], Daniel Baumgarten[2], Boris Mizaikoff[2]

[1] Departamento de Química Analítica, Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie, E-14071 Córdoba, España
[2] Institute of Analytical and Bioanalytical Chemistry, Ulm University, 89081, Ulm, Germany.

Conventional methods for the selective recognition of specific viruses remain complex to date. These methods have major drawbacks including long analysis times, low sensitivity, high cost, and the need for trained personnel. To overcome these problems, imprinted polymer-based sorbent materials with specific virus recognition properties (VIPs) have been recently employed. The outstanding material properties of imprinted polymers (i.e., tailorability, robustness, versatility, etc.) enable applications even in harsh conditions, in biotechnological scenarios, and in medical/clinical scenarios. However, the main challenge of imprinting entire viruses primarily originates from the need to execute the polymerization at conditions close to their natural environment avoiding the destruction of the virus, the infectious nature of the virus template, and their size and fragility. Our group is focused on the preparation of synthetic materials which selectively bind to specific virus types without the need of an infectious template. For that, we used the so-called surrogate templates mimicking real viruses during the polymerization/imprinting step. Thereby, the virus was replaced by a robust and non-infectious surrogate template, while after the templating procedure the real/infectious virus may be bound. As it can be seen in Figure 1, the surrogate template may either be a fragment of the initial target microorganism (e.g., protein, peptide sequence, etc.), or a 'dummy particle', which emulates the microorganism in size, shape, and surface functionality.

A.16 Magnetic Solids Based on Carbon Nanotubes Prepared from Pickering Emulsions

Beatriz María Fresco-Cala[1], Ana Gálvez-Vergara[2], Soledad Cárdenas[2]

[1] Institute of Analytical and Bioanalytical Chemistry. Ulm University, 89081, Ulm, Germany.
[2] Departamento de Química Analítica, Instituto Universitario de Investigación en Química Fina y Nanoquímica IUNAN, Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie, E-14071 Córdoba, España.

Two types of magnetic solids based mainly on carbon nanotubes, such as monolithic solids and spherical microparticles, have been developed by photopolymerization emulsion templating. Water-in-oil (W/O) and oil-in-water (O/W) Pickering emulsions were tested using polystyrene-modified magnetic nanoparticles as stabilizers. It should be highlighted that employing polystyrene-modified magnetic nanoparticles as stabilizers in water/chloroform mixtures, stable W/O and O/W Pickering emulsions can be achieved being possible to continuously switch from one to another. In addition to this, magnetic nanoparticles provided magnetic character to the obtained solids in the presence of an external magnetic field fulfilling thus a double mission. Moreover, the incorporation of carbon nanotubes was equally significant, because without the presence of them the polymerization reaction was not successfully completed. The two types of Pickering emulsions led to structurally different final solids despite being formed by the same components. On one hand, W/O Pickering emulsions produced monolithic solids. On the other hand, O/W Pickering emulsions formed spherical magnetic microparticles. The morphology of both magnetic solids containing carbon nanotubes was characterized by scanning electron microscopy (SEM). Finally, a comparison between the extraction efficiency of magnetic monolithic solids and microparticles was carried out using polycyclic aromatic hydrocarbons as target analytes. The best results were obtained with the magnetic microparticles obtaining limits of detection (LODs) between 1 and 4 $\mu g \cdot L^{-1}$ and excellent recovery values (99-108 %) in chamomile tea samples.

A.17 Innovative Biopolymers for Inorganic and Organic Pollutants Removal in Water Treatment

Giulia Costamagna, Claudio Cecone, Marco Ginepro, Francesco Trotta

Department of Chemistry, University of Turin

Human activities, such as intensive cultivation and industrial activities inevitably lead to water and soil pollution. Aquatic environment contamination due to heavy metals or pesticides and their potential toxicity/bioaccumulation is a serious concern for humans and ecosystem. Usually, metal and herbicides contamination derive from the run-off of agricultural lands, contaminated soils and mineral deposits. Other metal contamination sources could be industries, agricultural activities. Heavy metal such as Cr (VI) and As(III) and As(V) are quite largely diffuse and not so easily removing. For example, Cr (VI) contamination derives from galvanic chromium plating processes, textile and iron&steel industry. Arsenic contamination, instead, has a natural source: this is a big issue that involves about 140 million people in over 50 countries worldwide. In agricultural field, Glyphosate is one of the most common organic herbicides that is the active ingredient of the Roundup Monsanto commercial product. In 2015 International Agency for Research on Cancer classified Glyphosate as "probable carcinogenic to humans". The Huge use of this herbicide have contaminated soils and water. To try to solve these big issues, the research is focused on innovative maltodextrin-based biopolymers for the removal of different types of pollutants. Maltodextrins are a family of oligosaccharides achieved from starch (potatoes, corn, peas starch). Specific cross-linking agents use allows to get a hyper-cross-linked biopolymer having an eco-compatible and biocompatible polymeric structure. Laboratory tests were performed to assess the capacity and potential retention of heavy metals and organic compounds and anions. Several absorption tests were performed: the results achieved were up to 80-99%. These new materials are innovative, biodegradable and eco-compatible that have shown noticeable potential for future application in water treatment.

A.18 Rod-Coil Block Copolymer:Fullerene Blend Water-Processable Nanoparticles: How Molecular Structure Addresses Morphology and Efficiency in NP-OPVs

Stefania Zappia[1], Silvia Destri[1], Anna Maria Ferretti[2], Marianna Diterlizzi[1], Guido Scavia[1], Umberto Giovanella[1], William Porzio[1], Tersilla Virgili[3], Lucia Ganzer[3], Varun Vohra[4]

[1] Istituto di Scienze e Tecnologie Chimiche "Giulio Natta" (SCITEC), via A. Corti 12, 20133 Milano, Italy
[2] Istituto di Scienze e Tecnologie Chimiche "Giulio Natta" (SCITEC), via G. Fantoli 16/15, 20138 Milano, Italy
[3] Istituto di Fotonica e Nanotecnologie (IFN-CNR), P.zza Leonardo Da vinci 32, 20132 Milano, Italy
[4] University of Electro-Communications 1-5-1 Chofugaoka, Chofu, Tokyo 182-858, Japan

Water-processable nanoparticles (WPNPs) of semiconducting materials recently emerged as a new tool for sustainable optoelectronic applications due to their simple fabrication and tunable properties. The WPNP-based approach could be appealing to control active layer morphology in optoelectronic devices, in particular organic photovoltaics (OPVs). Moreover, WPNPs allow to reduce the use of chlorinated solvents in the device fabrication and to process organic semiconducting materials into aqueous medium.[1] Here we will present a series of four amphiphilic low band gap (LBG) rod-coil block copolymers (BCPs), constituted by a LBG polymer, PCPDTBT, as the electron donor material, and differing for the poly-4-vinylpyridine (P4VP)-based flexible blocks with various length and chemical composition.[2] The BCPs were used for the sustainable fabrication of NP-OPV devices , in blend with a fullerene acceptor material. The goal of this work is the study of the relatioship between the morphology of the nanodomains of the two active materials and the hydrophilic coil molecular structures. We correlated the design of the materials with the device performances, exploiting TEM and EFTEM microscopy on WPNPs, with the contribution of AFM and spectroscopic techniques. We investigated the influence of the chemical design over material properties.[3,4,5] In particular, BCP5 displayed a coil block of five repeating units of 4-vinilpyridine (4VP). It led to working devices with a high short-circuit current density and an efficiency comparable to the convetional ones (Jsc=11.5 mA·cm^{-2}, PCE 2.5%).[6] Moreover, we will report on the case of a more crystalline LBG investigating an alternative morphology to the core-shell one and how this morphology influence the performance in the devices.

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References
[1] *ACS Nano* **2021**, *15*, 3927-3959.
[2] *Polymer* **2015**, *80*, 245-258.
[3] *Polymer* **2019**, *174*, 61-69.
[4] *Phys. Chem. Chem. Phys.* **2020**, *22*, 26583-26591.
[5] *Nanomaterials* **2022**, *12*, 84.
[6] *Adv. Sustain. Syst*. **2018**, *2*, 1700155.

A.19 Innovative Edible Biomaterials with Natural Essential Oils for Powdered Supplements: New Strategies to Improve Food Quality and Reduce Waste from Disposable Packaging

Roxana Gheorghita (Puscaselu)[1], Gheorghe Gutt[2]

[1] *Faculty of Medicine and Biological Sciences, Stefan cel Mare University of Suceava, Romania*
[2] *Faculty of Food Engineering, Stefan cel Mare University of Suceava, Romania*

Lately, the amount of waste from multi-layer plastic packaging has far exceeded the expectations of statisticians. Unfortunately, this problem results in intense pollution of the environment, but also the continuous use of non-renewable resources. Government organizations and NGOs around the world are trying to warn the population of the risks, but also to support the scientific world to identify strategies for developing new materials that can be used to package products and strengthen a green economy concept/system. Food supplements include a wide range of products, from natural powders to drugs or active substances, with role in the well-being of the population. Unfortunately, they are usually packaged in conventional materials, with successive layers of polyethylene or polypropylene, metal, glue, paints, etc. The present study focused of the development of biopolymers packaging materials, from agar and sodium alginate, plasticized with glycerol. To improve the packaged products properties, natural essential oils have been incorporated, such as lemon, grapefruit, oranges, cinnamon, cloves, in proportion of 0.5 and 1% w/v. The addition of essential oil favored the development of more homogeneous, thinner, finer films, with very good optical properties (transmittance, opacity, color), and mechanical properties (tensile strength and elongation) comparable to those of classic packaging. The microbiological safety assessment aimed at identification of the incidence and proliferation of the most common microorganisms found in the food industry: total number of germs, coliforms, enterobacteria, *E. coli*, *S. aureus*, *L. monocytogenes*, yeasts or molds. According to the data obtained, these edible materials, obtained entirely from natural substances, accepted for consumption in *quantum statis* doses represent an important pawn in the development of the concept of green economy. The obtaining technology is easy to apply at industrial level, without the need for special and expensive equipment, and the raw material can be obtained from agro-industrial waste or seaweed.

A.20 Vanillin Acrylate-Based Antimicrobial Shape Memory Polymers

Auksė Navaruckienė[1], Justinas Jaras[1], Danguole Bridziuviene[2], Vita Raudoniene[2], Egidija Rainosalo[3], Jolita Ostrauskaitė[1]

[1] Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilenu Rd. 19, LT-50254 Kaunas, Lithuania
[2] Biodeterioration Research Laboratory, Nature Research Center, Akademijos Str. 2, LT-08412 Vilnius, Lithuania
[3] Centria University of Applied Sciences, Talonpojankatu 2, FI-67100 Kokkola, Finland

Bio-based materials increase the interest of the scientific community as an ecological and economical alternative to petrochemical-based materials [1]. Lignin is the main source of plant-derived vanillin, which is considered as natural bio-based vanillin [2]. The aim of this study was to develop novel bio-based antimicrobial shape memory polymers using commercial vanillin derivatives.

In this study, three commercial vanillin acrylates, vanillin diacrylate (VD), vanillin dimethacrylate (VDM), and vanillin hydroxypropane dimethacrylate (VHDM), were tested in photopolymerization with 1,3-benzenedithiol (BDT). Ethyl(2,4,6-trimethylbenzoyl)phenylphosphinate (TPOL) was selected as the photoinitiator. By varying the ratio of acrylate to thiol (from 1:1 to 1:0.5), the rate of thiol-acrylate photopolymerization and free radical photopolymerization was tuned and polymers with different mechanical and thermal properties were obtained.

Photorheometry was used to monitor the evaluation of thiol-acrylate photopolymerization and the free-radical photocross-linking process. The highest final rigidity was demonstrated by dual cured polymers with 1 mol of vanillin derivative (VD, VDM or VHDM) and 0.5 mol of thiol (BDT) in comparison to polymers with 1 mol of thiol (BDT). Another advantage of the dominant radical homopolymerization of acrylates was the increase of the reaction speed, as resins with 0.5 mol of thiol polymerized faster. However, polymers with 0.5 mol of thiol shrunk more than polymers with 1 mol of thiol during photopolymerization.

Differential scanning calorimetry was used to study the thermal properties of vanillin acrylate-based photocross-linked polymers. The glass transition temperature of the polymers synthesized with 1 mol of BDT (-3–17 °C) was significantly lower than that of the polymers synthesized with 0.5 mol of BDT (40–46 °C). The specimens of all synthesized vanillin-based polymers were able to obtain new shape while heated above their glass transition temperature, maintain temporary shape after cooling below their glass transition temperature, and return to their primary shape after heating above their glass transition temperature. These properties determined them as shape memory polymers.

All vanillin acrylate-based polymer films showed significant antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*, which was similar to that of the chitosan film. Vanillin-based polymer films also showed antifungal activity against *Aspergillus flavus* and *Aspergillus niger.*

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References

[1] Nasseri R., Deutschman C. P., Han L., Pope M. A., Tam K. C.: Cellulose nanocrystals in smart and stimuli-responsive materials: a review. *Materials Today Advances*, **2020**, *5*, 100055.
[2] Ciriminna R., Fidalgo A., Meneguzz, F., Parrino F., Ilharco L. M., Pagliaro, M.: Vanillin: the case for greener production driven by sustainability megatrend. *ChemistryOpen*, **2019**, *8*, 660–667.

A.21 The Adsorption of Methylene Blue and Rhodamine B by Pullulan-graft Superabsorbent Hydrogels

Buse Sonmez, Ayse Nur Celikkol

Hisar School

Pullulan is produced by a yeast-like fungus Aureobasidium pullulans and it is non-toxic, non- mutagenic, non-hygroscopic, edible, biocompatible and biodegradable. Pullulan is soluble in water, which makes it inapplicable for wastewater treatments [1]. Hydrogels have porous structures which facilitate them to adsorb various water contaminants like dyes and metal ions from wastewater. Grafting various hydrophilic moieties to the base unit of the hydrogel augments the sorption ability of the hydrogel [2]. Textile dyes, their removal from aqueous solutions and the disposal of industrial wastes that contain various dyes have gained wide attention in wastewater treatment [3]. Recently, designing and developing new polymeric adsorption mechanisms which yield efficient and economically friendly ways to treat aqueous pollutants such as dyes has been on the research focus [1]. Industries such as textiles, dyeing, printing, food colouring, plastics, cosmetics, papermaking, and pharmaceuticals use dyes extensively [4]. The discharge of dyes from the environment needs urgent attention for both toxicological and esthetical reasons [5]. The presence of dyes in wastewater can cause health problems such as skin irritation, allergic dermatitis. Additionally, most of the dyes have toxic, carcinogenic and mutagenic effects on aquatic organisms and humans [6,7]. This study aims to synthesize two pullulan based hydrogels by solution polymerization which adsorb methylene blue and rhodamine B, two cationic dyes, from wastewater and desorb the dyes effectively. The hydrogels' swelling capacities, dye adsorption-desorption properties and their reusabilities were investigated throughout this study and the data analysis shows promising results for the removal of methylene blue from wastewater by the synthesized hydrogels. The effect of adsorbent dosage, initial dye concentration and pH were also investigated on the adsorption abilities of the hydrogels. Fourier Transform Infrared Spectroscopy (FTIR), Thermal Gravimetric Analysis (TGA), and Scanning Electron Microscopy (SEM) were used to determine the characterization of the hydrogels. Ultraviolet-Visible Spectroscopy was used to investigate the dye adsorption-desorption capacities of the hydrogels.

References

[1] Sugumaran, K. R.; Ponnusami, V. *Carbohydrate Polymers* **2017**, *173*, 573-591.
[2] Sinha, V.; Chakma, S. *Journal of Environmental Chemical Engineering* **2019**, *7(5).*
[3] Saber-Samandari, S.; Gulcan, H. O.; Gazi, M. *Water, Air and Soil Pollution* **2014**, *225(11).*
[4] Wang, L.; Zhang J.; Wang, A. *Desalination* **2011**, *266(1-3),* 33-39.
[5] Métivier-Pignon, H.; Faur-Brasquet, C.; Le Cloirec, P. *Separation and Purification Technology* **2003**, *31(1)*, 3-11.
[6] Chen, K-C.; Wu, J-Y.; Huang, C-C.; Liang, Y-M.; Hwang, S-C. J. *Journal of Biotechnology 101* **2003**, 241-252.
[7] Islam, A.; Ali, I.; Karim, S. M. A.; Firoz, S. H.; Chowdhury, A-N.; Morton, D. W.; Angove, M. J. *Journal of Water Process Engineering* **2019**, *32*, 100911.

A.22 Study of Degradation and Chemical Recycling by Glycolysis of Urban and Marine PET Waste.

Eider Mendiburu-Valor, Arantxa Eceiza, Cristina Peña Rodriguez

UPV/EHU

The poly (ethylene terephthalate) (PET) residues are one of the most abundant plastics founded in the sea due to the high production, becoming a big environmental problem. The degradation of two different PET bottle samples coming from urban waste (PET-uw) and marine waste (PET-mw) has been studied, comparing their properties with post condensed PET, raw material for bottle fabrication (PET-pc). Through the study by FTIR and DSC it has been confirmed that both the PET-mw and PET-uw residues were degraded, significant changes have been observed in the crystallinity and polymer chain structure. In addition, the water contact angle measurements (WCA) have been confirmed that marine samples have become more hydrophilic, decreasing considerably their contact angle due to the generation of carboxylic and hydroxyl groups during the degradation process caused by hydrolysis. The melt flow index (MFI) values have also shown a decrease in the viscosity of two PET residues. Due the viscosity is a critical parameter for the mechanical recycling of PET, a recycling alternative has been evaluated for both waste: chemical recycling through glycolysis to obtain BHET. In order to optimize the PET recycling process, the kinetics of the depolymerization reaction have been analyzed by analyzing the results in short periods of time from 10 to 180 minutes. Results indicates that the depolymerization of both residues can be carried out at 220 °C for 30 min, obtaining yields between 55.3 and 67.8 %. For both cases almost pure BHET monomer has been obtained: 96.5 and 96.7 % for PET-mw and PET-uw respectively, higher than those obtained for PET-pc. Obtained results indicate that the initial degradation of PET wastes increases the BHET monomer content in the glycolyzed PET sample. The BHET recycled by the glycolysis of PET marine residues can be used for the synthesis of polymers as polyurethanes.

A.23 Elucidating Enzymes Selectivity and Thermostability in Short-Esters and Polyesters Synthesis

Filippo Fabbri[1], Federico Adolfo Bertolini[2], Gerog M. Guebitz[1, 2], Alessandro Pellis[2, 3]

[1] Austrian Centre of Industrial Biotechnology, Konrad Lorenz Strasse 20, 3430 Tulln an der Donau, Austria
[2] Department of Agrobiotechnology, Institute of Environmental Biotechnology, University of Natural Resources and Life Sciences, Vienna, Konrad Lorenz Strasse 20, 3430 Tulln an der Donau, Austria
[3] Department of Chemistry and Industrial Chemistry, University of Genova, via Dodecaneso 31, 16146 Genova, Italy

Various bio-based aliphatic building blocks, such as adipic acid, itaconic acid, sebacic acid and 1,4-butandiol were investigated for the biocatalyzed synthesis of polyesters [1]. Different hydrolases, namely *Candida antarctica* lipase B (CaLB), *Humicola insolens* cutinase (HiC), and the in-house produced *Thermobifida cellulosilytica* cutinase 1 (Thc_Cut1) [2,3] were successfully adsorbed onto polypropylene beads [4] and evaluated using a full-factorial design of experiments (DoE) for the synthesis of short-esters. The activity of the biocatalysts in transesterification was screened in a broad range of temperatures (50-90 °C) considering different carbon chain lengths for alcohols and acids (C_4, C_8 and C_{12}). The DoE allowed to obtain a 4D contour response, which indicated CaLB, HiC and Thc_Cut1 temperature optima at 85 °C, 70 °C, and 50 °C, respectively. Furthermore, CaLB and HiC exhibited their selectivity towards long-chain alcohols and acids as substrate in contrast to Thc_Cut1, which was more active on short-chain monomers. Finally, the obtained model was verified by biocatalyzed synthesis of polyesters through polycondensation reactions, using the previously investigated immobilized hydrolytic enzymes. CaLB and HiC showed the best synthetic activity when used with dimethyl sebacate (DMSe) while a decrease in polymers M_w was observed with dimethyl adipate (DMA) and dimethyl itaconate (DMI). On the other hand, Thc_Cut1 led to polyesters with lower molecular masses, despite the high conversion rate achieved with DMA. These results fully confirmed our model for all of the three enzymes.

References:
[1] Pellis, A., Corici, L., Sinigoi, L., D'Amelio, N., Fattor, D., Ferrario, V., ... & Gardossi, L. (2015). Towards feasible and scalable solvent-free enzymatic polycondensations: Integrating robust biocatalysts with thin film reactions. *Green Chemistry*, *17*(3), 1756-1766.
[2] Herrero Acero, E., Ribitsch, D., Steinkellner, G., Gruber, K., Greimel, K., Eiteljoerg, I., ... & Guebitz, G. (2011). Enzymatic surface hydrolysis of PET: effect of structural diversity on kinetic properties of cutinases from Thermobifida. *Macromolecules*, *44*(12), 4632-4640.
[3] Pellis, A., Ferrario, V., Cespugli, M., Corici, L., Guarneri, A., Zartl, B., ... & Gardossi, L. (2017). Fully renewable polyesters via polycondensation catalyzed by Thermobifida cellulosilytica cutinase 1: an integrated approach. *Green Chemistry*, *19*(2), 490-502.

[4] Weinberger, S., Pellis, A., Comerford, J. W., Farmer, T. J., & Guebitz, G. M. (2018). Efficient physisorption of Candida Antarctica Lipase B on Polypropylene Beads and application for polyester synthesis. *Catalysts*, *8*(9), 369.

A.24 Plastic and Aluminium Recycling from Multilayer Packaging Waste Using Biogenic Sulfuric Acid

Klemens Kremser[1], Patrick Gerl[1], Alessandro Pellis[1, 2], Georg M Guebitz[1], Felice Quartinello[3]

[1] University of Natural Resources and Life Science Vienna BOKU, Dept. of Agrobiotechnology, IFA-Tulln, Inst. of Environmental Biotechnology
[2] Department of Chemistry and Industrial Chemistry, University of Genova, via Dodecaneso 31, 16146 Genova, Italy
[3] University of Natural Resources and Life Science, Vienna, Institute of Environmental Biotechnology, Department of Agrobiotechnology Konrad-Lorenz Starße 20, A-3430 Tulln an der Donau

Multilayer packaging provides favourable properties on the one hand but accounts for a huge waste generation on the other. Due to their complex structure, comprising different layers and materials like polymers, aluminium, paperboard and adhesives, full recycling of all materials is challenging. Existing recycling technologies are capable of removing paperboard, but plastic-aluminium fractions go to incineration for energy recovery most of the times. Bacterial production of sulfuric acid was investigated in this study to provide an environmentally friendly and effective way to separate aluminium and plastics from multilayer waste. Waste elemental sulfur is a by-product in gas and petroleum refining arising in huge quantities. Application of extreme acidophilic, sulfur-oxidizing bacteria resulted in generation of an around 1.4 M sulfuric acid, which was afterwards applied in aluminium and polymer recovery from different waste materials like aluminium-polyethylene reject material from liquid beverage packaging and pharmaceutical blisters. Within a maximum of 7 days, aluminium was fully removed and selectively precipitated, allowing full aluminium and polymer recycling without harming the polymer properties. The recycled polymers where afterwards characterised regarding re-processability and re-use. Characterization of recycled polyethylene from reject material revealed similar properties compared to virgin PE, highlighting it´s potential to be used in re-processing. Within the conducted work, a bio-based method for aluminium and plastic recovery was investigated, revealing a potential new recycling way for multilayer waste materials.

A.25 Highly Antioxidant Composite Bioplastic Films from Avocado Residues for Food Packaging Applications

Danila Merino

Istituto Italiano di Tecnologia

The industrial processing of avocados annually generates more than 1.2 million tons of avocado peels (AP) and avocado seeds (AS) that have great potential in the production of active bioplastics, although they have never been considered for this aim until now. Separately the AP and AS, as well as a combination of avocado peels and seeds (APS) were evaluated in this work for the first time for the preparation of antioxidant films, with application in food packaging. Films were prepared by casting, after their processing by three different methods: (1) hydrolysis in acid media, (2) hydrolysis followed by plasticization with polyglycerol-3 (G3), and (3) hydrolysis and plasticization with G3 followed by blending with pectin polymer in different proportions (25 and 50 wt. %). The results indicate that the combination of hydrolysis, plasticization, and pectin blending is essential to obtain materials with competitive mechanical properties, optical clarity, excellent oxygen barrier properties, high antioxidant activity, biodegradability, and migration of components in TENAX suitable for food contact applications. In addition, the materials prepared with APS are advantageous from the point of view of the industrial waste valorization, since the entire avocado wastes are used for the production of bioplastics, avoiding further separation processes for their valorization.

A.26 Lemon Peel Derived Bioplastics Intended for Agricultural Applications

Danila Merino

Istituto Italiano di Tecnologia

Water-based polymer solutions that form a protective layer when sprayed onto the soil represent a groundbreaking step towards utilizing biomass for mulching. In this work, lemon peel waste, usually used as a source of pectin, was hydrolyzed and blended with low methoxyl pectin (LMP) in a 25, 50, and 75 wt.%. LMP can crosslink with calcium cations naturally present in the soil, and therefore, their bioplastics may show potential for mulching. The bioplastic films were produced by casting in the presence of 30 wt.% of polyglycerol-3 plasticizer. The formulation with 50 wt.% of LMP presented the best mechanical properties and was selected to prepare insect repellent mulch films. For that, neem essential oil (NEO) was added in 0.5 and 1.5 wt.%. Besides, lemon peel biochar (LPB) particles were added in a 5 or 10 wt.% to prepare opaque materials for photosynthetically active radiation (400-700 nm), potentially preventing weeds' growth. Results indicate that NEO did not affect materials properties significantly, showing limited insecticidal activity against green peach aphids. Bioplastics with a 10 wt.% of LPB showed reduced mechanical resistance and water vapor barrier. Instead, composites with 5 wt.% of LPB presented acceptable properties, and both concentrations of LPB avoided the passage of light. Tested materials showed a fast biodegradability in soil, considering a 50% weight loss during the first week of the experiment.

A.27 Greening Polyester Synthesis: Investigating Enzymatic Polycondensations in Novel Bio-based Solvents.

Cicely Warne[1], Rob McElroy[2], Georg Guebitz[1, 3], Alessandro Pellis[3, 4]

[1] acib GmbH, Konrad-Lorenz-Strasse 20, 3430 Tulln an der Donau, Austria.
[2] Department of Chemistry, University of York, Heslington, York, YO10 5DD.
[3] Institute of Environmental Biotechnology, University of Natural Resources and Life Sciences Vienna Konrad-Lorenz-Strasse 20, 3430 Tulln an der Donau, Austria.
[4] Universitá di Genova, Dipartimento di Chimica e Chimica Industriale, via Dodecaneso 31, 16146, Genova (GE), Italy

Polyesters are useful materials with a wide range of applications, but there is increasing concern over their sustainability. Synthesis is one of the areas in which this can be improved, with enzymatic synthesis representing a sustainable alternative to traditional chemical catalysis. Although considered a green method of catalysis, enzymatic transformations are still performed in organic solvents with serious environmental issues such as toluene and diphenyl ether (DPE)[1]. As DPE is a petroleum-based solvent that is toxic to aquatic life and classed as highly hazardous, new solvents need to be investigated to replace it. Cyrene is a bio-based dipolar aprotic solvent that has been used as an NMP substitute[2], and has recently seen success as a solvent in polyester synthesis[3]. It has several functional groups, allowing for the synthesis of derivative solvents with different properties. In this work, Cyrene and several derivatives (dioxolane Cygnet 0.0 and dioxepane Cygnet) were tested in the polycondensation of bio-based adipic acid and either 1,4-butanediol or 1,8-octanediol, using *Candida antarctica* lipase B (CaLB) as the biocatalyst. To make the entire process more sustainable, it was a secondary aim to optimise the reaction and substitute the methanol and chloroform utilized in the workup procedure with greener alternatives. This was successful; chloroform and methanol were effectively substituted for Cyrene and water, respectively. Dioxolane Cygnet was found to be the preferred solvent, giving polymers with a Mn of >22000 Da. Surprisingly, although dioxepane Cygnet produced neither consistently better nor worse molecular weights compared to Cyrene, it gave polymers with lower yields. Finally, these solvents were used to polymerize several other bio-based monomers, showing their versatility in the production of bio-based polymers.

References

[1] Pellis et al. 2020, European Polymer Journal **130**, 109680.
[2] Sherwood et al. 2014, Chem. Commun. **50**, 9650–9652.

[3] Milescu et al. 2021, ChemSusChem **14**, 3367.Biosurfactants and wetting of chosen polymers.

A.28 Biosurfactants and Wetting of Chosen Polymers

Edyta Rekiel, Anna Zdziennicka, Bronisław Jańczuk

Department of Interfacial Phenomena, Institute of Chemical Sciences, Faculty of Chemistry, Maria Curie-Skłodowska University

Wetting is one of the most important processes occurring in industrial production and household. The visual measure of wetting is contact angle which is measured at the point were liquid-vapour interface meets solid body and it can be expressed in a quantitative manner using the Young equation. In consequence, finding out how different kinds of substances influence on the solid wetting – especially when it comes to polymers – seems to be crucial from practical point of view.

Biosurfactants are surface active compounds – mainly of microbial origin – that became very popular in the past couple of years. They are biodegradable, non-toxic, and they have similar or often better physico-chemical properties in comparison to their synthetic counterparts. For this reason, they are treated as promising green chemistry alternatives. Despite high surface activity, biosurfactants have rather poor wetting properties. In this case, it is necessary to modify these properties, for example, by the addition of short-chain alcohols. Such alcohols may influence on the water structure and – in result – on the hydration of head and tail of (bio)surfactant molecules and – in consequence – on the wetting of different solids.

In this research, we studied wettability of two polymers widely applied in practice and regarded as model solids: polytetraflouroethylene (PTFE) and polymethyl metacrylate (PMMA) by aqueous solutions of rhamnolipid and surfactin in the presence and in absence of ethanol. The obtained results were analysed in the light of surface tension components of the solid bodies, water, ethanol, as well as head and tail of biosurfactant surface tension.

A.29 Effect of UV Irradiation on Epoxy and Oligophosphonate S–IPNs

Cristian-Dragos Varganici, Liliana Rosu, Dan Rosu

Centre of Advanced Research in Bionanoconjugates and Biopolymers, "Petru Poni" Institute of Macromolecular Chemistry, 41A Gr. Ghica-Voda Alley, 700487 Iasi, Romania

Epoxy resins are polymers which possess a wide palette of properties, due to the versatility of the oxirane ring, capable of reacting with many classes of compounds. Due to this aspect, epoxies generally possess outstanding properties: excellent addition to different substrates, resistance to abrasion, chemicals and corrosion, etc. [1]. However, epoxy resins also show major drawbacks, such as low thermal stability and fire resistance and brittleness and release of toxic gases in the environment [2]. Furthermore, when exposed in the environment, like most polymers, they become vulnerable in time to environmental factors action, such as: humidity, micro-organisms and especially UV light. It is therefore important to overcome the disadvantages of epoxy resin properties with respect to recycling and environmental impact.
Herein, authors report the obtaining of three semi–interpenetrating polymer networks (S–IPNs) based on an epoxy resin, diglycidyl ether of bisphenol A (DGEBA), hardened with aromatic, cycloaliphatic and aliphatic curing agents and having an aromatic oligophosphonate, as linear component. The structures were designed as potential future wood protective coatings against environmental factors action.
The obtained S–IPNs were subjected to photochemical aging at a wavelength value of 365 nm for 500 hours. The colour and structural modifications of the structures during UV exposure were monitored as functions of irradiation time and dose. The influence of UV irradiation on the flame resistance capacity of the S–IPNs was also assessed.

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References
[1] R. Thomas, P. Vijayan, S. Thomas, Recycling of thermosetting polymers, *Transworld Research Network*, (2011) 122-129
[2] A. Toldy, A. Szabó, Cs. Novák, J. Madarász, A. Tóth, Gy. Marosi, *Polym. Degrad. Stab.*, 93 (2008) 2007

A.30 The Thermal Behavior of Epoxy Resins Cross–Linked with Bio–Based Curing Agent

Dan Rosu, Cristian-Dragos Varganici, Liliana Rosu, Fanica Mustata

Centre of Advanced Research in Bionanoconjugates and Biopolymers, "Petru Poni" Institute of Macromolecular Chemistry, 41A Gr. Ghica-Voda Alley, 700487 Iasi, Romania

Thermosetting networks from epoxidized vegetable oil (EVO) and bio–based curing agents are usually soft materials, having flexible structures. In order to enhance the mechanical properties, parts of bio–based curing agents must be replaced with small molecular curing agents. Their presence can also improve the thermal stability of the thermoset. This research describes the study of the thermal behavior of a green thermoset based on EVO cured with castor oil maleic anhydride derivative (COMA) and methyl nadic anhydride (MNA). The MNA improved the hardness and glass transition temperature of the obtained thermoset. The curing and thermal degradation mechanisms of the bio–based thermoset were determined via simultaneous TG/FT-IR/MS and differential scanning calorimetric (DSC) analyses. The kinetic parameters and the curve shapes of the activation energy as a function of conversion degree were obtained for both the curing and thermal decomposition processes, via the multivariate linear regression method (MLR) from "Thermokinetics–3" software. Based on the variation of the kinetic curves shapes for both curing and thermal degradation processes, and also the DSC and DTA curves, it was accepted that both processes occured in multi-step kinetics. The MLR method allows the estimation of the most probable thermal mechanisms of the bio–based thermosets.

A.31 Epoxy and Oligophosphonate S–IPNs. Morphological Study

Liliana Rosu[1], Ana-Lavinia Vasiliu[2], Cristian-Dragos Varganici[1], Dan Rosu[1], Fanica Mustata[1]

[1] Centre of Advanced Research in Bionanoconjugates and Biopolymers, "Petru Poni" Institute of Macromolecular Chemistry, 41A Gr. Ghica-Voda Alley, 700487 Iasi, Romania
[2] "Petru Poni" Institute of Macromolecular Chemistry, 41A Gr. Ghica-Voda Alley, 700487 Iasi, Romania

There were obtained three phosphorus based flame retardant semi–interpenetrating polymer networks (S–IPNs) having as linear component an aromatic oligophosphonate (2% P) and as cured matrix an epoxy resin cross–linked with three different curing agents: 4,4'–diaminodiphenylsulfone, 1,3–bis(aminomethyl) cyclohexane and octamethylene diamine. The morphologies of the films were investigated in detail by scanning electron microscopy (SEM) on a SEM Quanta 200 device (USA), operating at 30 kV with secondary and backscattering electrons and in high vacuum mode. The SEM studies were performed on uncoated samples fixed on aluminum supports. The cured networks, without oligophosphonate, exhibited smooth glassy cracks accompanied by parallel fracture lines. The curing agents generated higher rigidity in them, increasing brittleness and the crosslinking degree (Figure 1) [1]. The S–IPNs show the same relative texture, accompanied by more ridges and torsions along the cracks, indicating a good miscibility of the oligophosphonate into the cured epoxy matrices [2].

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References

[1] F. Mustata, N. Tudorachi, I. Bicu, Thermosetting resins obtained via sequential photo and thermal crosslinking of epoxy resins. Compos. Part B: Eng. 55, 470–478, 2013
[2] I.–D. Carja, D. Serbezeanu, T. Vlad–Bubulac, C. Hamciuc, A. Coroaba, G. Lisa, C.G. López, M.F. Soriano, V.F. Pérez, M.D.R. Sánchez, J. Mater. Chem. A 2, 16230–16241, 2014

A.32 The Facile Synthetic Route of Advanced Copolymer and Patterned Surface-Grafted Brushes with Pendant Functional Groups

Joanna Smenda, Karol Wolski, Szczepan Zapotoczny

Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387 Krakow, Poland

Surface functionalization plays a key role in the formation of nano/microdevices with a layered structure. Polymer brushes that offer various architectures and physicochemical properties are promising for that purpose. Moreover, they can replace hardly available and difficult to process inorganic materials in some applications. Homogeneous coatings with desirable properties may be obtained by grafting polymer brushes from the surfaces via metal-free surface-initiated atom transfer radical polymerization (SI-ATRP). This approach provides control over the layer thickness and architecture without using toxic complex compounds based on transition metals and the necessity of providing demanding conditions.

Therefore, we present here the synthesis of advanced structured polymer brushes with pendant thiophene and acetylene groups using metal-free SI-ATRP. The applied reaction setup required only initiator-decorated substrate, microlitre volumes of the reaction mixture and organic photocatalyst active in the visible light. In the research, we indicated that polymer chain end activity was maintained after the polymerization completion. As a consequence, polymer chains were prone to elongation allowing the synthesis of block copolymer brushes in two sequential polymerizations. Furthermore, we synthesized patterned polymer brushes using easily accessible photomasks such as TEM grids. AFM measurements of the obtained patterns revealed great spatial resolution and formation of highly ordered structures.

The research presents a simple and economic strategy in the synthesis of homopolymer and copolymer brushes. This method is suitable for difficult to polymerize and/or precious monomers as it is carried out in small volumes and with low reagent consumption. The high spatial control over substrate decoration shows a future possibility of creating designed patterned layers in one synthetic step which is crucial in a scaling-up of processes.

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A.33 Effect Of Nanoclays Addition On The Structural and Mechanical Properties of Polypropylene Random Copolymer

Nikolaos Bikiaris[1], Evangelia Delli[2], Dimitris Gkiliopoulos[3], Konstantinos Chrissafis[2]

[1] Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, Greece
[2] School of Physics, Laboratory of Advanced Materials and Devices, Aristotle University of Thessaloniki, GR-541 24, Thessaloniki, Greece
[3] Laboratory of Chemical and Environmental Technology, Department of Chemistry, Aristotle University of Thessaloniki, Greece

Polymer-matrix based composite materials exhibiting robust mechanical and thermal properties are of immense technological significance for a wide variety of applications including aerospace and civil/structural engineering. Polypropylene random copolymer (PPR), copolymerized from propylene and ethylene monomers, has received a significant deal of industrial attention due to the higher impact strength, excellent thermal stability, and mechanical properties. Certain applications of it include pipes manufacturing, packing plastic, automobiles etc. Recently clays are considered as a fundamental reinforcing element in nanocomposites. It is well established that the incorporation of nano additives is an effective method to further enhance physical and mechanical properties of polymeric materials. Herein, five polypropylene (PPR112)/nanoclays composites using different filler concentrations (1-15 %wt.) were prepared via melt-mixing extrusion and thoroughly examined. The structural characteristics of the composites were investigated using Fourier-transform Infra-red spectroscopy (FTIR), X-ray Diffractometry (XRD) and Scanning Electron Microscopy (SEM), while Tensile strength and Impact strength were measured to evaluate the mechanical behavior of the prepared nanocomposites.

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A.34 Electrical Conductivity Enhancement of Polyaniline/Polycaprolactone Composites through Thermal Processing and Solution Casting

Aurora Lasagabáster-Latorre[1, 2, 3], Carla Fernández Blanco[4, 5, 6], Isabel Vázquez-Rodríguez[4, 5, 6], Ana Isabel Ares Pernas[4, 5, 6], Goretti Arias-Ferreiro[4, 5, 6], Sonia Dopico-García[4, 5, 7], Silvia Lage-Rivera[4, 5, 6], Victoria González-Rodríguez[4, 5, 6], María José Abad López[4, 5, 6]

[1] *Universidad Complutense de Madrid*
[2] *Facultad de Óptica y Optometría*
[3] *Departamento Química Orgánica*
[4] *Universidade da Coruña*
[5] *Campus Industrial de Ferrol*
[6] *Grupo de Polímeros-CIT*
[7] *Laboratorio de Química-CIT*

Conducting polymer composites based on polyaniline (PANI) and biodegradable polymers as polycaprolactone (PCL) have the potential to substitute metallic materials in electronic applications, with the additional advantage of mechanical flexibility, simple processability and environmental impact reduction [1]. In this work two different approaches were explored to enhance the electrical conductivity of PANI:PCL composites depending on their processing technique. Compatibilizers were added to improve the PANI dispersion in PCL composites obtained by extrusion while different solvents were compared using solution processing.

Preparation of PANI-DBSA/PCL composites by thermal processing: blends of PANI doped with dodecylbenzenesulfonic acid (DBSA) at 30% (v/v) and PCL were obtained by extrusion at 65 ˚C. Three compatibilizers, poly(propyleneglycol)-blockpoly(ethylene-glycol)-block-poly(propylene-glycol) (PPG-PEG-PPG), acetyltributyl citrate (ATBC) or sorbitan mono-ester (Span 60), were added in the range 0-15%.

Preparation of PANI-HCl/PCL composite films by solution casting: the mixture of PANI doped with hydrochloric acid (PANI-HCl) and dissolved PCL was sonicated (3x3 minutes) and solvent evaporation was carried out at room temperature. The solvents tested were acetone, tetrahydrofuran or dichloromethane and mixtures of dichloromethane with glycerol, toluene or tetrahydrofuran.

PANI-PCL composites with electrical conductivities in the order of 10^{-1} S·cm^{-1} were obtained both by extrusion and solution casting, only one order of magnitude lower than neat PANIs.

For thermal processing the use of compatibilizers was paramount, achieving the best results with PPG-PEG-PPG followed by Span 60. The electrical percolation threshold of the PANI-DBSA in the composite PANI-DBSA/ PPG-PEG-PPG/PCL was 9.7% (v/v), maintaining the ratio of PANI-DBSA/PPG-PEG-PPG 2:1.

Concerning PANI-HCl/PCL composites obtained by solution casting, a careful selection of the solvent was required. The highest conductivity was attained with 1:1 dichloromethane: tetrahydrofuran with an electrical percolation threshold of 3.3% (v/v).

References:

[1] Pud, A.; Ogurtsov, N.; Korzhenko, A.; Shapoval, G. Prog. Polym. Sci. 200, 28 (12), 1701

A.35 Synthesis and Investigation of Vitrimers from Glycerol and Vegetable Oils

Sigita Grauželienė, Jolita Ostrauskaitė

Department of Polymer Chemistry and Technology, Kaunas University of Technology

Vitrimers have gained great attention from scientists as they behave like thermosets at low temperatures when the exchange reactions are long and flow like viscoelastic liquids due to the thermoactivated bond exchange reactions at high temperatures. This behavior allows to reshape, repair, and reprocess vitrimers by various modern methods such as 3D printing and also to obtain many structural and fast acting devices such as actuators for soft robotics. Recently, biobased monomers have started to be used for the synthesis of vitrimers as they are safer and fulfill the main ideas of green chemistry and green engineering, which aims to reduce the negative impact on the environment and human health. The increase in biodiesel production from vegetable oils and animal fats leads to an increase in glycerol yield as a by-product. In order to avoid the surplus, glycerol could be used for the synthesis of vitrimers as already has been used as a starting material for the manufacturing of chemical intermediates or products in several industrial segments, e.g. food, plastics, and pharmaceutical industry. Vegetable oils are also attractive for the synthesis of vitrimers due to their low toxicity and high biodegradability. Therefore, the idea of this research was to use monomers obtained from renewable raw materials for the synthesis of vitrimers. Consequently, several resins have been prepared by mixing the monomers at different ratios with the photoinitiator and transesterification catalyst and cured under UV/Vis light. Real-time photorheometrical study showed that the rigidity of the vitrimers decreased slightly with increasing the amount of functionalized glycerol. However, the amount of this monomer had no influence on the gel point and reduced the viscosity of the resin required for optical 3D printing. The resin containing the highest amount of functionalized glycerol was chosen for vitrimer synthesis as this resin had the highest amount of hydroxyl and ester groups that are beneficial for transesterification reactions. Moreover, the synthesized vitrimer showed shape-memory properties and self-healing with an efficiency of 45 %.

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A.36 Sustainable 3D Printing Filaments Based on Recycled Polypropylene and Rice Husk: Effects of Fiber Particle Size and Maleic Anhydride-Grafted-Polypropylene Implementation

Maria Alejandra Morales[1], Alicia Porras[1], Veronique Michaud[2], Alejandro Marañon[1]

[1] *Universidad de los Andes*
[2] *École Polytechnique Fédérale de Lausanne*

Nowadays, scientists and industry are concerned with the protection of the planet, by enhancing the development of more sustainable materials and the change towards a circular economy. In addition, the development of additive manufacturing techniques enables to locally produce parts with minimal waste, and would benefit from the use of renewable raw materials. Our work presents the development and characterization of 3D printing filaments based on recycled polypropylene (rPP) and rice husk (RH). The influence of two different particle sizes and the implementation of maleic anhydride-grafted-polypropylene (MAPP) as additive on the 3D printing process and 3D printed parts was evaluated. For the analysis, warping effect, thermal, mechanical, and morphological (SEM) analyses were performed. Thermal behavior was evaluated through TGA (ASTM D3418) and DSC (ASTM E1131). Mechanical properties, as tensile (ASTM D3039), flexural (ASTM D790) and impact (ASTM D256) were determined. Results showed an improvement in mechanical properties and reduction of warping when MAPP was implemented together with the use of smaller particle size of the RH. According to the morphological analysis, this improvement was caused by an improved interfacial adhesion between the polymeric matrix and the fiber achieved with the MAPP, and the better fiber distribution achieved when smaller particle size is used. The study demonstrates the potential of recycled polymers and agroindustrial waste to be used in new manufacturing techniques, as 3D printing, contributing to the change to a circular economy industrial model.

A.37 Development of Ternary Biopolymer Blends: Mechanical and Rheological Characterization

Alberto Frache, Rossella Arrigo

Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Alessandria site, Viale Teresa Michel 5, 15121 Alessandria, Italy

In the last years, the increasing concerns related to the environmental impact of plastic wastes has stimulated a growing research effort towards the formulation of green polymer-based systems, potentially suitable for replacing traditional fossil-based thermoplastics. In this context, a wide range of biodegradable and/or bio-based polymers were developed. However, many of them suffer from processing difficulties and high cost; besides, their physical and functional properties are often poorer than those of traditional thermoplastics. Therefore, there is an urgent need to formulate new biopolymers-based systems, derived from a combination of existing biopolymers, offering final performance compared to those of fossil-based polymers, possibly at an equivalent cost. In this work, ternary biopolymer blends based on polylactic acid (PLA), poly-butylene succinate (PBS) and polyhydroxybutyrate-co-hexanoate (either unfilled (PHBH) or containing embedded talc particles (tPHBH)), were obtained by melt compounding using a twin-screw extruder and fully characterized through morphological observations and rheological and mechanical characterizations. A preliminary study of the interfacial properties of the biopolymers through contact angle measurements allowed predicting a partial wetting between PBS and PHBH when PLA is the continuous phase; differently, in PLA/PBS/PHBt blends with PLA and PHB as matrix, a complete wetting between the phases is expected. Morphological and rheological analyses confirmed the theoretical calculations, as all the formulated systems showed a uniform microstructure with a good compatibility between the phases especially when the amount of PBS increases. The results of the mechanical tests demonstrated that PLA/PBS/PHBH systems exhibit a ductile behavior, particularly when the content of PBS is higher than 30 wt.%, in contrast to the intrinsic brittle character of both PLA and PHBH. Conversely, for PLA/PBS/PHBHt blends, the presence of talc in PHBHt hinders the achievement of similar elongation at break values and the introduction of higher amounts of PBS is required to obtain a ductile behavior.

A.38 Hierarchically Porous S/N/O Codoped Carbons from Polyacrylonitrile-Based Block Copolymers for Selective Separation Of Industrial Pollutants

Lidia Domínguez-Ramos, Diego Gómez-Díaz, M. Sonia Freire, Julia González-Álvarez, Massimo Lazzari

Universidade de Santiago de Compostela, Spain

Due to their peculiar mesophase separation and ease of processing polyacrylonitrile (PAN)-based block copolymers (BCs) are an ideal precursor for preparing activated carbons for applications as selective adsorbents, for the purification of a variety of industrial streams.

It is well known, and industrially exploited, e.g. for carbon fibre fabrication, that controlled pyrolysis of PAN may led to the formation of regular graphitic carbons. In the case of BCs, the volatilization of a sacrificial second block as poly(methyl methacrylate) (PMMA), results in the development of a porous carbon with interconnected mesopores that are almost regularly shaped and uniformly distributed. This behaviour is attributed to the crosslinking of PAN at high temperatures, which hinders the expected cylindrical or gyroid microphase separation of the PAN-*b*-PMMA BC.

Residual N atoms from PAN remains in the porous carbon in form of pyridinic and pyrrolic N-centres, whereas other different functional groups could be introduced through selective doping treatments. S-containing groups were introduced by sulphuration through a controlled thermal treatment of elemental sulphur/PAN-based 4/1 mixture, whereas the presence of O-containing groups, mainly hydroxyl and carbonyl groups could be modulated through pre-oxidation and activation processes. It is worth citing that the activation process also allowed controlling the microporosity (2 nm), finally fine-tuning an overall process of fabrication of hierarchically porous activated carbons.

Structural and morphological characterization of precursors and carbons was carried out mainly by electron microscopies (TEM and SEM), X-ray photoelectron spectroscopy (XPS, Raman spectroscopy, and an automated gas sorption analyser Brunauer-Emmett-Teller (BET) for surface area and pore size distribution (total pore volume, macro-, meso- and microporosity) determination. Preliminary results on the application of selected activated carbons for dye removal from aqueous solutions will also be showed.

A.39 Solvent Free Mechano-Synthesis of Cyclodextrin Crosslinked Polymers

Alberto Rubin Pedrazzo[1], Marco Zanetti[1, 2], Claudio Cecone[1], Gjylije Hoti[1], Francesco Trotta[1]

[1] *Università di Torino*
[2] *ICxT Centre*

Cyclodextrin nanosponges (CD-NS) are cross-linked polymers made up of cyclodextrins, characterized by a three-dimensional nano-structure. The reactive hydroxyl groups of CDs allow them to act as polyfunctional monomers, permitting them to crosslink with many bi or multifunctional chemicals [1]. The most common NSs synthetic pathway consists in dissolving the chosen CD in organic polar aprotic liquids (e.g.dimethylformamide or dimethylsulfoxide), which may affect the final result, especially for potential biomedical applications. We are here reporting new green syntheses of nanosponges through different mechanochemistry approaches. Mechanochemistry involves the application of mechanical forces to drive and control chemical reactions by transferring energy to chemical bonds. Mechanochemistry applied to inorganic chemistry is well established and in recent years there has been a growing interest in mechanochemistry applied to organic synthesis: esterification and etherification of starch and the possibility of obtaining CD derivatives with a solid state reaction using ball milling or reactive extrusion, have been reported recently [2]. The green synthetic routes here proposed permits to obtain a cross-linked polymer, exhibiting the same characteristics as CD-NS synthesized in batch, without using any solvent [3]. CD-based carbonate NSs, traditionally synthetized in DMF, which is a toxic and suspected carcinogenic solvent, were synthesized using 1,1-carbonyldiimidazole as a crosslinker. Moreover, we tested a mechanochemical approach that involves the use of a Twin-Screw Extruder (TSE) as a chemical reactor: TSE is capable of fine temperature control and, furthermore, TS Extrusion is a continuous process and not a batch process. Among the many available CD-NS syntheses, we tested this different solvent-free approach on a β-CD/citric acid (CA) system: the traditional synthesis is carried out in heated vessel under vacuum, using water as solvent. The polycondensation leads to an insoluble cross-linked polymer. The use of a mechanochemical approach, using TSE, permitted us to obtain the same polymer in a considerably shorter time and without using a vacuum pump. Moreover, the use of a continuous screw system is particularly interesting for a possible scale up. The polymers obtained from both symphyses were deeply characterized and various applications were tested for a comparison with the classical synthesis.

References:

1. F.Caldera, M.Tannous, R.Cavalli, M.Zanetti, and F.Trotta. *Int. J. Pharm*. 531(2), 470–479, ***2017***.

2. L. Jicsinszky, M. Caporaso, E.C. Gaudino, C. Giovannoli, G. Cravotto, B. Martel. *Mol.* vol. 22, no. 3, pp. 1–16, ***2017***.
3. Trotta, F.; Rubin Pedrazzo, A. Process for Preparing a Nanosponge. WO2021053039A1, ***2021***.

A.40 Bioderived Furanoate Polyesters for Sustainable Packaging: Effect of Blending and Nanofiller Addition on the Thermomechanical and Functional Properties

Giulia Fredi[1, 2], Andrea Dorigato[1, 2], Mauro Bortolotti[1, 2], Dimitrios Bikiaris[3], Riccardo Checchetto[4], Alessandro Pegoretti[1, 2]

[1] *Department of Industrial Engineering, University of Trento, Trento, Italy*
[2] *National Interuniversity Consortium of Materials Science and Technology (INSTM), Florence, Italy*
[3] *Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece*
[4] *Department of Physics, University of Trento, Trento, Italy*

Poly(alkylene 2,5-furandicarboxylate)s (PAFs) are a new class of bioderived polymers, emerging as a sustainable and biobased alternative to fossil-derived poly(alkylene terephthalate)s (PATs), widely used for packaging applications. One of the main obstacles to their industrialization is the lack of knowledge of their thermomechanical behavior. Therefore, this work aims to characterize their properties in the form of films (a) as neat homopolymers, (b) in blend with other biopolymers (e.g., polylactide, PLA), and (c) added with carbon nanofillers such as carbon nanotubes (CNTs) and reduced graphene oxide (rGO).

The long-alkyl-chain PAFs poly(decamethylene 2,5-furandicarboxylate) (PDeF) and poly(dodecamethylene 2,5-furandicarboxylate) (PDoF) have been synthesized with a two-step polycondensation procedure. Multi-walled carbon nanotubes (CNTs) Nanocyl NC7000 and NatureWorks Ingeo PLA 4032D were used as received. rGO was obtained by thermo-chemically reducing a commercial Graphenea graphene oxide (GO) suspension. Nanocomposite films were prepared by solution casting in chloroform and hexafluoroisopropanol.

For the nanocomposites PDeF/CNTs (CNT up to 2 phr), the homogeneously distributed and well-debundled CNTs positively homogenize the microstructure, enhance the crystallization kinetics, and improve the strength, stiffness, and creep behavior of PDeF. Surprisingly, the strain at break also increases (+71 % with 0.25 phr of CNTs than neat PDeF), due to a more homogeneous microstructure. For the nanocomposite blends PLA/PDoF/rGO (PDoF up to 10 wt%, rGO up to 2 phr), PDoF and PLA are immiscible and PDoF is visible as homogeneously distributed spheroidal domains. The morphology of such domains changes after the addition of rGO, as they become rougher and smaller and with an increased interfacial interaction with the surrounding PLA matrix. Interestingly, PDoF and rGO synergistically contribute to the crystallization kinetics of PLA. The addition of 10 wt% of PDoF to PLA leads to a slight decrease in the tensile modulus and strength and to a noticeable increase in the strain at break (+145 %), thus tackling one of the main drawbacks of PLA, i.e., its brittleness. rGO and PDoF also improve the gas

barrier properties of PLA, by decreasing the permeability and the diffusivity to CO_2, O_2, and N_2.

This work highlights the positive impact of bioderived long-alkyl-chain PAFs on the ductility of PLA and the interesting multifunctional role of rGO and CNTs in PAF and PLA/PAF blends. The resulting films exhibit interesting thermomechanical and gas barrier properties, very promising for packaging applications.

A.41 New Generation Bioplastics of Ductile Poly(phenol)s with Poly(butylene succinate)

Maninder Singh, Tatsuo Kaneko

[1] *Graduate School of Advanced Science and Technology*
[2] *Energy and Environment Area*
[3] *Japan Advanced Institute of Science and Technology*

The current situation of enormous plastic waste in the sea, on the land, has been creating havoc as these plastics pile up and remain there for centuries destroying marine and terrestrial life as well. Fabrication of environmental friendly polymers are in great demand these days because they are derived from naturally occurring molecules which degrade easily into the environment with no harm and can be useful for solving environmental problems. One such environmentally benign, the high-performance polymer was synthesized using phenolic monomer i.e. poly(4HCA-co-DHCA) which has high thermal and mechanical strength than usual aliphatic polyesters such as poly(lactic acid) which makes the resulting polymer highly rigid in nature. Also, these polymers have liquid crystalline behavior which sometimes dramatically increases the mechanical strength. Because of the high rigidity, these polymers cannot be used in applications that require flexible polymers. Poly(4HCA-co-DHCA) is brownish in color and look-alike wood but it is very rigid in nature. This polymer can be a good candidate to be explored further to obtain a flexible polymer. Moreover, these aromatic polymers are proven to be safer to use and biodegradable[1,2]

Biodegradable rigid poly(4HCA-co-DHCA) can be made flexible by introducing an aliphatic chain into the polymer. The poly(butylene succinate) (PBS) was hybridized as a flexibility inducer into rigid poly(4HCA-co-DHCA). Since PBS is biodegradable in nature. It degrades into water and carbon dioxide much faster than poly(butylene adipate terephthalate) (PBAT) and poly(lactic acid) (PLAs).[3] In this report, we will present the formation protocol for composites of rigid poly(4HCA-co-DHCA) with different weight percent (PBS 0%, PBS 10%, PBS 20%, PBS 30%, PBS 40%, PBS 50%, and pure PBS) of flexible PBS and in-depth analysis of the composite structure was done using various characterization techniques to study the toughness (PBS 0% 2 MJ/m3, PBS 10% 2 MJ/m3, PBS 20% 7 MJ/m3, PBS 25% 18 MJ/m3, PBS 30% 69 MJ/m3, PBS 40% 76 MJ/m3) and flexibility of the synthesized biocomposite material.

References

[1] T. Kaneko, T.H. Thi, D.J. Shi, M. Akashi Nature Mat. **2006**, *5*, 966.
[2] M. Chauzar, S. Tateyama, T. Ishikura, K. Matsumoto, D. Kaneko, K. Ebitani, T. Kaneko Adv. Funct. Mat. **2012**, *16*, 3438.
[3] M.R. Nobile, A. Crocitti, M. Malinconico, G. Santagata, P. Cerruti AIP Conf. Proc. **2018**, 020180.

A.42 Enzymatic Synthesis of Biobased Furan Based Polymers

Dina Maniar, Katja Loos

Macromolecular Chemistry and New Polymeric Materials, Zernike Institute for Advanced Materials, University of Groningen

Over the past two decades, environmental problems due to plastic pollution have become so common that a huge effort to develop sustainable polymer alternatives from renewable sources has become necessary. Molecules derived from biomass form excellent biobased chemical platforms for polymer building blocks. Among the wide variety of bio-based monomers, furan chemistry occupy a special place in polymer chemistry. Similarities between furan and benzene rings offer opportunities for bio-based alternatives to phenyl polymers. For example, polyethylene furoate (PEF) is a prevalent alternative to polyethylene terephthalate (PET) commonly used as packaging material. However, furan building blocks are highly temperature sensitive and, unlike their phenyl analogs, require mild reaction conditions. Alternative synthetic routes need to be established to overcome significant degradation risks during traditional polymer synthesis. In this regard, green and robust enzymatic polymerization is very attractive and has the potential to meet the needs of sustainable polymer chemistry.

Therefore, we have developed a variety of novel furan based polymers with diverse properties, focusing on environmentally friendly synthetic methods. A series of furan based polymers have been successfully produced by enzymatic polycondensation of biobased furans with various comonomers. Their polymerization kinetics was studied using immobilized *Candida antarctica* lipase B (CALB) as a biocatalyst. To provide a completely green approach to polymerization, we investigated enzymatic synthesis in ionic liquids and solvent-free conditions and compared the results with those in organic solvents.

The structural characterization of the obtained products shows that our method is effective for the production of furan-based polymers, overcoming the shortcomings of traditional chemical routes. The efficiency of an enzymatic process is related to important parameters such as monomer structure, polymerization technique, and solubility of the final product in the system. This study provides a fundamental understanding of the fabrication of bio-based furan based polymers and their properties by an efficient and environmentally friendly process.

B.1 Wool Keratin: Extraction, Processing and Applications in the Biomedical Sector

Marina Zoccola [1], Parag Bhavsar [2], Giulia Dalla Fontana [2], Alessia Patrucco [2]

[1] CNR-STIIMA - Italian National Research Council - Institute of Intelligent Industrial Technologies and Systems for Advanced Manufacturing – C.so G. Pella 16 – 13900 Biella (Italy)
[2] CNR-STIIMA, Italian National Research Council - Institute of Intelligent Industrial Technologies and Systems for Advanced Manufacturing– C.so G. Pella 16 – 13900 Biella (Italy)

Keratins are proteins characterised by a high sulphur amount and by the presence of strong disulphide bonds which make keratins water insoluble and resistant to different chemical agents.
Wool keratin can be extracted by the cleavage of the cystine bonds by treatment with reducing agents or by sulphitolysis or using oxidising agents. From these extractions intact proteins with molecular weight ranging from less than 10 and 60 kDa are obtained. The hydrolysis of keratins can be obtained by the cleavage of peptide bond using strong acids or strong bases. Recently, green processes such treatments with superheated water and treatment by steam-explosion have been proposed with the aim of avoiding the use of harmful agents. In these cases, due to the cleavage of peptide bonds, protein material with lower molecular weight is obtained.
Keratin biomaterials possess many distinct advantages over conventional biomolecules, including a unique chemistry afforded by their high sulfur content, remarkable biocompatibility, biodegradability, hygroscopicity, propensity for self-assembly, and intrinsic cellular recognition.
Proteins extracted from wool can be processed as pure keratin, or in blend with other polymers, with cross-linking agents, or in presence of additives (e.g. plasticisers).
Films, sponges, nanofibres, microcapsules, hydrogels, powders and solutions can be obtained by the extraction or hydrolysis of wool keratin and by the following processing.

B.2 Polyhydroxy Butyrate Nano Spheres Incorporated with Drug for Medical Applications

Eglė KUMPIKAITĖ, HALEEMA KHANZADA

Kaunas University of Technology

The purpose of present study was to develop noospheres of polyhydroxy butyrate (PHB) with narrow size distribution for drug encapsulated for medical textiles. After achieving optimized recipe the drugs loaded Nano-spheres of PHB were fabricated by using solvent evaporation method. Ciprofloxacin based antibiotic drugs were used as core material during the encapsulation. The scanning electron microscope (SEM) images showed that the drug loaded noospheres were spherical in shape. In this research, formulation of drug loaded noospheres, particle size and release of drug in vitro were studied. A formulation based on maximum release of drug with time was selected, and after that these Nano sphere loaded with antibiotic drug were applied on different type of textile matrices by using pad and cure method. Finally, these noospheres loaded with drug were subjected to SEM, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and analysis of drug release. The physical and mechanical properties of the treated samples were also investigated. The treated samples showed increased stiffness and decreased tensile strength. The treated sample showed antibacterial activity against both the Gram positive and Gram negative bacteria. The samples treated with the drug loaded noospheres showed a control approximately 90 percent drug was released after 24 h.

B.3 Cyclodextrin-Based Nanosponges as Stabilizer and Promotor of the Anticancer Activity of Nisin Against Colon and Breast Cancer Cells

Yousef Khazaei Monfared[1], Mohammad Mahmoudian[2], Claudio Cecone[1], Fabrizio Caldera[1], Parvin Zakeri-Milani[3], Adrián Matencio[4], Francesco Trotta[1]

[1] Department of Chemistry, University of Turin
[2] Faculty of Pharmacy, Tabriz University of Medical Sciences, Tabriz, Iran
[3] Liver and Gastrointestinal Diseases Research Centre and Faculty of Pharmacy, Tabriz University of Medical Sciences, Tabriz, Iran
[4] University of Turin

The great variability of cancer types demands novel drugs with broad spectrum, as nisin, a polycyclic antibacterial peptide that recently has been considered for prevention of cancer cells growth. The aim of present study to investigate the protective effect of two different β-cyclodextrin-based nanosponges (carbonyl diimidazole and pyromellitic dianhydride) and their anticancer enhancement effect of nisin encapsulated with against colon (HT-29) and breast (MCF-7) cancer cells was carried out. The physicochemical properties, loading efficiency, release kinetics and stability in presence of pepsin of Nisin complexes were studied. In addition, the cytotoxicity and cell membrane damage of Nisin Z were evaluated by using the MTT, LDH assay and flow cytometry. The results indicate that CD-NS are able to complex Nisin with an encapsulation efficiency around 90%. A protective effect of nisin complexed with CD-NSs was observed in presence of pepsin. An increase in the percentage of apoptotic cells was observed when the cancer cells were exposed to nisin complexed with nanosponges. Interestingly, Nisin free and loaded on PMDA/CDI-NSs is more selectively toxic towards HT-29 cells than MCF-7 cancer cells. These results suggest the novel application of nanosponges for protecting peptides and deliver drugs against cancer.

B.4 Nanocomposite Hydrogels Based on Poly(n-Vinyl Pyrrolidone) and Laponite Xlg

Ionela Alice PODARU[1], Paul Octavian STĂNESCU[2], Gabriela TOADER[3], Ștefania STOLERIU[2], Raluca Elena GINGHINĂ[4], Bogdan TRICĂ[5], Mircea TEODORESCU[2]

[1] Military Technical Academy „Ferdinand I", 39-49 G. Cosbuc Blvd., Bucharest, 050141, Romania University Politehnica of Bucharest, 1-7 Gh. Polizu Street, Bucharest, 011061, Romania
[2] University Politehnica of Bucharest, 1-7 Gh. Polizu Street, Bucharest, 011061, Romania
[3] Military Technical Academy „Ferdinand I", 39-49 G. Cosbuc Blvd., Bucharest, 050141, Romania
[4] Research and Innovation Centre for CBRN Defense and Ecology, 225 Şos. Olteniţei, Bucharest, Romania
[5] National Institute for Research and Development in Chemistry and Petrochemistry, 202 Splaiul Independentei, Bucharest, 060021, Romania

Nanocomposite (NC) hydrogels crosslinked by Laponite clay represent a special category of hydrogels, which have been initially developed by Haraguchi and coworkers[1]. They are characterized by largely superior mechanical properties in comparison to the fragile chemically crosslinked hydrogels, in addition to other very useful properties like high transparency, good thermal conductivity or rapid swelling/de-swelling process. The monomers employed to synthesize these hydrogels are mostly vinyl monomers containing an amide group within the molecule, like N-isopropylacrylamide, *N,N*-dimethylacrylamide, acrylamide, N-vinylpyrrolidone (NVP), etc., but monomers from other classes such as oligo(ethylene glycol) metacrylates or N,N-dimethyaminoethyl methacrylate have been proved to produce NC hydrogels as well. Among these monomers, NVP seems to be the least studied from this point of view[2], although poly(N-vinylpyrrolidone) hydrogels display important applications.

The present work deals with the preparation and detailed structural characterization of nanocomposite hydrogels based on NVP monomer and Laponite XLG as cross-linker/reinforcing agent. The nanocomposite hydrogels were synthesized by the radical polymerization of NVP using 2,2-azobisisobutyronitrile as the initiator, with or without *N,N'*-methylenebisacrylamide as chemical crosslinker, and different concentrations of Laponite XLG. The hydrogels obtained were characterized by FT-IR, XRD, TGA, SEM-EDX, TEM analyses, compression tests and rheological measurements.

The results showed the existence of interactions between the inorganic clay and organic polymer matrix which led to the formation of exfoliated nanocomposites. Also, during the formation of the nanocomposite hydrogels, Laponite XLG functioned as both reinforcing agent and multifunctional cross-linking agent by its own. In comparison with the chemically crosslinked hydrogel, the NC hydrogels exhibited optical transparency, good flexibility and much better mechanical properties.

References:
1. K. Haraguchi. Nanocomposite hydrogels, Current Opinion in Solid State and Materials Science. 11, ***2007***, 47–54.
2. Y. Wang, D. Shang, Z. Niu. Removal of Heavy Metals by Poly(Vinyl Pyrrolidone)/Laponite Nanocomposite Hydrogels. *Adv. Mater. Res.* 631–632, ***2013***, 291–297.

B.5 The Potential of Using Chitosan in the Biotechnological Production of Proteins

Monika Sikora[1], Michał Arabski[2], Maria Wiśniewska-Wrona[3]

[1] Department of Medical Biology, Institute of Biology, Jan Kochanowski University, University Street 7, 25-406 Kielce, Poland Lukasiewicz Research Network - Institute of Biopolymers and Chemical Fibers Skłodowskiej-Curie Street 19/27, 90-570 Lodz, Polan
[2] Department of Medical Biology, Institute of Biology, Jan Kochanowski University, University Street 7, 25-406 Kielce, Poland
[3] Lukasiewicz Research Network - Institute of Biopolymers and Chemical Fibers Skłodowskiej-Curie Street 19/27, 90-570 Lodz, Poland

Biosynthesis of proteins and therapeutic peptides is currently one of the developing strategies and an alternative to proteolysis. The advantage of using bacterial expression systems is the relatively fast growth of culture on cheap substrates, a high degree of genome characterization and a large selection of vectors and strains. The production of recombinant proteins using bacterial systems also has some drawbacks. For medical purposes it requires purification from LPS as one of the key steps. Llipopolysaccharide (LPS) is a thermostable molecule in the outer cell membrane of Gram-negative bacteria and shows a strong immune response in the human body. The currently used purification procedures may lead to changes in environmental conditions, resulting in a reduction the stability of the proteins. It is important to precisely select the purification conditions similar to natural during the purification process and storage. Therefore, there is still a search for new methods with high degree of purification and minimized to zero the risk of degradation and changes in the structure and activity of the protein.
Chitosan is a linear, semi-crystalline polysaccharide, obtained in deacetylation process of the natural polymer- chitin, from the exoskeleton of crustaceans. Chitosan is appropriate biomaterial due to unique properties: biodegradability, biocompatibility, non-toxicity, antibacterial and antifungal properties. Due to the high biological activity and the ability to bind micro and macroparticles, this biopolymer may be a suitable candidate for use in the process of purifying protein products from endotoxin. The research issues of the presented results concern the technology of production a chitosan-based polymer bed for the purification of protein products from LPS and their biological activity. The produced functional forms of the tested biopolymers were characterized in terms of physicochemical properties, their ability to bind LPS molecules and biological effect on living cells.
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B.6 A New Material for Protective Face Masks and Respirators with High Breathability

Monica Torsello[1], Carlo Gotti[2, 3], Riccardo Onesti[4], Gianmarco Tanganelli[5], Marco Roselli[4], Davide Fabiani[3, 5], Andrea Zucchelli[2, 3], Cristiana Boi[4, 6], Maria Letizia Focarete[1, 6]

[1] Department of Chemistry "G. Ciamician", University of Bologna, Bologna, Italy
[2] Department of Industrial Engineering, University of Bologna, Bologna, Italy
[3] Advanced Mechanics and Materials–Interdepartmental Center for Industrial Research (CIRI-MAM), University of Bologna, Bologna, Italy
[4] Department of Civil, Chemical, Environmental and Materials Engineering (DICAM), University of Bologna, Bologna, Italy
[5] Department of Electrical, Electronic, and Information Engineering "G. Marconi", University of Bologna, Bologna, Italy
[6] Health Sciences and Technologies – Interdepartmental Center for Industrial Research (HST-ICIR), Alma Mater Studiorum - Università di Bologna, Ozzano dell'Emilia, Bologna, Italy

Electrospinning is a versatile technique able to produce sub-micrometric spun fibers with high surface to volume ratio. Fibers are obtained applying a high voltage to a polymer solution or melt. Thanks to the strong electric field, electrospun fibers are electrostatically charged; for this reason, non-woven electrospun materials can be exploited in respiratory protective devices, since their properties are similar to those of electret fibrous materials commonly used in face masks. In fact, face masks and respirators owe their incredibly high efficiency to different filtration mechanisms, among these, the electrostatic filtration plays an important role, being responsible for the protection against viruses and other particles that are smaller than the ones that could be retained by size exclusion.
In this work, a novel electrospun material for face mask able to provide both effective protection and comfort was developed. Polyvinylidene fluoride (PVDF) was chosen for its polarized structure and high charge stability. A commercial layer of spunbond polypropylene (PP), commonly used for face masks production, was selected and coated with PVDF ultrafine fibers, then coupled with a second spunbond PP layer. Surgical face masks were then tailored starting from this composite material. The electrospun filter was thoroughly characterized and its features were optimized to meet the requirements of the current regulation for face masks (EN14683:2019) in terms of differential pressure and bacterial filtration efficiency. Because of their architecture, traditional microfiber filters are usually associated with high pressure drops, thus resulting in a poor breathability. Instead, these face masks demonstrated to block more than 98% of bacteria and, at the same time, offer a respiratory resistance way lower with respect to the commercial surgical masks, providing an effective advantage in terms of comfort for the wearer and representing a promising alternative to traditional solutions.

B.7 Poly(lactic Acid)/Poly(ethylene Adipic Acid) Copolymers for Paclitaxel Delivery

EVANGELIA BALLA, Evi Christodoulou, Dimitrios Bikiaris

Aristotle university of Thessaloniki

Controlled drug delivery is a developing field, promising to improve the efficacy of pharmaceutical treatments and limit their secondary effects. In this context, aliphatic polyesters, and notably poly(lactic acid) (PLA) and poly(lactic-co-glycolic acid), have gained much attention. Among the different criteria to select a polymer for drug delivery, biodegradability is a crucial issue, as the accumulation of the polymeric carrier in the body can pose significant health risks. In the present study, PLA/poly(ethylene adipic acid) (PEAd) copolymers were prepared to modulate PLA slow degradability. Two PLA/PEAd copolymers with different ratios were prepared *via* reactive melt mixing and characterized by infra-red and by nuclear magnetic spectroscopy. The enzymic hydrolysis of these copolymers and their cytotoxicity were comprehensively assessed. Finally, the preparation of nanoparticles via oil/water emulsification - solvent evaporation method was also investigated. These copolymers exhibited interesting characteristics and Paclitaxel-loaded nanoparticles will be further prepared.

B.8 N-Isopropylacrylamide-based Composite Hydrogels Containing Carbon Nanotubes: Synthesis by Two-Step Photopolymerization and Characterization

Gianluca Ciarleglio, Elisa Toto, M.Gabriella Santonicola

Department of Chemical Engineering Materials Environment (DICMA), Sapienza University of Rome

Biocompatible and conductive polymer hydrogels are the subject of intensive research in the bioengineering field because of their use in bioelectronic devices and for the fabrication of electro-responsive tissues and drug delivery systems. In this study, we report the synthesis of conductive nanocomposite hydrogels consisting of a poly(N-isopropylacrylamide) (pNIPAM) matrix embedding carboxyl-functionalized multi-walled carbon nanotubes (MWCNT-COOH) using a novel two-step photopolymerization method**.** Functional hydrogels with controlled hydrophilicity and conductivity were prepared varying the carbon nanotube concentration in the range 0 - 3 wt. %. The thermo-responsive properties of the NIPAM-based nanocomposite hydrogels were measured by differential scanning calorimetry with both ultrapure water and PBS solution as swelling liquid. Results show that the endothermic peak associated with the temperature-dependent volume phase transition (VPT) shifts to higher temperatures upon increasing the concentration of the nanotubes, indicating that more energy is required to dissociate the hydrogen bonds of the polymer/filler network. In PBS solution, the swelling ratios and the VPT temperatures of the nanocomposite hydrogels are reduced as a result of salt-induced screening of the oppositely charged polymer/filler assembly, and the electrical resistivity decreases by a factor of 10 with respect to the water-swollen hydrogels.

B.9 Curcumin-Usnic Acid-Loaded Electrospun Nanofibers Based on Hyaluronic Acid as Potential Targeted Drug Delivery System

Petr P. Snetkov, Svetlana N. Morozkina, Roman O. Olekhnovich, Vladislava I. Klimshina, Mayya V. Uspenskaya

ITMO University

Modern medicine urgently needs for safe drug delivery systems. Biopolymers, especially polysaccharides, are the optimal matrix for the development of such systems. For example, hyaluronic acid binds to various cell receptors and regulates not only biological responses, and also, when loaded with the drugs, provides safe effects on the target organ.

Natural substances such as polyphenolic drugs have a wide range of biological activities such as antiviral, antibacterial, anti-inflammatory, etc. At the same time, such compounds have practically no side effects, which opens their wide use in the various fields of medicine. A significant disadvantage of such compounds is their hydrophobic nature, which limits application. The use of biopolymer matrices leads to significant increase of their solubility and bioavailability.

Electrospun nanofibers are one of the most promising types of targeted delivery systems. Electrospinning is a highly efficient method for the nanofibers formation from either polymer solutions or melts. However, the fabrication of polysaccharide-based fibers is difficult, and researchers use different approaches and methods, such as toxic co-solvents, modifying polymers, etc.

The paper presents the results of the development and investigation of nanofibrous systems based on native hyaluronic acid with different loading well-recognized biologically active agents, such as curcumin and usnic acid. Note that no modifying polymers were used to fabricate the fibers and no toxic catalysts were used to create the bioactive complex “polymer matrix-bioactive substances”. Particular attention is given to the technological parameters that affect both the stability of the electrospinning and the morphological characteristics of the fibers.

This finding is expected to broad the comprehension of the hydrophobic drug loading and electrospinning process of hydrophilic biopolymers like hyaluronic acid, which results in the development of modern drug delivery systems.

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B.10 Synthesis and Characterization of Dacarbazine Loaded Chitosan Polymersomes

Alina Gabriela Rusu[1], Aurica P. Chiriac[1], Loredana Elena Nita[1], Vera Balan[2]

[1] Natural Polymers, Bioactive and Biocompatible Materials Laboratory, "Petru Poni" Institute of Macromolecular Chemistry, 41A Gr. Ghica–Voda Alley, 700487, Iasi, Romania
[2] Faculty of Medical Bioengineering, Grigore T. Popa University of Medicine and Pharmacy of Iasi, 700115 Iasi, Romania

Over the years self-assembled polymeric systems have been utilized as drug delivery carriers [1, 2]. Amphiphilic polysaccharides, like glycopeptides composed of hydrophobic and hydrophilic segments, have the ability to self-assemble into core–shell systems with tunable size, nanostructures called polymersomes [3]. They are versatile carriers that can encapsulate not only hydrophilic, but also hydrophobic drugs with a high encapsulation efficiency [4]. Moreover, this unique platform has the ability to integrate both drug delivery and medical imaging capabilities, holding promise for more effective treatments. In this study, we designed a polymersome system for the controlled release of dacarbazine (DCB) as an antineoplazic drug with the main objective of improving the loading efficiency of the drug as well as achievement of an efficient control on the release rate of the drug from the new network. In the main step, the synthesis of a functionalized chitosan-*g*-poly(L-leucine) (MAC-pLeu) system was realized, and its self-assembly into polymersomes was achieved by employing the solvent shift method. To widen the potential of these nanocarriers in cancer therapy, magnetic nanoparticles immobilized with an oxidative enzyme (glucose oxidase – GOx) were loaded in the MAC-pLeu polymersomes. The new nanocarriers were characterized from their physico-chemical and morphological point of view. The size and shape of the pristine polymersomes and the ones containing also GOx-immobilized magnetic nanoparticles were studied by dynamic light scattering (DLS) and transmission electron microscopy (TEM). Furthermore, degradability was studied by incubating the polymersomes with lysozyme and after loading dacarbazine in the magnetic polymersomes, the drug release process was assessed. The obtained results indicated that these magnetic polymersomes have a great potential to be utilized in cancer therapy.

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References

[1] J.J. Milligan, S. Saha, I.C. Jenkins, A. Chilkoti, Genetically encoded elastin-like polypeptide nanoparticles for drug delivery, Current Opinion in Biotechnology, 74 (2022) 146–153.

[2] C.A. Stevens, K. Kaur, H.-A. Klok, Self-assembly of protein-polymer conjugates for drug delivery, Advanced Drug Delivery Reviews, 174 (2021) 447–460.
[3] A. Brito, S. Kassem, R.L. Reis, R.V. Ulijn, R.A. Pires, I. Pashkuleva, Carbohydrate amphiphiles for supramolecular biomaterials: Design, self-assembly, and applications, Chem, 7 (2021) 2943–2964.
[4] M. Hasannia, A. Aliabadi, K. Abnous, S.M. Taghdisi, M. Ramezani, M. Alibolandi, Synthesis of block copolymers used in polymersome fabrication: Application in drug delivery, Journal of Controlled Release, 341 (2022) 95–117.

B.11 Hydrogels Based on Amino Acids and Gelling Polymers

Alexandra Croitoriu, Alexandru Mihail Serban, Aurica P Chiriac, Alina Gabriela Rusu, Alina Ghilan, Loredana Nițǎ

Petru Poni Institute of Macromolecular Chemistry Grigore Ghica Voda Alley 41-A, RO-700487 Iasi, Romania

Physical gels are an attractive class of soft and responsive materials which present high potential for use in various applications due to their special and unique properties. The gels applications in the biomedical field are severely limited by their low mechanical performance. Nevertheless, a multicomponent approach offers the possibility to generate enhanced mechanical properties and functionality for this class of materials. Developing hydrogels based on polymers with high capacity of gelation and amino acids (polypeptides) is an effective way to improve the mechanical behavior and biocompatibility of this soft material class. The aim of this study is to enhance the properties of hydrogels based on amino acids by addition of polysaccharides (agarose) in the system network. The new hydrogels were characterized by Fourier-Transform Infrared and UV-VIS spectroscopic analyses, thermal analysis and scanning electron microscopy. The used methods of characterization provided as well a better understanding of the gelation process, the nature of the intermolecular interactions, and of the dynamics and morphology of the new synthesized hydrogel systems.

Acknowledgments

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References:

[1]. Norioka, C., Inamoto, Y., Hajime, C., Kawamura, A., Miyata, T., A universal method to easily design tough and stretchable hydrogels, *NPG Asia Materials*, **2021,** 13(1), 13-34.

[2]. Nowak, B., & Ravoo, B. J., Photoresponsive hybrid hydrogel with a dual network of agarose and a self assembling peptide. *Soft Matter*, **2020**, 16, 7299-7304.

[3]. Cui, J., Puza, F., Zheng, Y., Han, L., & Xue, L., Physical Entanglement Hydrogels: Ultrahigh Water Content but Good Toughness and Stretchability, *Polymer Chemistry*, **2020**, 11, 2339-2345.

B.12 3D Printed Thermosensitive Antibacterial Patches for Wound Healing Applications

Zoi Terzopoulou[1], Ioanna Koumentakou[1], Anna Michopoulou[2], Dimitrios N Bikiaris[1]

[1] Laboratory of Chemistry and Technology of Polymers and Dyes, Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
[2] Biohellenika Biotechnology Company, Leoforos Georgikis Scholis 65, 555 35, Thessaloniki, Greece

The skin is the largest organ of the body, accounting for about 15% of the total body weight in adults. Surgeries, traumas, abrasions, burns and other factors which cause cutaneous wounds require effective treatment to prevent morbidity or mortality. Wound healing is an intricate process and wound dressings form a significant segment of wound care management.
3D printing has shown great potential assisting and promoting the wound healing process. 3D printing facilitates the production of more flexible matrices, possessing well defined architecture and physical orientation. A wide range of biocompatible synthetic and natural polymeric hydrogels have been used for the fabrication of 3D printed dressings.
In this study, a 3D printed hydrogel based on chitosan (CS), gelatin (Gel), Pluronic and polycaprolactone (PCL) was developed for wound dressing application. CS is a naturally derived polymer, non-toxic and biodegradable. It promotes the proliferation of osteoblasts and mesenchymal stem cells, while it also presents antimicrobial and hemostatic properties. Gelatin was selected to improve the printability of chitosan and the tissue repair capacity of the dressing due to its cell adhesion, migration, and proliferation abilities. The hydrogel was reinforced with nontoxic, biodegradable, and biocompatible synthetic polymers Pluronic and PCL to improve the mechanical properties of the dressings. Different ratios of CS, Gel, PCL and Pluronic were used to synthesize hydrogels for 3D printed patches.
The successful synthesis of hydrogels was confirmed by FTIR spectroscopy, their crystallinity was studied by XRD, and their thermal properties were studied using DSC. Moreover, the swelling in water and the stability of the 3D printed patches were investigated.
This research has been co-funded by the European Regional Development Fund (ERDF) and from national resources through the Operational Program "Competitiveness, Entrepreneurship and Innovation", NSFR 2014-2020, under the call "Aquaculture"-"Industrial materials"-"Open innovation in culture" (project code: Т6УВП-00288).

B.13 Fabrication of 3D Printed Thermosensitive Dressings for Wound Healing Applications

Ioanna Koumentakou[1], Zoi Terzopoulou[1], Anna Michopoulou[2], Dimitrios Bikiaris[1]

[1] *Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki*
[2] *Biohellenika Biotechnology Company*

Three-dimensional printing has seen rapid technological development over the last two decades. 3D printed patches are fabricated for tissue engineering applications, promising solutions for medical treatments, particularly for the healing of chronic wounds. 3D printing technology fabricates scaffolds with flexible matrices with high precision, possessing well-defined architecture and physical orientation. A wide range of biocompatible synthetic and natural polymeric hydrogels have been used for the fabrication of 3D printed dressings. In this study, a 3D printed hydrogel based on chitosan (CS), gelatin (Gel), Pluronic (Pl) and poly (vinyl alcohol) (PVA) was developed for wound dressing application. CS is a naturally derived polymer, non-toxic and biodegradable. It promotes the proliferation of osteoblasts and mesenchymal cells, while it also presents antimicrobial and hemostatic properties. Gelatin was selected to improve the printability of chitosan and the tissue repair capacity of dressing due to its cell adhesion, migration, and proliferation ability. The hydrogel was reinforced with nontoxic, biodegradable, and biocompatible synthetic polymers thermosensitive Pl and PVA to improve the mechanical properties of the dressings.

The successful synthesis of hydrogels was confirmed by FTIR spectroscopy, their crystallinity was studied by XRD and their thermal properties were studied from DSC thermograms. Moreover, the water swelling and stability capacity of 3D printed patches were investigated.

Acknowledgement

This research has been co-funded by the European Regional Development Fund (ERDF) and from national resources through the Operational Program "Competitiveness, Entrepreneurship and Innovation", NSFR 2014-2020, under the call "Aquaculture"-"Industrial materials"-"Open innovation in culture" (project code: Τ6ΥΒΠ-00288)

B.14 Langmuir-Blodgett Technique - A Research Method Helpful in the Design of Biocompatible Coatings for Implants

Klaudia Szafran, Małgorzata Jurak, Agnieszka Ewa Wiącek

Department of Interfacial Phenomena, Institute of Chemical Sciences, Faculty of Chemistry, Maria Curie-Skłodowska University in Lublin, Poland

The Langmuir-Blodgett (LB) technique makes possible to obtain thin films with an ordered and strictly defined structure. One of the fields in which LB technique can be used is tissue engineering (TE). TE is an interdisciplinary science whose task is to regenerate and maintain or improve the functioning of tissue. The materials employed in TE should be non-toxic and biocompatible. One of the polymers applied in TE is polyethylene terephthalate (PET). However, due to hydrophobicity, and poor biocompatibility its usage is limited. To improve properties its surface should be modified. An example is the LB deposition of biological or biologically active substances, such as phospholipid 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC), chitosan (Ch), cyclosporine A (CsA) and/or lauryl gallate (LG). DOPC occurring in natural membranes can improve the compatibility of the implant, as well as imitate membrane-artificial material interactions. Ch is widely used in TE as a scaffold which has ability to transport and release drugs, e.g. CsA. CsA is a strong immunosuppressant applied to prevent transplant/implant rejection. However, CsA-treatment causes extensive production of reactive oxygen species harmful to the body. To avoid this side effect, LG with antioxidant activity can be used.

The aim of studies was to examine the properties of PET surface, covered with the Ch film, and mixed DOPC-CsA-LG monolayers by means of the LB method. Using the LB technique allows to design and characterize biocompatible coatings with desired topography, molecular orientation and chemical composition, as well as wettability. Such properties that define the implant biocompatibility can be determined by atomic force microscopy, time-of-flight secondary ion mass spectrometry and contact angle measurements.

The carried out studies confirmed effective LB deposition of layers onto PET substrate as well as the effect of the type and quantity of compounds present in the layer on the change of polymer wettability and surface topography.

B.15 CO_2 Capture and Separation, the First Step toward Circular Economy; a Regenerable, Bio-Based, Polymerized, Ionic Liquid Membranes

Sergio Bocchini[1], Silvia Mazzotta[2, 3], Giulio Latini[1]

[1] *Istituto Italiano di Tecnologia, Center for Sustainable Future Technologies*
[2] *Istitutor Italiano di Tecnologia, Center for sustainable future technologies*
[3] *IUSS Scuola universitaria superiore Pavia*

Air can be considered as a source of CO_2, with concentrations of approximately 408 ppm reported in 2018 and predicted levels expected to reach 600−1550 ppm in 2030. Direct air capture (DAC) from the atmosphere is considered as a CO_2 separation technology that can be realized and a source of CO_2 exploitable as building block for utilization. The use of solid amines for CO_2 adsorption following a two-steps process: the adsorption of CO_2 from the direct air and the separation of CO_2 from the sorbent. The separation of CO_2 from amines is relatively easier than from strong liquid bases as it requires less energy due to the weaker bonds between CO_2 and the solid sorbent. The benefit of the DAC technology is that it can be implemented anywhere because of the fast mixing of CO_2 in the air. However this technique rely on the preparation of amine sorbed on solid inorganic substrate such as silica substrate and even if durable are quite difficult to regenerate once spent. Our substrate is based on polymerized ionic liquid that use as functional amino acid anions as active sorbent.

Ionic liquids (ILs) are organic salts that melts below 100°C been studied as innovative material for CO_2 capture. Polymerized ionic liquids (PILs) merge ILs and macromolecules peculiarities resulting in a novel class of material that features high tunability and ionic exchange ability as well as easier handling, processability typical of polymer. PILs have been studied for gas separation and demonstrated, higher CO_2 loading than common ILs, as well as faster absorption/desorption rate. However, despite the chemical absorption of CO_2 in ILs is a well-established concept divided as capture by chemisorption or by physisorption in PILs the majority of the studies focus on material without CO_2 reactive species and no explicit reference to chemical nor physical sorption materials.

Different PILs with amino acid anions were developed and tested for CO_2 absorption in solid phase. The research on PILs aimed to explore different AA anions as well as different polymeric structures. Ionic exchange procedures were tuned depending on the solubility property of the starting PIL with several AA. All synthetic procedures aimed to avoid toxic and hazardous chemicals. Obtained PILs were identified and were tested for CO_2 and water absorption and desorption.

B.16 SBS-Based Anion Exchange Membranes for Water Electrolysis

Andrea Roggi[1], Marco Turriani[1], Elisa Martinelli[1], Gabriele Agonigi[2], Antonio Filpi[2]

[1] *University of Pisa*
[2] *Enapter s.r.l*

Producing hydrogen using anion exchange membrane (AEM) water electrolysis is a promising approach to address the severe energy crisis facing human society. AEM electrolysis can be integrated with intermittent and renewable energy sources, utilize low-cost electrocatalysts and other inexpensive components in stacks. To enable commercially viable hydrogen generation, improvement of the AEM component is imperative. In recent years, various polymeric systems have been studied for the development of innovative AEM with increased ionic conductivity, water transport, mechanical robustness, chemical and thermal stability and reduced hydrogen crossover and cost.[1,2] However, the goal of fabricating a membrane, in which all these requirements are combined and optimized in a synergistic way, still represents a challenging task that nowadays limits the large-scale application of AEM technology.[2,3] The present work was, therefore, aimed at addressing several unique features of AEM for implementation in an industrially scalable, cost-effective and sustainable energy- production process through a suitable synthetic strategy that involved the post-modification of a commercially available poly(styrene)-*b*-poly(butadiene)-*b*-poly(styrene) triblock copolymer (SBS) matrix by grafting side chains of vinylbenzyl chloride (VBC), which provides functional groups that are easily convertible into quaternary ammonium cationic groups. The obtained SBS-based graft copolymers were, therefore, used for the fabrication of AEM by solution casting followed by quaternization reaction with trimethylamine (TMA) for the quantitative conversion of $–CH_2Cl$ into $–CH_2(CH_3)_3N^+$ groups. Obtained films were thermally, mechanically and electrochemically characterized. By varying the VBC functionalization degree of the copolymer it was possible to modulate the ionic exchange capacity, conductivity, water uptake and mechanical properties of the membrane derived therefrom. Several key properties were found to be comparable or even better than those of the commercial *benchmark* membrane. The more promising polymers and membranes were selected for testing in electrolytic cells under real operating conditions.

References:

[1] M. Mandal, *ChemElectroChem* **2021**, *8*, 36–45.
[2] D. Henkensmeier, M. Najibah, C. Harms, J. Žitka, J. Hnát, K. Bouzek, *J. Electrochem. Energy Convers. Storage* **2021**, *18*, DOI 10.1115/1.4047963.
[3] H. A. Miller, K. Bouzek, J. Hnat, S. Loos, C. I. Bernäcker, T. Weißgärber, L. Röntzsch, J. Meier-Haack, *Sustain. Energy Fuels* **2020**, *4*, 2114–2133.

B.17 Hydrolysed Polyacrylamide Adsorption onto Calcium Carbonate

Jin Hau Lew[1], Paul F. Luckham[1], Omar K. Matar[1], Erich A. Müller[1], Myo Thant Maung Maung[2]

[1] *Imperial College London*
[2] *PETRONAS Research Sdn Bhd*

The strengthening of carbonate rocks using chemical techniques is a mitigation strategy to prevent excessive fines migration during oil and gas production. We provide herein a study of the adsorption of hydrolysed polyacrylamide (HPAM) onto calcium carbonate ($CaCO_3$) particles to provide information on the plausible applicability of this chemical treatment. In this study, three types of HPAM of different molecular weight (F3330S, 11-13MDa; F3530S, 15-17MDa; F3630S, 18-20MDa;) were adsorbed onto $CaCO_3$ particles, and the results are compared to different adsorption isotherm and kinetic models. The adsorption of all three HPAMs onto $CaCO_3$ is best described by Langmuir isotherm with very high relation coefficient ($R^2 > 0.97$). The equilibrium parameter (R_L) also ranges between 0 and 1, which suggests that HPAM adsorbs favorably in the form of a monolayer onto $CaCO_3$. The adsorption also follows pseudo-second order kinetics which indicates the interaction of HPAM with $CaCO_3$ is largely dependent on the adsorbate concentration. The optimum HPAM adsorption time is also studied by stirring the HPAM – $CaCO_3$ mixtures for 1h, 6h, 18h, 24h and 72h. Results indicate that HPAM adsorption reached its maximum after 18h of stirring, with negligible increment beyond this stir time. The effect of HPAM molecular weight was also studied by plotting the adsorbed amount of polymer against polymer concentration. Results show that the amount of HPAM adsorbed onto $CaCO_3$ at equilibrium increases with higher polymer molecular weight; the equilibrium adsorbed values for F3330S, F3530S and F3630S are approximately 0.24 mg/m^2, 0.31 mg/m^2, and 0.43 mg/m^2, respectively. Zeta potential analysis shows that $CaCO_3$ has a zeta potential of +12.32 mV, which transitions into negative values upon introducing HPAM. The point of zero charge (PZC) is observed at HPAM dosage between 10 to 30 ppm, in which the pH here lies between 9–10.

B.18 A Facile and Ecofriendly Synthesis of Polymer Brushes Bearing Pyridine Groups

Anna Hatalak, Artur Wójcik, Karol Wolski

Jagiellonian University, Faculty of Chemistry, Department of Physical Chemistry and Electrochemistry, Nanoengineering of Functional Polymeric Materials Group, Cracow, Poland

Polymer functionalized surfaces find applications in many fields, such as biomedicine and electronics. In comparison to traditional polymer coatings, polymer brushes have highly-ordered structure and nanometric sizes. They consist of densely packed polymer chains with extended conformation attached by one end to the substrate. Polymer brushes are usually synthesized by reversible deactivation radical polymerizations (RDRPs) where atom transfer radical polymerization (ATRP) plays the major role.
However, copper-based ATRP is problematic in case of polymerization of some challenging monomers such as pyridine-based ones that demonstrate high complexation affinity of transition metal ions. Moreover, modern approaches in the synthesis of polymer brushes are focused on increasing their environmental friendliness in accordance with the rules of green chemistry. This can be done by reducing the number of reagents or replacing harmful compounds by nontoxic ones.[1]
In response to that, we present a facile and controlled strategy for decoration of solid substrates by polymer brushes bearing pyridine groups eliminating toxic copper compounds from the polymerization solution. The developed strategy allowed the synthesis of thick brushes (up to 100 nm) within short reaction times with minimal consumption of reagents. The obtained materials were post-polymerization functionalized by quaternization of pyridine groups via alkyl halides modifying the properties of the initial films. The prepared brushes were characterized by, inter alia, grazing-angle Fourier transform infrared spectroscopy (GA FT-IR) and atomic force microscopy (AFM).

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References
[1] Ślusarczyk, K., Flejszar, M., Chmielarz, P. *Polymer* **2021**, *233*, 124212.

B.19 Recycling Liquid Glass Modified Waste-Lignin Into Bio-Based Polyurethane Foam Composites for Building Materials Industry

Agnė Kairytė, Saulius Vaitkus, Sigitas Vėjelis, Giedrius Balčiūnas, Arūnas Kremensas

Vilnius Gediminas Technical University, Faculty of Civil Engineering, Institute of Building Materials, Laboratory of Thermal Insulating Materials and Acoustics

Local governments around the world are pursuing pretentious zero waste policies with the aim to reduce methane and CO_2 emissions, release of solid particles to the atmosphere and minimize the waste which are landfilled. Lignin, as a secondary raw material for the wood industry, is obtained by hydrolysis of polysaccharides (cellulose) from shredded wood. It landfilled in Lithuania as a precursor for further use in the production of biofuel, as a binding material for straw briquettes and wood pellets and as a substrate for plants as it improves the soil structure. Furthermore, lignin is characterized by favorable properties such as low water permeation and mechanical support and can have even wider application areas such as building materials industry. Theoretically, lignin particles can be immobilized in polymer matrices such as bio-based rigid polyurethane (PUR) foams. However, existing hydroxyl groups in lignin cause expansion and dimensional instabilities. Consequently, the present study investigates the possibility of "locking" the hydroxyl groups on the surface of lignin particles by using liquid glass and vacuum infusion technique. The obtained PUR foam composites with 2.5-10% unmodified lignin particles had by ~15% lower tensile strength, by ~60% reduced compressive strength and unfavorable dimensional changes at 7.5% and 10% lignin particles while liquid glass infusion technique led to significant improvements of the mentioned properties and enabled the incorporation of higher amounts of particles. Moreover, thermal conductivity value of PUR foam composites with liquid glass modified lignin particles was in the range of (0.026÷0.028) W/(m·K) while water absorption was not affected indicating effective thermal insulation and moisture barrier behavior.

B.20 Investigating Adipic Acid as a Green Alternative for the Synthesis of Biobased Unsaturated Polyester Resins.

Lazaros Papadopoulos [1], Alexandra Zamboulis [1], Christina Kyriakou-Tziamtzi [1], Stavros Tsompanidis [2], Nikos Athanasopoulos [2], Electra Papadopoulou [3], Konstantinos Chrissafis [1], Dimitrios Bikiaris [1]

[1] *Aristotle University of Thessaloniki*
[2] *PHEE*
[3] *CHIMAR HELLAS SA*

Management of plastics has grown into a challenge for our society. On one hand, single use plastics have contributed substantially to the accumulation of waste in landfills and oceans, poisoning the environment through microplastics formation. On the other hand, crude oil, the primary raw material for plastics production, is a nonrenewable resource whose price has been fluctuating along with its projected availability. Therefore, the need for the development of polymers from renewable resources, the so-called bio-based polymers, has emerged.
Among others, unsaturated polyester resins (UPRs) are one of the most used polymer classes today. They are linear polycondensation products which contain unsaturated double bonds in the polymer backbone. They are then combined with unsaturated monomers, called reactive diluents, to create three dimensional networks via radical polymerization, which can be thermally or UV induced. The aim of this work is the production of novel UPRs based on adipic acid, a biobased monomer with a huge market and environmental potential. Several characterization methods were utilized to examine the physicochemical properties of the materials.

B.21 Turning Additive Manufacturing Green: Exploring the Potential of Biobased Polyester Resins Into UV 3D Printing Applications.

Lazaros Papadopoulos [1], Tobias Robert [2], Dimitrios Bikiaris [1]

[1] *Aristotle University of Thessaloniki*
[2] *Fraunhofer WKI*

Additive manufacturing (AM), also known as three-dimensional (3D) printing, is a production technique for products of high customization regarding their size, shape, and design. Guided by Computer Aided Design (CAD) software, objects are printed layer by layer, achieving accuracy and significantly less waste material compared to traditional processing techniques.
AM can employ different types of polymers, depending on the specifications of the 3D printer. In UV-curing processes, polyester- and polyurethane acrylates are widely used. However, acrylic acid based materials can possess allergenic and irritation potential, can be volatile and toxic, especially at low molecular weights, while also not being produced from renewable resources. Therefore, alternative biobased monomers and resins are of high interest.
In this work, we developed unsaturated polyester resins, of high biobased content, and studied their properties and printability with a DLP 3D printer. To this end, monomers from renewable resources were utilized for the synthesis of the polyesters, like itaconic acid, succinic acid and 1,3-propanediol. The produced resins were evaluated regarding their physicochemical properties and the thermomechanical properties of materials produced via 3D printing were characterized.

B.22 Extraction Of Olive-Tree Byproducts Biomass And Its Characterization For Wood-Based Panels

Georgia Michailidou[1], Theopoula Asimakidou[2], Electra Papadopoulou[3], Konstantinos Chrissafis[2], Dimitrios Bikiaris[1]

[1] Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Macedonia, Greece
[2] Solid State Physics Section, Physics Department, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece
[3] CHIMAR HELLAS SA, 15 km National road Thessaloniki-Polygyros, 57001 Thermi, Thessaloniki, Greece

The awareness of the worldwide population into the exploitation of nature along with the environmental crisis has led to an ever-growing need for eco-friendly, biobased products. Since the wood processing industry is a key pillar to the world economy, substitution of wood with lignocellulosic materials derived from agricultural crops in furniture and interior constructions is mandatory. Through this perspective, the present project aims into the application of olive-tree byproducts including small branches, olive leaves, and olive-pomace into the production of particleboards and adhesive mixtures for plywood panels. Furthermore, extraction of the olive wastes will be conducted, with the intention to further utilize the high-value organic compounds in new applications. The water swelling capacity of the various olive-tree byproducts will be evaluated through swelling measurements. In a further step, the surface of extracted and non-extracted byproducts will be examined in detail through scanning electron microscopy while element analysis will be performed via energy dispersive X-ray analysis. Finally, the chemical structure of both extracted and non-extracted byproducts will be assessed through infra-red spectroscopy and X-ray diffraction analysis. Our X-ray diffraction analysis, infra-red and swelling results indicate the high quality of the derived from olive-tree wastes biomass which is suitable for further application in particleboards and plywood.

Acknowledgements
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B.23 Comparison of Enzymatic Hydrolytic Mechanisms on Different Bio-Based Plastics

Chiara Siracusa [1], Felice Quartinello [1], Alessandro Pellis [2], Georg M Guebitz [1]

[1] *Austrian Centre of Industrial Biotechnology (Acib)-Tulln an der Donau Address: Konrad-Lorenz-Straße 20, 3430 Tulln an der Donau*
[2] *Università degli Studi di Genova | UNIGE · Department of Chemistry and Industrial Chemistry*

Among the recently developed bioplastics, poly (butylene 2,5-furanoate) (PBF) and poly (1,4-butylene 2,5-thiophenedicarboxylate) (PBTF) are particularly promising. They can be stretched in films, they reach the thermal and mechanical features of the petrol-derived polyesters yet fulfilling "green" polymer requirements. These bioplastics can be derived at large scale from biomass, without the accumulation of toxic bioproducts and polyesters derived from 2,5-furandicarboxylic acid (FDCA) are faster decomposed by enzymes than the terephtalic acid (TA) based counterparts [1].
Upon the introduction of new bio-based materials, the next future goal is optimizing and customizing the protocols for an efficient decomposition. To close the loop of production and recycling, an environmentally friendly degradation based on enzymes is the strategy of choice [2].
The results of the incubation of PBF and PBTF films with two commercial cutinases, *Humicula insolens* cutinase (HiC) and *Thermobifida cellulosilytica* cutinase 1 (Thc_Cut) demonstrated a similar amount of released products, quantified through High Performance Liquid Chromatography (HPLC), but a slightly faster rate for PBF films. Furthermore, a closer investigation directed towards the surface by Scansion Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FT-IR) analysis suggested a different mechanism of hydrolysis performed by the enzymes. PBF appears to be degraded in an exowise manner, unlike the PBTF films. The structure itself of PBF establishes more interchain interactions, that could explain the different behaviour of the enzymes on these substrates [3].

References

[1] Pellis A, Haernvall K, Pichler CM, Ghazaryan G, Breinbauer R, Guebitz GM. Enzymatic hydrolysis of poly(ethylene furanoate). J Biotechnol. 2016 Oct 10;235:47-53. doi: 10.1016/j.jbiotec.2016.02.006. Epub 2016 Feb 17. PMID: 26854948.
[2] Maurya A, Bhattacharya A, Khare SK. Enzymatic Remediation of Polyethylene Terephthalate (PET)-Based Polymers for Effective Management of Plastic Wastes: An Overview. Front Bioeng Biotechnol. 2020 Nov 19;8:602325. doi: 10.3389/fbioe.2020.602325. PMID: 33330434; PMCID: PMC7710609.
[3] Gigli M, Quartinello F, Soccio M, Pellis A, Lotti N, Guebitz GM, Licoccia S, Munari A. Enzymatic hydrolysis of poly(1,4-butylene 2,5-thiophenedicarboxylate) (PBTF) and poly(1,4-butylene 2,5-furandicarboxylate) (PBF) films: A comparison of mechanisms. Environ Int. 2019 Sep;130:104852. doi: 10.1016/j.envint.2019.05.046. Epub 2019 Jun 10. PMID: 31195223.

B.24 A Circular Economy Approach: Efficient Cellulases Recovery in Enzymatic Polymer Separation

Sophia Mihalyi [1], Felice Quartinello [2, 3], Georg Guebitz [1, 3]

[1] *University of Natural Resources and Life Sciences, Vienna, Department of Agrobiotechnology, IFA-Tulln, Institute of Environmental Biotechnology, Konrad-Lorenz-Strasse 20, 3430 Tulln an der Donau, Austria*
[2] *University of Natural Resources and Life Sciences Vienna, Department of Agrobiotechnology, IFA-Tulln, Institute of Environmental Biotechnology, Konrad Lorenz Straße 20, 3430 Tulln an der Donau, Austria*
[3] *Austrian Centre of Industrial Biotechnology, Konrad Lorenz Strasse 20, 3430 Tulln an der Donau, Austria*

Separation of polymer blends is a challenging task in circular economy approaches. Textile waste often consists of blended fibers that require specific targeting for fiber separation in recycling processes. Enzymatic hydrolysis enables specific depolymerization of e.g. natural fibers (cellulose) in blends with synthetics (polyester) and thus recovery of the building blocks for valorization approaches. Cellulosic fibers can be specifically hydrolyzed by cellulases that are commercially available. However, their recycling in textile depolymerization and separation processes would reduce cost and resource requirements. Only 1 % of textile waste is recycled into new clothes and 87 % is being landfilled or incinerated in Europe [1]. To contribute to the progression towards increased textile-to-textile recycling this concept enables the reutilization of remaining synthetic fibers after hydrolysis of the natural fibers for textile production through fiber re-spinning. It was shown in this study, that the economic impact of the textile industry could be further reduced by reutilization of the cellulases for at least five times in cellulose depolymerization processes without decreasing the enzymatic activity and hydrolysis yield. The cellulase activity was measured through the filter paper assay still displaying 95 % of the initial activity in the fifth cycle. The recovered glucose concentration was detected through HPLC analysis, indicating the release of equal glucose concentrations between the primary hydrolysis experiment and the fifth round with recovered enzymes. Therefore, the recycling of cellulases is feasible in a textile recycling process to save costs and resources and contribute to the development towards a circular bioeconomy.

Reference:

[1] European Parliament. https://www.europarl.europa.eu/news/en/headlines/society/20201208STO93327/the-impact-of-textile-production-and-waste-on-the-environment-infographic. (Accessed 07.01.2022)

B.25 Formation of Antibacterial Polylactide-Based Films With an Addition of Berberine As Potential Food Packaging Materials

Ewa Olewnik-Kruszkowska[1], Magdalena Gierszewska[1], Agnieszka Richert[2]

[1] Nicolaus Copernicus University in Toruń, Faculty of Chemistry, Gagarina St. 7, Toruń, Poland
[2] Nicolaus Copernicus University in Toruń, Faculty of Biological and Veterinary Science, Lwowska St. 2, Toruń, Poland

Recently, antimicrobial food packaging starts to be one of the most innovative concepts of active packaging where interactions with the product are envisioned to reduce, inhibit or delay the growth of microbes, which may be present in the packed food or on the surface of the packaging materials, and extend the shelf life of the preserved foodstuffs. Such films are commonly produced by incorporating active antimicrobial compounds, e.g. quercetin or tee tree essential oil - into conventional polymeric materials [1,2]. One of the possible food preservatives is berberine. Berberine is an abundant flavonoid, widely present in nature, with numerous biological properties, and used as a potent antioxidant. Polylactide (PLA) was chosen to be used as a biodegradable matrix derived from renewable resources such as corn or sugar beet. Currently, biodegradable packaging materials made of PLA are considered an alternative solution for reducing the ecological problems that are caused by petroleum-based plastic packaging. Furthermore, PLA-based packaging materials have been regarded as safe which places them in a unique position in terms of applications in the food processing industry. Taking into account the biodegradable properties of polylactide and biocidal capacity of berberine, novel antibacterial films were formed. Structural, thermal, and mechanical properties of obtained materials were analyzed. Moreover, the antibacterial properties of PLA-based films, with the addition of berberine, were also evaluated. It was established that the introduction of 1wt% berberine into a polylactide matrix is sufficient to obtain materials impeding the proliferation of *Staphylococcus aureus* and *Escherichia coli*.

Literature:
[1] Materials 2021, 14(7), 1643.
[2] Materials 2020, 13(21), 4953

B.26 Nanocellulose Based Materials: Barrier and Viscoelastic Properties.

Sara Dalle Vacche

Politecnico di Torino, Torino, Italy

Nanocellulose, in the form of microfibrils or nanocrystals, has emerged as a sustainable biobased material with interesting applications in several domains. Nanocellulose can be processed in the form of films, which can be used for packaging. While in dry environments their mechanical and barrier properties are satisfactory, these materials are very sensitive to moisture. To overcome this issue, nanocellulose can be mixed with polymeric matrices to produce composite films, tuning their permeability and mechanical resistance.
In this work, the viscoelastic properties and the permeability to oxygen and water vapor of nanocellulose films based either on commercial wood-derived microfibrillated cellulose (MFC) or on nanocellulose obtained from hemp waste through an original defibrillation procedure (HNC) are characterized. Then the nanocellulose fibrils are combined with polymeric matrices, that can undergo photoinduced crosslinking, including biobased ones derived from soybean oil and cardanol, to obtain nanocellulose/polymer composite materials. Their photocrosslinking is followed by infrared spectroscopy. Then, the main parameters influencing the dynamic mechanical behavior and gas barrier properties of the composite materials are investigated, namely the polymer/cellulose ratio, the type of cellulose and of polymeric matrix, the crosslinking of the matrix.

B.27 Microliter Scale Synthesis of Polymer Nanobrushes Based on Poly(3,4-propylenedioxythiophene).

Justyna Bała, Gabriela Grześ, Karol Wolski

Jagiellonian University, Faculty of Chemistry, Department of Physical Chemistry and Electrochemistry, Gronostajowa 2, 30-387 Cracow, Poland

Rapid development of polymer chemistry and the wide range of potential applications of polymeric materials result in discovering innovative methods for synthesis of well-defined structures and complex polymer architectures. One of them are polymer nanobrushes which can be described as nanostructured materials made of stretched, densely packed polymer chains, covalently attached with one end to the substrate. Polymer brushes can be used in many various applications e.g., to change surface properties such as wettability, friction or electrical resistance. Due to this fact, a particularly important task is to optimize their synthesis leading to a decrease in costs and the negative impact of the whole process on the environment.
This work demonstrates an efficient method that allows obtaining polymer brushes based on poly(3,4-propylene-1,4-dioxythiophene) in microliter volumes via light mediated organocatalyzed atom transfer radical polymerization (O-ATRP). The produced nanobrushes were analyzed and characterized using Atomic Force Microscopy (AFM) and Fourier Transform Infrared Spectroscopy. The presented synthesis route allowed obtaining of well-defined polymer structures based on poly(3,4-propylene-1,4-dioxythiophene) with adjustable thickness and high grafting density showing conductive properties. This microliter scale technique, mediated by light and organic-based catalyst allowed to exclude toxic transition metals and hence material's contamination by these compounds. Furthermore, it should be noted that the economic and ecological aspects of the demonstrated method follow the trends of sustainable chemistry.

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B.28 Eco-Friendly Synthesis of a New Copolymacrolactone Amphiphilic System

Aurica P. Chiriac[1], Loredana Elena Nita[2], Alina Gabriela Rusu[2], Alexandru Serban[2], Florica Doroftei[2]

[1] *Petru Poni Institute of Macromolecular Chemistry*
[2] *Institutul de chimie macromoleculara Petru Poni, Iasi, Romania*

The growing interest for the ring-opening polymerization of macrolactones is entire justified and derived from the sustainable or renewable feed stocks for these monomers. They are able to conduct to preparation of new potentially degradable polymeric materials boasting a diversity of properties that allow various applications including in the biomedical field due to the biocompatibility of the synthesised compounds. Recently we synthesized poly(ethylene brassylate-co-squaric acid) (PEBSA) copolymer by ring-opening of ethylene brassylate macrolactone and condensing with squaric acid, a process performed in 1,4 dioxane homogeneous system. [1] The amphiphilic behaviour of the copolymer allowed the entrapment of thymol, and the antimicrobial activity of the new bioactive complex was confirmed against eight different reference strains. The present investigation was carried out in the context of the necessity for environmental friendly polymer materials preparation for sustainable development. PEBSA copolymer can be successfully included in this category due to the biobased ethylene brassylate comonomer and also owing to the biodegradability of the synthesised copolymacrolactone system. The presented study was devoted to the aqueous dispersion preparation of the PEBSA copolymer by using Na dodecylbenzene sulfonate as anionic tensioactive compound. The copolymer chemical structure was confirmed by spectroscopic analyses, while the microstructure was evaluated by SEM micrographs. Comparative data concerning the molecular weight and the size measurement of PEBSA samples synthesised by the two methods are presented.

References

1. Chiriac, A.P.; Rusu, A.G.; Nita, L.E.; Macsim, A.M.; Tudorachi, N.; Rosca, I.; Stoica, I.; Timpu, D.; Aflori, M.; Doroftei, F. Synthesis of Poly(Ethylene Brassylate-Co-squaric Acid) as Potential Essential Oil Carrier, Pharmaceutics, 2021, 13, 477. https://doi.org/10.3390/pharmaceutics13040477

B.29 Innovative Nonwovens with Addition of Feathers for Agricultural Applications

Krystyna Wrześniewska-Tosik [1], Tomasz Mik [2], Ewa Wesołowska [2], Tomasz Kowalewski [2], Michalina Pałczyńska [2], Damian Walisiak[2]

[1] Lukasiewicz Research Network- Institute Biopolymers and Chemical Fibres
[2] ŁUKASIEWICZ Research Network-Institute of Biopolymers and Chemical Fibres, Lodz, Poland

The aim of research is the manufacture innovative feather-based nonwovens characterised by added functionalities and advantages derived from the use of feather keratin such as: tailor-made biodegradation adjusted to the crops duration, input on organic nitrogen to the soil, zero waste at their end of life and cost competitive materials. The nonwovens obtained by needle punching method consists of wool and feather-based keratin fibres and can be used for agricultural applications.

There are many reasons why developed nonwovens are suited for agricultural uses:

- Friendly to the environment and human health ensuring the reduction of biomass waste in the form of feathers, deposited and polluting the environment.
- Biodegradability - the developed innovative nonwovens are made of biodegradable raw materials of natural origin
- Ability to control the time of microbial decomposition by the share of feather fractions in the nonwoven
- High efficiency with low financial outlay - market price of the developed products, due to the fact that they are made of waste materials, will be much lower than that of fossil based products
- Fertilizing properties - nonwovens made of waste natural resources can be used in 100% as soil improvement agents, because they contain significant amounts of fertilizing ingredients in their structure which are used to meet the nutritional needs of crops.

Elaborated nonwoven, due to above mentioned functionalities can improve productivity and efficiency of agricultural production, increase crop yield and reduce the need for pesticides.

B.30 Structure and Physical Properties of Biopolymer Glass Composites Prepared with Ionic Liquids

Teodoro Klaser [1], Luka Pavic [1], Željko Skoko [2], Ana Šantić [1]

[1] *Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia*
[2] *Department of physics, Faculty of science, Bijenička cesta 32, 10000 Zagreb, Croatia*

Over the past decade, a significant research effort has been directed toward developing biopolymers obtained from renewable raw materials which would replace environmentally harmful synthetic polymers. Generally, biopolymers such as starch, cellulose, chitosan, zein, gelatin or polylactic acid (PLA) offer many benefits but their poor mechanical properties often limit their application. In order to overcome this disadvantage and produce an environmentally friendly polymer with superior physicochemical properties, various composites with different combinations of matrix biopolymer and fillings have been developed. Also, biopolymers generally have low solubility in conventional solvents, so for the preparation of biopolymer-based materials novel class of solvents called ionic liquids (IL) has been used. ILs are low-temperature molten salts composed of bulky organic cation and smaller inorganic or organic anion which are considered ideal “green” solvents for synthesis and catalysis due to their non-volatility, non-flammability, and chemical and thermal stability.

In this work, we present a series of composites based on polylactic acid (PLA) and different glass fillers (bioglass, phosphate-based glasses containing various alkali and transition metal oxides, glass waste from Kelteks company) prepared using imidazolium- and pyrrolidinium-based ILs as solvents. The thermal, structural, mechanical and electrical properties of these novel composites were thoroughly studied using differential scanning calorimetry (DSC), X-ray diffraction, microscopy techniques, IR spectroscopy and impedance spectroscopy. The results show that selected ILs efficiently dissolve PLA and can be used in the preparation of PLA-glass composites with various (micro)structural and physical properties.

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B.31 Chitosan Films Crosslinked with Dialdehyde Starch as Novel Food Packaging Materials

Magdalena Gierszewska, Ewa Olewnik-Kruszkowska

Nicolaus Copernicus University in Toruń, Faculty of Chemistry, Gagarina St. 7, Toruń, Poland

The food packaging industry comprises almost a fifth of the entire net revenue of the plastic industry, mainly due to the ease of processing, low cost, and low density of synthetic polymers (e.g. polyethylene terephthalate, high-density polyethylene, polypropylene) that are widely used in the packaging manufacturing process [1]. Many of these materials are not easily recyclable and are difficult to degrade completely in nature, creating environmental problems. This problem can be solved by substituting these polymers with natural, easily biodegraded ones [2]. Along with biodegradability, biopolymers will mitigate the migration of health-hazardous additives into the food and in some cases, provide an additional benefit of having antibacterial properties. Chitosan, a biopolymer obtained through chemical deacetylation of chitin, is one of such promising polymers [3].

Many researchers have obtained chitosan-based films by casting, coating, layer-by-layer assembly, etc., and succeeded in modifying their characteristics. Moreover, they have added other functional materials into chitosan to produce composite films with enhanced, e.g. preservative, properties. As neat chitosan films do not present reasonable physical properties from the package industry point of view like tensile strength and elasticity, many efforts are needed to develop the chitosan-based films to meet the practical application criteria and can successfully compete with the petroleum-based packaging films.

The main problem arises from the solubility of Ch-based films in contact with water and aqueous media, in many cases the main components of food.

The aim of this study assumes the possible crosslinking of the Ch with natural starch derivative, dialdehyde starch (DAS), to prevent Ch films swelling and solubility in an aqueous environment. The chemical structure, surface morphology, mechanical properties of Ch/DAS films was evaluated. Special attention was devoted to the swelling properties in different external fluids (water, biological buffers, simulated food fluids).

B.32 Making ATRP Greener: Light-Mediated Synthesis of Functional Polymer Brushes

Kamila Chajec, Monika Słowikowska, Joanna Smenda, Karol Wolski

Jagiellonian University, Faculty of Chemistry, Department of Physical Chemistry and Electrochemistry, Gronostajowa 2, 30-387 Cracow, Poland

Polymer chains attached by one chain end to a substrate (called polymer brushes) are of great interest due to their interesting properties and applications in many fields such as biomedicine (e. g., for controlled drug release). Several polymerization techniques are used to obtain these polymer nanostructures using the "grafting-from" approach. One of the most popular is atom transfer radical polymerization (ATRP). Until recently, classical ATRP has mainly been studied for copper-based catalysts, but their negative impact on the environment has forced the need to develop new synthetic techniques that are compatible with "green chemistry".

In response to this challenge, we developed two simple variations of the visible light-mediated ATRP methods for facile decoration of flat inorganic substrates. The first one, surface-initiated photo-ATRP with iron-based catalyst (SI-photo-Fe-ATRP), was used for the synthesis of poly(methyl methacrylate) (PMMA) brushes, allowing the replacement of deleterious copper compounds and minimizing the amount of catalyst to only 200 ppm. In contrast, a second surface-initiated atom transfer radical polymerization with a photoactive organic catalyst (O-SI-ATRP) was used to synthesize poly(3-trimethylsilyl-2-propyl methacrylate) brushes with more sophisticated architecture using only microliter volumes of reagents. Additionally, it allowed elimination of transition metals from the entire process. Both polymerizations were carried out in order to obtain highly ordered layers with adjustable thicknesses. The brushes were examined by atomic force microscopy (AFM) and FT-IR spectroscopy.

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B.33 Biodegradation of Polystyrene via *Zophobas Morio* Larvae and Guts Deriving Bacteria

Edoardo Miravalle [1], Sabela Balboa Mendez [2], Ana Maria Otero Casal [2], Marco Zanetti [1], Massimo Lazzari [2]

[1] *University of Turin*
[2] *University of Santiago de Compostela*

Polystyrene (PS) is one of the most produced and used polymers worldwide, and its degradation or biodegradation are matters of great interest. The interaction of different larvae with PS is already known in the literature and, in this study, particular attention was attributed to the superworm *Zophobas Morio* and its gut's bacteria. The ability to live on a sole polymer diet was assessed during a 28-day-period, and parameters like survival rate and plastic consumption were evaluated. PS ingestion and degradation were defined by analyzing the frass by ATR-FTIR and NMR spectroscopies and size exclusion chromatography (SEC). Following the guts of the larvae were retrieved, and the bacteria contained were used to evaluate degradation activity on the surface of PS disks on a novel agar-bacteria-plastic interface. The degradation has been carried out on isolated strains and consortia, and its effects were evaluated via ATR-IR analysis after implementing a specially developed cleaning process without aggressive reagents. SEM and confocal images have been acquired to understand the degradation process better. A two-month enrichment process in a PS rich aqueous media has been performed in different conditions to refine the degrading consortia. In conjunction with this process and during the other phases of the study, changes in consortia composition were evaluated by metabarcoding analysis, which revealed the presence of strains not previously reported in literature. Finally, the enriched consortia were used in a 30-days respirometry test in which the production of CO_2 was monitored via GC-MS analysis, and the degradation process on PS was followed by SEC analysis.

B.34 Biodegradable Plastics: Revisiting the Science and Offering a New Sustainable Solution

Yelena Kann

Radical Plastics Inc.

Limited ability of current biodegradable plastic technology to address increasing amount of plastic waste in the natural environment calls for additional research in this area. This presentation analyzes the limitations and problems of current biodegradable plastics and offers a new approach to achieve environmental biodegradation. According to the presented research, addition polymerized plastics, such as polyethylene and polypropylene, biobased or petroleum based, can be re-designed with a novel, natural, non-toxic fine mineral-based redox catalyst. The proposed catalyst promotes oxidative abiotic degradation of the mentioned polymers and is based on abundant fine mineral matter which was identified through the zero-waste initiative and has a unique chemical and morphological composition. The abiotically degraded plastics are then enzymatically degraded at ambient conditions by natural soil microorganisms which convert them to biomass, water, and carbon dioxide. These plastics, redesigned with the proposed catalyst, are still mechanically recyclable, but will not accumulate as waste if leaked into the environment. The redesigned plastics could alternatively be used in applications requiring functional soil biodegradability, e.g., agricultural mulch films, which are used to increase crop yield, reduce water, energy and fertilizer usage.

The proposed technology offers the most sustainable and economical solution compared with other developments, is scalable, and can be easily implemented.

The data demonstrating how the efficiency of oxidation can be dramatically improved with the proposed catalyst will be provided. We hope to provoke additional ideas in this area of science which has high relevance to achieving sustainability goals and reducing plastics pollution. We will only achieve our lofty sustainability goals and solve this global plastic pollution crisis if we are willing to open the aperture of approaches.

B.35 Novel Bio-Based Indirect Polyurea Resins

Liudmyla Gryshchuk [1], Sergiy Grishchuk [2], Maurice Gilberg [1]

[1] *Leibniz-Institut fuer Verbundwerkstoffe GmbH, Erwin-Schroedinger-Strasse 58, 67663 Kaiserslautern, Germany*
[2] *Kaiserslautern University of Applied Sciences, Carl-Schurz-Str. 10-16, 66953 Pirmasens, Germany*

Many available plastics are made from petroleum-based resources. The substitution of these materials in plastics production by sustainable bio-based materials is of high public and economic interest. One type of resin suitable as alternative component in bio-based materials is the indirect polyurea (IPU) resin. IPU is a two component organomineral resin containing an isocyanate (diphenylmethane diisocyanate -PMDI), water glass (WG) and an emulsifier to achieve a stable water-in-oil emulsion. It is applied e.g. as matrix for fiber reinforced composite liners in construction applications. IPU is a cold-curing reactive resin and is primarily processed into fiber-reinforced plastics by hand lamination. In the past, organic phosphate esters were used as emulsifiers, which might unfortunately release ecologically harmful phosphates into the environment. The replacement of the esters by bio-oils resulted in an improvement of properties as well as the increase of bio-content in IPU.
Our current research focused on the development of novel IPU formulations using bio-based materials. The resin formulations were adapted for the rheological properties requirements of a resin infusion process. For this purpose, several bio-based emulsifiers like mustard seed oil, linseed oil and cardanol based products were applied. As key requirements the reduction of viscosity and the reaction speed together with an increase of pot life were realized. With the novel bio-based emulsifiers, the reaction could be slowed down. The reference resin showed a viscosity of 24 Pa*s after one hour and with mustard seed oil as emulsifier it was reduced to 4 Pa*s. By adding terpenes as bio-based additives the viscosity was reduced to a value below 1 Pa*s, and thus it is in a range that allows the processing by infusion. As further benefit, by substitution of petroleum-based products with bio-based materials improvements in the mechanical properties of IPU could be reached.

B.36 Fabrication of Microcrystalline Cellulose/ZnO Hybrid Composite by Hydrothermal Synthesis and Its Application in Rubber Compounding

Supparoek Boopasiri, Chomsri Siriwong

Department of Chemistry, Faculty of Science, Khon Kaen University

With great concern of environmental threats, attempts have been made to reduce the consumption of zinc oxide (ZnO) in rubber products. This research aims at fabricating a new type of ZnO by depositing ZnO on microcrystalline cellulose (MCC) surface using an ultrasonic-assisted hydrothermal process. The concentration ratio of $Zn(NO_3)_2$ to NaOH is varied from 1:1 to 1:4. The obtained products, namely MCC-ZnO, are characterized by various techniques such as FESEM, FTIR, XRD, BET, and TGA. Results show that the amount of deposited ZnO and the specific surface area of MCC-ZnO increase continuously with increasing NaOH concentration. The MCC-ZnO (1:3) containing approximately 55.6 wt% of deposited ZnO is selected for investigating the curing efficiency in natural rubber (NR) and compared with the commercial ZnO (C-ZnO). Obviously, the state of cure progressively increases with increasing either MCC-ZnO or C-ZnO content. At the same content, MCC-ZnO exhibits a significantly higher crosslink density than C-ZnO leading to the superior elasticity and mechanical properties. This could be explained by the greater specific surface area and, thus, the higher reactivity of MCC-ZnO. Clearly, a considerably lower quantity of MCC-ZnO is required to attain a similar level of crosslink density or mechanical properties as compared to C-ZnO.

B.37 Influence of the Nanoadditive on the Structural and Thermal Properties of Polypropylene/SiO_2 Composites for Heating/Cooling Pipe Systems

Eleftheria Xanthopoulou [1], Evangelia Delli [2], Dimitrios Gkiliopoulos [3], Konstantinos Chrissafis [4], Dimitrios N Bikiaris [5]

[1] Department of Chemistry, Aristotle University of Thessaloniki,GR-541 24,Thessaloniki, Greece
[2] Physics Department, Aristotle University of Thessaloniki, GR-541 24, Thessaloniki, Greece
[3] Laboratory of Chemical and Environmental Technology, Department of Chemistry, Aristotle University of Thessaloniki, Greece
[4] School of Physics, Laboratory of Advanced Materials and Devices, Aristotle University of Thessaloniki, GR-541 24, Thessaloniki, Greece
[5] Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, Greece

Nowadays, polyolefins, such as polyethylene and polypropylene, are a series of polymeric materials that are extensively used in piping networks to substitute metallic systems owing to their unique properties, such as lower weight, and superior resistance to abrasion and chemical corrosion. Nevertheless, the low thermal conductivity and mechanical properties of these polymers in comparison to counterpart metal materials utilized in these systems limit their advantages, creating a necessity for further advancement. In this context, the development of polymer-matrix composites has raised the interest of both academic and industrial communities towards the preparation of materials with enhanced physicochemical and mechanical properties. Herein, the structural and thermal properties of polypropylene (PPR112)/SiO_2 composites were investigated. Five materials with different filler concentrations (from 1-15 %wt.) were prepared via melt-mixing. The structural features of the composites were examined with the implementation of multiple techniques such as X-ray Diffractometry (XRD) and Fourier-transform Infra-red spectroscopy (FTIR), while Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Polarized Light Microscopy (PLM) were applied to assess the thermal characteristics of the synthesized polymers.

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B.38 Preparation and Characterization of Pyrenyl Terminated Polycaprolactones for the Development of and Nanocomposites and Nanopapers Based on Graphite Nanoplates

Giacomo Damonte[1], Alberto Vallin[1], Daniele Battegazzore[2], Alberto Fina[2], Orietta Monticelli[1]

[1] Dipartimento di Chimica e Chimica Industriale, Università degli studi di Genova, Via Dodecaneso 31, 16146 Genoa, Italy
[2] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino-sede di Alessandria, Viale Teresa Michel, 5, 15121 Alessandria, Italy

This work focused on the development of novel polymers based on polycaprolactone (PCL), with suitable features to be combined with graphene and related materials (GRM) for the preparation of nanocomposites and nanopapers, i.e. materials characterized by a predominant amount of polymer and GRM, respectively. Indeed, polymers with different architecture, linear or star-shaped, and molecular mass were synthesized, all ending with a pyrene group, namely a functionality that can promote specific interactions with the GRM surface. The specific interactions occurring between the synthesized pyrenyl terminated PCL and graphite flakes, were confirmed by UV measurements. A linear polymer (Pyr-PCL) was applied as polymer additive in the development of nanocomposites based on a commercial PCL and graphite nanoplates (GNP). In this case, the interaction pyrene/GNP turned out to affect the nanofiller dispersion in the nanocomposites. Indeed, with respect to the systems prepared by directly adding GNP to the molten polymer, the addition of Pyr-PCL allowed to obtain a finer dispersion and stronger adhesion of GNP to the polymer matrix. It is relevant to underline that Pyr-PCL-compatibilized nanocomposites exhibited better electrical conductivity than that reported in the literature for other PCL/graphite systems. A star polymer, terminated with four pyrene moieties, was exploited in the preparation of GNP-based nanopapers. The pyrenic functionalities and the peculiar polymer shape allowed not only specific interactions with the surface of graphitic flakes but also promoted their binding, thus favouring the formation of tightly packed GNP systems. Nanopapers, prepared starting from solution containing the functional polymer, showed much higher ductility and higher thermomechanical resistance compared to those based on the neat GNP, while maintaining elevated thermal diffusivity. Beside the application as low temperature heat exchanger materials, several other exploitations may be envisaged, including in the biomedical field, taking advantage of the biocompatibility and degradability of the PCL chains.

B.39 Experimental Study and Additive Model to Predict Rheological and Mechanical Properties of Reprocessed Monopolymer Blend

Francesco Paolo La Mantia[1,2], Maria Chiara Mistretta[1], Vincenzo Titone[1,2]

[1] Department of Engineering, University of Palermo, Viale delle Scienze, 90128 Palermo, Italy
[2] INSTM, Via Giusti 9, 50125 Firenze, Italy

A very popular operation in the plastic industry is to mix virgin polymer with the same reprocessed polymer coming from their scraps. In this work, a polypropylene random copolymer sample, under commercial name Hostalen PP H5416, was reprocessed in a single screw extruder until five successive extrusion cycles. Virgin polymer was mixed with 30% of recycled polymer. This reprocessed fraction contained different amounts of polymer reprocessed more times. Tensile properties tests were carried out using in an Instron (Instron, UK) universal testing machine (mod. 3365) according to ASTM D638. The rheological characterization was performed using an ARES G2 (TA Instruments, USA). In order to predict the rheological and mechanical properties of monopolymer blends made from virgin and reprocessed components an additive model has been proposed:

$P(Ri) = xP(A) + (1-x)[xP(_{Ai-2})+(1-x)(xP(_{Ai-1}) + (1-x)P(A_i))]$

where P(A) is the property of the virgin sample and P(Ai) that of the polymer extruded i times. The results obtained showed that the Newtonian viscosity is reduced with increasing the amount of reprocessed material and with increasing the number of reprocessing steps present in the monopolymer blend. The elongation at break shows the same feature of the Newtonian viscosity. It decreases with increasing the amount and the number of reprocessing steps of reprocessed component in the monopolymer blend. The theoretical values of Newtonian viscosity, of the elongation at break and of the other mechanical properties fit well the experimental values.

B.40 Hemp Fibers Modified with Graphite Oxide as Green and Efficient Solution for Water Remediation

Gianluca Viscusi, Elena Lamberti, Francesca D'Amico, Giuliana Gorrasi

Department of Industrial Engineering University of Salerno

A novel system based on the use of an agro-based waste material, such as hemp fibers modified with graphite oxide, has been fabricated as an innovative and sustainable adsorbent for the removal of organic dye (methylene blue) from aqueous solutions. The amount of dye was found to be highly dependent on pH regime, initial concentration of dye, ionic strength and slightly dependent on temperature. The pH level has important bearing on adsorption content indicating that weak electrostatic interactions could exist between cationic dye and electron rich sites of surface. The experimental data follow a pseudo second order model whose parameters allowed to evaluate the activation energy of the process at pH=7.5 and C_0=5 mg/L. The evaluation of thermodynamic parameters allowed to state that the process is little endothermic, even if at room T a very high recovery % has been obtained. The DoE methodology combined with analysis of regression was applied in evaluating the previsional model based on experimental data and optimizing the conditions of maximum adsorption of MB. Regeneration studies showed 5% drop in adsorption capacity after 7 cycles. The produced adsorbent is chemically stable, showing no noticeable leaching of GO. It follows that hemp fibers modified with carbons could be used as an easily available adsorbent. A small amount of adsorbent was able to completely decolorize an aqueous solution of MB (5 mg/L-35 mg/L) just after 2 h. So, it is raising up as an alternative for costlier adsorbent materials used in waste water treatment processes.

B.41 Novel Polyurethane Binders Designed for ‘Green’ Composite Energetic Materials

Gabriela Toader[1], Florin Marian Dirloman[1], Traian Rotariu[1], Andreea Elena Moldovan[1], Raluca Elena Ginghina[2], Aurel Diacon[3], Edina Rusen[3]

[1] *Military Technical Academy*
[2] *Research and Innovation Center for CBRN Defense and Ecology*
[3] *Faculty of Applied Chemistry and Materials Science, University ‘Politehnica’ of Bucharest*

The current study highlights the development of a set of novel polyurethane polymers that can be used as binders for 'green' composite energetic materials. These new binders were synthesized by employing the polyester - polyols resulted from the degradation of polyethylene terephthalate (PET) waste. Because inappropriate disposal of PET has resulted in significant environmental damage in recent years, our research proposes a PET recycling option in an attempt to address some of these difficulties. Polyurethanes obtained from PET degradation products (polyols) were afterwards used as binders in a variety of rocket propellant composites that also included 'green' oxidizers. The polyurethane networks were softened with an energetic plasticizer (triethylene glycol dinitrate, TEGDN) to improve the exothermic decomposition performances of these rocket propellants and to generate composites with the appropriate mechanical behavior. Our subscale rocket motor experimental investigations (Figure 1) showed that the developed ecologically friendly composites can be successfully utilized as ‘green’ rocket propellants. Specific analytical tools were used to characterize the components of the energetic formulations: 1H - NMR, FT-IR, SEM-EDX, DTA and TGA, tensile and compression tests, DMA, and micro-CT.

B.42 Benzothiadiazole Based Poly(rod-coil) Polymers as Promising Materials for Mechanical Oriented Films with Polarized Emission

Benedetta Maria Squeo [1], Fabio Bertini [1], Guido Scavia [1], Michela Unsleghi [2], Ettore Fois [3], Mariacecilia Pasini [1], Chiara Botta [1]

[1] Istituto di Scienze e Tecnologie Chimiche "G. Natta", Consiglio Nazionale delle Ricerche, CNR-SCITEC, via Corti 12, 20133 Milan, Italy
[2] IASF-INAF via A. Corti 12, 20133 Milano, Italy
[3] Department of Science and High Technology, University of Insubria and INSTM, 22100, Como, Italy

Thin organic films with polarized emission properties are ideal materials for OLED applications requiring polarized electroluminescence, such as backlights for commercial LC displays. Polarized emission can be obtained by macroscopic orientation of an organic film composed by linear-chain conjugated molecules or polymers, which are intrinsically anisotropic.
Generally, system possessing liquid-crystal (L-C) properties can easily oriented by mechanical force, in this context we have designed and synthesized small molecules based on the highly emissive benzothiadiazole moiety to produce oriented films with polarized emission in the green/yellow and red regions. The scarce film forming properties combined with poor morphological stability of the molecules led to the development of suitable polymeric materials.
Here we propose the unusual approach of poly(rod-coil) polymers based on alternate definite conjugated and non-conjugated segments. The alkyl chains are optically inactive while the conjugated rod acts as photoactive polymeric core assuring the necessary optical properties are retained. We interconnect the conjugated molecule with long alkoxy soft linkers via Suzuki coupling. The thermal analysis of the polymers evidences a LC behavior that strongly depends on the length of the non-conjugated alkyl segments and the polymer molecular weight. The optical properties of the polymers in solution are identical to those of molecule. Films oriented by mechanical rubbing display absorption anisotropies and emission polarization up to 5. According to the chromophore molecular structure, the oriented films display either stable (polymers) or mechano-sensitive (molecules) polarized emissions with fluorescence efficiencies up to 1.

C.1 The Fabrication of PVA - Chitosan Nanofibers by Electrospinning Method as Drug Delivery System for Mangiferin

Thi Hong Nhung Vu, Svetlana N. Morozkina, Petr P. Snetkov, Mayya V. Uspenskaya

ITMO University

The development of new safe targeted drug delivery systems for biologically active compounds, especially for not water-soluble natural antioxidants, which have the wide range of applications from the treatment of diseases of the gastrointestinal tract to diabetes and obesity, - is very actual last decade due to unique properties of natural antioxidants for the prevention of many diseases, because they affect mainly by modulation of immune system. One of the most powerful natural antioxidant is mangiferin, which is isolated from the leaves, bark, stem, fruit peel and root of Mangifera indica (mango), and is also found in many other plants.

Since its isolation from mango (*Mangifera indica L.,* family *Anacardisaceae*) in 1908, many studies have been carried out to elucidate its structure and biological effects as well *in vitro* as *in vivo*. Mangiferin is a xanthonoid or more specifically it is a glucoside of norathyriol.

In folk medicine, plants rich in mangiferin are used to treat various diseases: cardiovascular diseases, various infections, hypoglycemia, burns, liver diseases, and many types of cancer. All *in vitro* and *in vivo* studies confirm that mangiferin has excellent biological activity but until now this compound has not received enough attention. The reason for this is the low solubility and low oral bioavailability of mangiferin.

In order to overcome these disadvantages and at the same time increase the drug's targeting to diseased cells, we have developed and successfully fabricated PVA- chitosan nanofibers loaded with mangiferin. By using electrospinning with an aqueous solvent of a mixture of acetic acid and ethanol, we obtained PVA – chitosan - mangiferin filaments approximately 105 nm in size.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (agreement № 075-15-2021-1349).

C.2 Cellular and Mechanical Performance of 3D-Printed Poly(Lactic acid) and Cocoa Bean Shell-based Bone Scaffolds

Andres J. Garcia-Brand[1, 2], Alejandro Maranon[3], Carolina Muñoz-Camargo[1], Juan C. Cruz[1], Alicia Porras[2]

[1] Department of Biomedical Engineering, School of Engineering, Universidad de los Andes
[2] Grupo de Diseño de Productos y Procesos (GDPP), Department of Chemical and Food Engineering, School of Engineering, Universidad de los Andes
[3] Structural Integrity Research Group, Department of Mechanical Engineering, School of Engineering, Universidad de los Andes

Bone scaffolds fabricated using additive manufacture has significant advantages in providing porous structures with customizable architectures that could be further explored as bone fillers. The prevalent biomaterials for the three-dimensional (3D) printing of bone fillers remain to be amorphous polymers such as polylactic acid (PLA) and polycaprolactone (PCL) filled with calcium phosphates and nanostructured materials. However, despite the cutting-edge alternatives that intend to improve surface bioactivity and bone microenvironment mimicking, there are still issues regarding the limited cell attachment and their low tensile and compressive strength. Therefore, a promising avenue to overcome these issues is the use of polysaccharide-rich filler such as natural fibers (NFs), that have demonstrated improving tensile properties and antioxidant potential of synthetic polymers without compromising their biocompatibility, as is the case of cocoa bean shells (CBS). Hence, this work combined the fabrication of a sustainable and low-cost PLA and CBS filled composite with a Fused Deposition Modeling (FDM) approach via filament-based 3D printing to fabricate bioactive cylindrical bone scaffolds. The composite material was characterized by their tensile properties and compressive performance of the cylindrical scaffolds, together with an *in vitro* osteoblasts cell attachment and proliferation. The results showed tunable the tensile and compressive strength by the inclusion of CBS, approaching that of trabecular bone. *In vitro* assays studied by phalloidin and DAPI staining of human osteoblast exhibited an increase of cell attachment, distribution and proliferation after 7 days in the PLA/CBS composites. Compared with other PLA-based composites used for 3D printing approaches of bone fillers, the manufactured PLA/CBS composites provides a low-cost, eco-friendly and bioactive alternative to overcome lack of bioactivity and low mechanical performance of polymeric bone scaffolds that could be further explored to encourage a personalized approach for bone failures.

C.3 Determination of the Cross-linking Density and Monomer Composition of Cyclodextrin-based Nanosponges: a Multiple-Method Approach

Gjylije Hoti, Fabrizio Caldera, Claudio Cecone, Alberto Rubin Pedrazzo, Yousef Khazaei Monfared, Adrián Matencio, Francesco Trotta

Department of Chemistry/University of Turin

Cyclodextrin (CD)-based nanosponges (NSs) are extensively studied due to their particular characteristics. The degree of cross-linking is a fundamental property of this polymer network, especially in the applications of CD-based NSs as drug delivery systems, but its determination has been a very challenging task. The water absorption capacity (WAC) (1526 g H_2O/g dry sample), Flory-Rehner theory, and rheology have strongly shown that the final CD-based NSs network exhibited a cross-linker content-dependent behavior [1], [2]. In addition to these, the understanding of the monomer reactivity ratios is the key to estimating the polymer composition and tailoring polymers with applicable physicomechanical properties [3].

Therefore, this research aimed to further broaden the current knowledge of the structure-property correlation of NSs through the esterification cross-linking of β-CD with varying pyromellitic anhydride (PMDA) content (2, 3, 4, 5, 6, 7, 8, 9, and 10 moles of PMDA for each mole of β-CD), as a cross-linker, in a simple one-pot synthesis. The monomers (β-CD and PMDA) reactivity ratio was investigated for the first time. Fourier transform infrared spectroscopy (FTIR), potentiometric titration and zeta potential, and methylene blue adsorption, give positive evidence that the crosslinking reaction resulted in ester linkages and carboxylic acid groups. By the application of thermogravimetric and elemental analyses (TGA and EA), the monomer reactivity ratio is experimentally determined using a system of linear equations. The polymer network composition (βCD: PMDA-based NSs) exhibited strong linearity (assessed in terms of correlation coefficient (R^2) value of 0.9761) between the theoretical and experimental values of monomers' molar ratio, as the theoretical monomer molar ratio increased, the experimental one increased at a constant rate. This detailed study confirmed that the composition of the final polymeric network depends on monomers (β-CD and PMDA) reactivity ratios, respectively the quantity of cross-linker added. This is an essential study for tailoring novel polymeric systems with the prospect of increasing their exploitation in a countless number of industrial applications.

References

[1] G. Hoti et al., "Effect of the Cross-linking Density on the Swelling and Rheological Behavior of Ester-Bridged β-Cyclodextrin Nanosponges," Materials (Basel)., vol. 14, no. 3, pp. 1–20, 2021.

[2] I. Krabicová et al., "History of cyclodextrin nanosponges," Polymers (Basel)., vol. 12, no. 5, pp. 1–23, 2020.

[3] H. Abdollahi, V. Najafi, and F. Amiri, "Determination of monomer reactivity ratios and thermal properties of poly(GMA-co-MMA) copolymers," Polym. Bull., vol. 78, pp. 493–511, 2021.

C.4 Surface Characterization of Airbrushed Porous Fibrillar Composite Materials Based on Polysulfone (PSF) – Hydroxyapatite (HA).

Dania Olmos, David Ríos, Javier González-Benito

Universidad Carlos III de Madrid

Multifunctional composite materials based on polysulfone (PSF) and hydroxyapatite (HA) were prepared by solution blow spinning (SBS). Solution blow spinning is a versatile processing method that allows obtaining materials which morphology can vary from films to fibrillar or fibrillar mixed with corpuscles [1,2]. In this work, solution blow spinning (SBS) technique is used to prepare composite materials based on polysulfone/hydroxyapatite with potential applications as scaffolds in the field of bone regeneration. Samples with fibrillar morphology were obtained and characterized to evaluate the effect of porosity and particle content in surface properties of the materials. Morphological characterization was done and fiber size distributions were obtained, showing that a slight widening of the fibers occurred when adding the HA nanoparticles. Two different methodologies are proposed to evaluate the porosity of the prepared samples, one based the fraction of area occupied by the pores and another, based on an estimated volume fraction occupied by the pores, being the latter the most appropriate for this type of study. Surface properties were characterized with contact measurements. Finally, it was confirmed that the factors that most affect the surface properties of the materials are composition and porosity.

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References:

L. Daristotle, A.M. Behrens, Anthony D. Sandler, and Peter Kofinas, ACS Applied Materials & Interfaces 8 (51), 34951-34963 (**2016**).

Gao, J. Zhang, *Mater. Horiz.*, ,**8**, 426-446 (**2021**)

C.5 Preparation and Characterization of Biocompatible and Biodegradable Polylactic Acid/poly(ε-caprolactone) Solution Blow Spun Materials

Irene Ramón, Dania Olmos, Javier González-Benito

University Carlos III of Madrid

Among the most common applications of biodegradable polymers, sutures, bioabsorbable implants, stents, materials used in controlled released approaches for drug delivery and more recently, scaffolds for tissue engineering can be highlighted [1]. In this work, two common biodegradable and biocompatible polymers, polylactic acid (PLA) and poly(ε-caprolactone) (PCL), were selected to prepare blends constituted by submicrometric fibers. The materials were prepared by solution blow spinning (SBS), a versatile and very appropriate manufacturing method, specially for this kind of applications where highly porous materials are required. Polylactic acid (PLA) has been widely used in research concerning bone and skin tissue engineering. Poly(ε-caprolactone) (PCL) is used in tissue engineering applications due to its good viscoelastic behavior and its biodegradability [2]. PLA/PCL blends containing different weight percentages of PLA were prepared: PLA (100%); PLA-80 (80%); PLA-60 (60%); PLA-50 (50%); PLA-20 (20%) and PCL (0%). Morphological and structural characterization was carried out to understand the influence of sample composition on the final properties of the materials.

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References

1. Manavitehrani, A. Fathi, H. Badr et al. *Polymers,* 8, 20 (**2016)**.
2. Czarnecka, M. Wojasinski, T. Ciach, P. Sajkiewicz, Materials, 14, 1463, (**2021**).

C.6 Preparation by Solution Blow Spinning and Characterization of Biocompatible Nanocomposites Based on Polylactic Acid (PLA) Filled with Magnetite Nanoparticles

Raúl Reyes Riverol, Javier González-Benito, Dania Olmos

Universidad Carlos III de Madrid

In this work, porous polylactic acid (PLA) modified with magnetite nanoparticles (Fe_3O_4) were produced by solution blow spinning (SBS). Solution blow spinning is a versatile processing method that, under certain conditions, allows obtaining fibrous materials where the constituent fibers may have diameters at nanoscale [1, 2]. Considering that morphology is one of key factors affecting the final performance of this kind of materials one of the main challenges of this work is the preparation of materials with controlled orientation of fibers. For that purpose, from the point of view of processing conditions, two different approaches were used: i) the rotation speed of the collector in the SBS device and ii) the incorporation of different amount of Fe_3O_4 loadings. In the second approach, materials loaded with different amount of Fe_3O_4 nanoparticles were collected at a constant rotation speed but using a collector with a magnet to induce preferential orientation by the corresponding interaction with nanoparticles. Morphological characterization was done by optical microscopy, optical profilometry and scanning electron microscopy (SEM). Image analysis was used to obtain fiber size distributions and orientation as a function of processing conditions and particle content.

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References

Krichen, P. Sharma. *J. Appl. Mech. Trans. ASME*. 83, 1-5 (**2016**).
Gao, J. Zang, Y. Su, et al. *Mater. Horiz.,* 8, 426 446 (**2021**)

C.7 In Vitro Bioactivity and Biocompatibility of Alginate-Pullulan Based Composites

Klara Magyari[1, 2], Alexandra Dreanca[1, 3], István Székely[1, 4], Emma Bobu[4], Emőke Páll[3], Mihai Cenariu[3], Lucian Baia[1, 4, 5], Monica Baia[4, 5]

[1] Nanostructured Materials and Bio-Nano-Interfaces Center, Interdisciplinary Research Institute on Bio-Nano-Sciences, Babes-Bolyai University, T. Laurian 42, 400271 Cluj-Napoca, Romania
[2] Research Group of Environmental Chemistry, Department of Applied and Environmental Chemistry, Institute of Chemistry, University of Szeged, Rerrich B. sqr. 1., 6720, Szeged, Hungary
[3] Faculty of Veterinary Medicine, University of Agricultural Science and Veterinary Medicine, 400372 Cluj-Napoca, Romania
[4] Faculty of Physics, Babes-Bolyai University, M. Kogălniceanu 1, 400084 Cluj-Napoca, Romania
[5] Institute for Research-Development-Innovation in Applied Natural Sciences, "Babes-Bolyai" University, Fântânele 30, 400294, Cluj-Napoca, Romania

Nowadays, polysaccharide-based materials have applications in the biomedical field, such as tissue regeneration, controlled drug delivery systems, and cell immobilization. Alginate and pullulan, two polysaccharides, are able to stimulate tissue repair, are nontoxic, biocompatible and also biodegradable. The aim of the present study was to evaluate the behavior of the alginate-pullulan composites in a simulated environment. To the alginate the pullulan polysaccharides were added in different concentrations, and the composite materials were cross linked in $CaCl_2$ solution. The first step of the composites' analysis was their structural and morphological characterization, followed by *in vitro* bioactivity, biodegradability and *in vitro* biocompatibility studies on osteoblast and fibroblast cells. FT-IR and Raman spectra revealed the cross-linking between the polymers, indicating that oxygen atoms from alginate create hydrogen bonds with pullulan chains, and bivalent calcium cations are strongly chelated by the OH groups of pullulan and carboxyl group of alginate. SEM micrographs indicate that the 1:1 weight ratio of alginate to pullulan composites is too high, and that the pullulan content must be reduced. After 42 days of immersion in simulated body fluid, calcium oxalates appears on the surface of the composites. The polymeric composites displaying higher sensitivity on osteoblasts, whereas the fibroblastic culture remained unaffected, presenting values of concentrations of viable cells near to 100%. Although the composites were successfully synthetized and are practically nontoxic, the appearance of calcium oxalate on their surface after immersion in a simulated biological environment, may affect the material's performance, especially in soft tissue regeneration applications, and f and especially because of this it is important to find the optimal alginate to pullulan ratio. Finding the optimum ratio will result in better performing materials.

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C.8 Xylo-Oligosaccharides Derived from Wheat By-Products as Novel Carbohydrates for Potential Food Applications

Gabriela Precup[1], Bernadette Emőke Teleky[1], Ioana Delia Pop[2], Cristina Bianca Pocol[3], Floricuța Ranga[1], Monika Heierman[4], Roland Schneider[4], Joachim Venus[4], Dan Cristian Vodnar[1]

[1] Faculty of Food Science and Technology, Institute of Life Sciences, University of Agricultural Sciences and Veterinary Medicine, Cluj-Napoca, 400372, CJ, Romania
[2] Department of Exact Sciences, Horticulture Faculty, University of Agricultural Sciences and Veterinary Medicine, Cluj-Napoca, Calea Mănăștur 3-5, 400372 Cluj-Napoca, Romania
[3] Department of Animal Production and Food Safety, University of Agricultural Sciences and Veterinary Medicine, 400372 Cluj-Napoca, Romania; cristina.pocol@usamvcluj.ro
[4] Leibniz Institute for Agricultural Engineering Potsdam-Bornim, Potsdam, Germany

Current challenges of our food security system and increased interest of consumers towards healthier dietary choices triggered developments of novel and alternative foods.
Xylo-oligosaccharides (XOS) are considered non-digestible fibers that attained commercial interest due to their prospective application in the food industry, since they showed low caloric index and good stability at various temperatures and pH. They can be produced by autohydrolysis, chemical and/or enzymatic methods. Associations in the scientific literature linked XOS with potential beneficial health outcomes related to the gut microbiota, thus being reported as emerging "prebiotics".
The present work presents a holistic approach referring to production of biobased XOS from wheat straw by means of alkali, enzymatic treatment, and the combinations thereof, that were further purified with ion-exchange resins. The XOS fractions were assessed in fermentation experiments with *Bifidobacterium bifido* subsp. *lactis* (BB-12) on wheat-flour doughs to investigate the rheological and physicochemical properties for potential applications in bakery products. Additionally, considering that XOS were reported prebiotics, the perception of Romanian consumers on this topic was investigated via an online survey.
The results indicated that an alkaline and enzymatic treatment was suitable for XOS production and soluble sugars. The refining experiments showed efficient removal of salts, phenols and furan derivatives, however further optimization of the treatments is required. Furthermore, the fermentation experiments presented that XOS supplementation increased the viability of BB-12 and positively influenced the rheological properties of doughs. Thus, wheat straw could represent a low-cost source to extract XOS used as potential food ingredients. The lack of a common consensus regarding prebiotics was a potential cause of the scattered confusion among Romanian consumers regarding the concept's meaning. Future research should struggle more to confirm the causality between the health effects of XOS as emerging

prebiotics so that healthcare providers can develop evidence-based recommendations.

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C.9 Linecaps® -based Buccal Films for the Oral Delivery

Shoeb Anwar Mohammed Khawja Ansari, Monica Argenziano, Anna Scomparin, Francesco Trotta, roberta Cavalli

University of Turin

Nowadays, extensive research is being carried out on the design and development of innovative drug delivery systems to improve safety, efficacy, and patient compliance. Among those novel delivery systems, buccal films are an interesting drug administration tool. In particular, buccal films are fast-dissolving dosage form, convenient to swallow and easy to prepare; furthermore, these self-administrable systems can allow for controlled release of the drug. In addition, mucoadhesive buccal films have been developed as a promising and versatile platform being able to prolong the residence time and the drug delivery through the buccal mucosa.
This work aimed at the design and development novel buccal films based on Linecaps®, a biopolymer obtained from pea starch. Structurally it is a maltodextrin rich in linear and soluble amylose. A series of formulations of mucohadesive, drug-loaded buccal films was prepared mixing hydroxyethyl cellulose and Linecaps® at different ratio. Dexamethasone, a corticosteroid with very low water solubility was used as model drug. To incorporate Dexamethasone in the buccal film the drug was complexed with Beta cyclodextrin. The prepared film formulations were characterized by means of film thickness uniformity, folding endurance, weight uniformity, content uniformity, swelling behaviour, percentage moisture loss, tensile strength, percentage elongation, surface pH, in vitro drug release studies and ex vivo mucoadhesion studies on rabbit buccal mucosa. The buccal films produced were uniform in drug content and thickness (ranging from 0.202 to 0.227 mm). All formulations have in vitro release in the range of 6 0–70% in 6 hours. The results suggest that Dexamethasone-loaded Linecaps®-based buccal films might be a potential tool to achieve oral drug release.

C.10 Alkyl Derivatives Of -Cyclodextrin Cationic Polymers: A Novel siRNA Delivery System

Anna Scomparin, Claudio Cecone, Elisa Giorgi, Monica Argenziano, Alfredo Brusco, Francesco Trotta, roberta Cavalli

University of Turin

Cyclodextrin (CD)-containing cationic polymers are expected to be promising tools for the delivery of small therapeutic oligonucleotides such as small interfering RNAs (siRNAs). They should be able to overcome many hurdles of siRNA cellular uptake such as the high molecular weight, polyanionic backbone and nuclease susceptibility. Although nanocarriers based on cationic polymers displayed the advantages of physical protection and colloidal stability, the toxicity associated with their high positive charge remains a challenge for the efficiency of these systems *in vivo*.
A way to enhance the biocompatibility and the cell membrane permeability of these cationic polymers is to design lipid nanoparticles (LNPs). This new generation of delivery systems is composed of both polymers and lipids, thereby acquiring the advantages of both types of molecules. LPNs display high structural integrity and bioavailability, improved encapsulation, loading and efficient cellular internalisation.
The aim of this work was the synthesis, preparation and characterization of new βCD-LNPs by using alkyl derivatives of β-cyclodextrin cationic polymers for the delivery of siRNA.
A novel series of alkyl derivative β-cyclodextrin cationic polymers with different length of the aliphatic tail (C0, C1, C5, C10) was synthesized and complexed, via electrostatic interaction, with siRNA at different N/P ratios. βCD-LNPs were characterized determining the pH, zeta potential (90Plus), average diameter and particles size distribution (Nanosight). Shape and morphology were evaluated using scanning electron microscopy (FE-SEM). Viability, on HUVEC cell line, and haemolysis assays were performed to assess the biocompatibility of the system.
Complexation of siRNA with alkyl derivative β-CD polymers was confirmed by gel retardation assay. The siRNA βCD-LNPs stability was investigated over time. The siRNA *in vitro* release from βCD-LNPs was studied in simulated cytosol. Alkyl derivatives β-CD polymers were able to form stable and non-toxic spherical complexes with a narrow size distribution according to the alkyl chain length.

C.11 Oxygen-loaded Dextran-nanodroplets Overcome Gemcitabine Resistant in Pancreatic Cancer

Anna Scomparin, Monica Argenziano, Chiara Dianzani, roberta Cavalli

University of Turin

Pancreatic cancer is one of the most hypoxic types of cancer in which the development of drug resistance is highly common. Indeed, the depleted levels of oxygen at the tumor site activate a cascade of events that make cancer more aggressive. Moreover, the gold standard for the treatment, represented by gemcitabine, commonly develops chemoresistance in cancer cells.
To overcome these limitations, we design and developed novel polymeric-coated nanodroplet (ND) exploiting an innovative triple co-delivery approach: oxygen, gemcitabine and curcumin. The ND are obtained by a previously set up method, using dextran sulfate (Mw= 100,000 Da) for the shell and 2H,3H-decafluoropentane for the inner core. All the ND nanosuspensions presented a pH in the physiological range of 5.50-6.80, with an average diameter lower than 250 nm and a negative zeta potential (-60 mV for the blank ND). The ND, with or without oxygen, present a high encapsulation efficiency (~ 66%) and loading capacity (9.4 and 8.2t respectively) of gemcitabine. After 24 hours incubation in phosphate-buffered saline (PBS) at pH 7.4, the drug released from the formulations was around 45%, and the kinetics was not affected by the oxygen. Similarly, sustained release of oxygen was observed up to 24h, following incubation at 37° C. The ND did not show any red blood cells lysis. The ND retain the in vitro pharmacological activity of gemcitabine, inhibiting proliferation and invasion of PDAC cancer cell, similarly to the free drug. In these settings, curcumin acts synergistically with gemcitabine and increases its anticancer efficacy. Finally, the oxygen-loaded NDs showed to restore normoxia regulating the expression of some genes related to HIF-1α, activated by the cells in response to low oxygen levels. This strategy shows a great potential to postpone the the onset of the chemoresistance in pancreatic cancer.

C.12 Poly P-dioxanone as Promising Biodegradable Polymer for Short-Term Medical Application

Stefanie Ficht[1], Lukas Schübel[1], Magdalena Kleybolte[2], Markus Eblenkamp[3], Jana Steger[1, 4], Dirk Wilhelm[4, 5], Petra Mela[1]

[1] Chair of Medical Materials and Implants, Technical University of Munich
[2] WACKER-Chair of Macromolecular Chemistry, Technical University of Munich
[3] TUM School of Engineering and Design, Technical University of Munich
[4] Research Group Minimally invasive Interdisciplinary Therapeutical Intervention (MITI), Klinikum rechts der Isar of Technical University of Munich
[5] Clinic and Policlinic for Surgery, Faculty of Medicine, Klinikum rechts der Isar of Technical University of Munich

Although 3D printing has shown great potential in medical technology and biodegradable polymers have become of increasing interest, there are only a few additively manufactured, biodegradable implants on the market. Additionally, there is a lack of research on appropriate sterilization techniques of thermosensitive polymers.
Within this work, printability of thermosensitive poly p-dioxanone (PPDO) via fused filament fabrication (FFF) was shown and assessed. Afterwards, the effect of two different low-temperature sterilization techniques, namely H_2O_2 plasma and gamma radiation, on the degradation behavior was evaluated compared to non-sterilized samples serving as control group. To quantify PPDO degradation the samples were immersed in phosphate buffered solution (PBS) over 4 weeks and surface morphology, thermal properties, molecular weight and inherent viscosity were investigated at regular time intervals.
Results show that we were able to successfully print PPDO and that printing did not significantly affect thermal properties, molecular weight (M_w) and inherent viscosity (IV). Investigation of sterilization reveals no significant changes of samples being exposed to H_2O_2 plasma while gamma radiation resulted in a 30 % decrease of M_w and statistically significant lower IV (p 0.001) compared to the control group.
During immersion in PBS a decrease in M_w and mechanical strength occurred for all samples. However, gamma sterilized samples were affected to a much higher extent compared to the two other sample groups both in final values and timeline. This was confirmed by scanning electron microscopy showing no changes of surface morphology of (non-sterilized) control samples, first microcracks appearing on plasma sterilized samples after two weeks while being present on gamma sterilized samples already immediately after radiation to then further deteriorate over immersion duration.
Based on our observations, FFF with subsequent plasma sterilization is a reliable process for manufacturing thermosensitive implants featuring short-term degradation behavior, which could be valuable for many medical applications.

C.13 Can Quantum-Mechanical Calculations Shed Light on Cyclodextrin-based Nanosponges (CD-NS) as Drug Delivery Systems?

Marta Corno[1], Riccardo Ferrero[2], Valentina Brunella[2]

[1] *Dipartimento di Chimica dell'Università di Torino*
[2] *Department of Chemistry, University of Torino*

In recent years, the interest in both the theoretical description and the structural modeling of cyclodextrin-based nanosponges (CD-NS) as carriers for a variety of guest molecules has risen. To this extent, previous studies have investigated the formation of non-covalent complexes between a guest molecule and β-cyclodextrin monomers, by applying different computational methods and different levels of theory. Among these, classical mechanics and semi-empirical levels were explored, as well as Density Functional Theory (DFT) methods, lastly.[1]

Due to the increasing complexity of these systems and their derivatives, especially considering β-cyclodextrin three dimensional networks, i.e. nanosponges,[2] it is necessary to employ a method combining the accuracy of density functionals with the computational cheapness ensured by force-field-based methods and standard semi-empirical ones. A promising candidate, aimed at bridging this gap, is the recently developed semi-empirical xTB-GFN2 method, proposed by Grimme's group. xTB-GFN2 has been employed in a large variety of systems, including different host molecules.[3,4]

Among several possible pharmacologically active molecules, we have chosen melatonin and investigated the melatonin/β-cyclodextrin inclusion complex as a testing ground for this novel method.[5] Its validation has concerned structure, energetics, and IR spectra predictions in comparison with more standard DFT-based approaches. Specific attention has been paid to solvent effects, for water, with implicit and explicit solvation. The aim was to define a robust, accurate and, at the same time, low-cost methodology to investigate these complexes. So far, results have indicated that the xTB-GFN2 method provides accurate computed observables, paving the way for modeling cyclodextrin-based nanosponges.

References

Nora, M. et al., *Incl. Phenom. Macrocycl. Chem.* **2020**, *96*, 43.
Trotta, F.; Zanetti, M.; Cavalli, R., *Beilstein J. Org. Chem.* **2012**, *8*, 2091.
Bannwarth, C.; Ehlert, S.; Grimme, S., *Chem. Theory Comput.* **2019**, *15,* 1652.
Boz, E.; Stein, M. *J. Mol. Sci.* **2021**, *22*, 1.
Ferrero, R. et al., *Molecules* **2021**, *26*, 5881.

C.14 Study on Gamma Radiation Protection Effectiveness of Nano/Micro MgO-reinforced Novel Silicon Rubber for Medical Applications

M. I. Sayyed[1], M. Elsafi[2], Aljawhara H. Almuqrin[3]

[1] *Isra university*
[2] *Alexandria university*
[3] *Princess Nourah bint Abdulrahman University*

In this work, we examined the potential of novel polymer composites for use in radiation protection applications. The prepared polymers are non-toxic compared to the lead and have potential as protection in different medical applications where low energy photons are utilized. We prepared silicon rubber (SR) with different concentrations of mico and nano-sized MgO. We used HPGe detector to measure some radiation attenuation factors at different photon energies ranging from 59.6 to 1408 keV. The effect of particle size on the attenuation parameters were reported and we found that the linear attenuation factors for the SR with nano-MgO are higher than that with micro-MgO. The mean free path (MFP) for the pure SR, SR with micro and nano-sized MgO were determined and we found that both the RS's with MgO (in micro and nano-sized) have a lower MFP than the pure SR. The linear attenuation coefficient results showed the importance of using these SR with high MgO contemts for low-energy radiation protection applications. Moreover, the half-value layer (HVL) results demonstrated that we need a small thickness of SR with nano-MgO to reduce the intensity of the low-energy photons.

C.15 Preparation, Characterization and Biological Activity of Chitosan-PVA-Ni Nanocomposite Film for Food Packaging

Gopal Krishna Mehrotra

Motilal Nehru National Institute of Technology Allahabad, Prayagraj- 211004, India

Among natural biopolymers Chitosan (Ch) holds a unique and promising position in the development of functional composite films for food preservation and transportation due to its low-cost, abundance, biodegradability, and good film-forming properties. Currently, use of metal nanoparticles which could safely impart intended 'smart' functionalities in the packaged foods is also one such brilliant idea worth investigation. In this context, in the present study Ni nanoparticles (Ni NPs) synthesized by a green synthetic route have been employed in the fabrication of Chitosan nanocomposite films with polyvinyl alcohol (PVA) as additional reinforcing agent. In the synthesis of Ni Nanoparticles an aqueous extract of the flower petals of rose (Rosa moschata) was used both as solvent as well as stabilizing agent. The Chitosan films named hereafter as *Ch-PVA-Ni nanocomposite films* were characterized and investigated physiochemically by FTIR, XRD, SEM and UV-vis spectroscopic techniques. Aiming their possible application in food packaging industry, the antibacterial and the antioxidant activities of *Ch-PVA-Ni nanocomposite film*s were also investigated and found exceptional as compared to native Chitosan films.

C.16 PVA/Biowaste-Derived Substances Electrospun Fibres: A Promising Sustainable Tool for Pollutant Removal

Maria Laura Tummino[1,2], Claudio Cecone[1], Giuliana Magnacca[1], Marco Zanetti[1], Pierangiola Bracco[1]

[1] Università degli studi di Torino
[2] Current address: Consiglio Nazionale delle Ricerche- STIIMA Biella

Water supply is an issue of major concern, since safe hydric resources are not accessible to a large part of the global population. In order to provide solutions to the pollution criticality, many depuration methodologies have been adopted [1]: a particular attention has been paid to the exploitation of innovative materials in tertiary water treatments, which provide a final depuration stage before water is reused, recycled or discharged into the environment.
In this framework, we prepared fibres of Polyvinyl alcohol (PVA) and biowaste-derived substances isolated from green compost (BBS-GC) by electrospinning technique. PVA is a non-toxic, biodegradable and biocompatible polymer with good film-forming ability due to the abundance of hydroxyl groups able in establishing intermolecular hydrogen bonding [2]. BBS-GC are water-soluble macromolecules with a complex lignin-derived structure containing acid and basic functional groups bonded to aromatic and aliphatic chains [1]. Although PVA has been widely employed to form fibres by electrospinning method [3], for the first time we blended it with BBS-GC. Such electrospun materials were prepared by using different ratios between the two macromolecules and, then, thermally treated in order to favour the condensation reaction between PVA hydroxyl groups and BBS-GC carboxylic groups. We observed fibres with diameters in the submicron range by scanning electron microscopy and we studied the physicochemical features by thermogravimetric analysis and infrared spectroscopy. Lastly, we applied such fibres in preliminary adsorption trials towards a cationic dye and caffeine as model pollutants.

References
[1] Tummino M.L., Testa M.L., Malandrino M., Gamberini R., Bianco Prevot A., Magnacca G., Laurenti E., *Nanomaterials*, **2019**, *9,* 162
[2] Choo K., Ching Y. C., Chuah C. H., Julai S., Liou N.S., *Materials*, **2016**, *9*, 644
[3] Anceschi A., Caldera F., Bertasa M., Cecone C., Trotta F., Bracco P., Zanetti M., Malandrino M., Mallon P. E., Scalarone D., submitted to Nanomaterials

C.17 Effect of Ionic Liquids on the Vulcanization and Properties of Natural Rubber Biocomposites

Magdalena Maciejewska, Anna Sowińska-Baranowska

Department of Chemistry, Institute of Polymer and Dye Technology, Lodz University of Technology

Environmental sustainability based on the use of renewable resources in a manner that satisfies present-day demands is an emerging concept of the modern development goals. Researchers are trying to explore for alternative solutions, i.e. those that will concern the production of biocomposites that will meet specific requirements for a given application. One such well known, renewable biobased polymer, that has been widely used in a wide variety of applications is natural rubber (NR).

In this study, the influence of ionic liquids (ILs) and their structure on the crosslinking process, crosslink density and properties of natural rubber (NR) composites was determined. ILs with different cations (alkylimidazolium, alkylpyrrolidinium and alkylpiperidinium) and anions (bromides, chlorides) were used to enhance the vulcanization and properties of natural rubber filled with nanosized silica. The effect of ILs on vulcanization parameters of NR compounds and functional properties of the obtained vulcanizates, including crosslink density, mechanical properties under static and dynamic conditions, hardness, thermal stability, and resistance to prolonged thermo-oxidation were investigated. ILs improved the rheometric properties of NR compounds, crosslink density, tensile strength, and hardness of the vulcanizates. Moreover, the activity of the filler was also improved, and its addition resulted in an improvement in the processing safety of the rubber compounds. The use of nanosized silica and ILs beneficially affected the thermal stability of the NR vulcanizates.

C.18 Model-Based Investigation of the Impact of Paraformaldehyde on the Ring-Opening Polymerization of Epoxides and Its Molecular Weight Distribution

Lynn Röver, Andreas Jupke

RWTH Aachen University - AVT.FVT - Fluid Process Engineering

Introduction

Polyols with a narrow molecular weight distribution (MWD) are a key component for the production of high quality polyurethanes (PUR). A common manufacturing process for polyols is the ring-opening polymerization of epoxides. In addition to the epoxides, starter molecules (e.g. propylene glycol) and a catalyst are required for the reaction.[1] While the industrially established polyol production meets the requirements concerning the narrow MWD, the whole production is petroleum-based. A promising method to reduce carbon dioxide (CO_2) emissions is the use of a CO_2-based long chain starter molecule, e.g. paraformaldehyde (pFA).[2,3,4]

In this work, we investigate the influence of pFA on the polymerization. We therefore extend a MWD model for the polyether polyol synthesis from liquid starters by Bachmann[5] and Klinger[6] by the dissolving behavior of pFA and reaction kinetics.

Methods

A dynamic population balance model for the reaction kinetics and molecular weight of polyol with pFA as initiator is developed considering experimental data. The key features of the model are the dissolving behavior of pFA present as a solid and its inhibiting effect on the catalyst. Given that both effects influence the reaction kinetics and the MWD, they should be included in an appropriate model for better accuracy. The modelare parameterized and validated with fed-batch experiments. The validated modelare transferred to continuous operation mode and the predicted data is compared with experimental results.

Results

PFA has an inhibiting effect on the catalyst and thus influences the reaction rate of epoxides. The reaction kinetic model developed in this work is able to describe this effect, including the decay of the inhibition, for different temperatures and catalyst concentrations in the fed-batch and the continuous operation mode. A consequence of inhibition is an accumulation of epoxides, especially at low temperatures. Considering the data from the reaction kinetic model and the catch-up kinetics, the model is able to reproduce the MWD for different temperatures and catalyst concentrations in the fed-batch and the

continuous operation mode. The model is be used to determine operating conditions under which high product quality and safe operation are possible.

References:
1.Ionescu, M. (***2005***), Chemistry and Technology of Polyols for Polyurethanes, Rapra Technology Limited, ISBN: 1–85957–491–2.
2. Lligadas, G., Ronda, J.C., Galia, M. and Cadiz, V. (***2010***), Plant Oils as Platform Chemicals for Polyurethane Synthesis: Current State-of-the-Art Biomacromolecules, 11 (11), 2825–2835. https://doi.org/10.1021/bm100839x.
3. Langanke, J., Hofmann, J., Gürtler, C. and Wolf, A. (***2015***), Facile synthesis of formaldehyde-based polyether(-carbonate) polyols. Polym. Sci. Part A: Polym. Chem., 53: 2071–2074. https://doi.org/10.1002/pola.27687.
4.Otto, Alexander: Chemische, verfahrenstechnische und ökonomische Bewertung von Kohlendioxid als Rohstoff in der chemischen Industrie. Dissertation. Techn. Hochsch, Aachen.
5. Bachmann, R., Klinger, M., Jupke, A. (***2021***), Molecular Weight Distribution in Di Metal Cyanide Catalyzed Polymerization1: Fundamental Distribution for Length Dependent Propagation Constant and Segments, Macromol Theor Simul.
6. Klinger, M., Bachmann, R., Jupke, A. (***2021***), Molecular Weight Distribution in Di Metal Cyanide Catalyzed Polymerization2: Numerical Simulation of Activation/Deactivation and Diffusion Effects , Macromol Theor Simul.

C.19 Thermal and Mechanical Behavior of PLA Plasticized by a Bio-derived Plasticizer

Adriana Nicoleta Frone, Denis Mihaela Panaitescu, Andreea Afilipoaei, George Mihail Teodorescu, Marius Stelian Popa, Augusta Raluca Gabor, Cristian Andi Nicolae, Catalina Diana Usurelu

National Institute for R&D in Chemistry and Petrochemistry ICECHIM

The excessive plastic consumption of the modern world has led to an alarming accumulation of waste[1]. Thus, the development of environmentally friendly processes and materials are nowadays crucial for a sustainable future. Polyesters are intensively studied for designing sustainable materials as a result of the ability of ester bonds along the polymer backbone to readily decompose[1]. Due to its biodegradability, non-toxicity, good biocompatibility and processability along with an increasing production and a decreasing price, poly(lactic acid) (PLA) has been largely investigated in studies that aim countless engineered applications starting from food packaging to biomedicine[2]. Still, it is a fragile and brittle material which causes a limitation in the elongation at break. Plasticization usually solves these issues through an improvement of PLA's processability and flexibility. This study aims to investigate the influence of a synthesized plasticizer on the properties of PLA. Bio-based blends of PLA/plasticizer with concentrations of 2.5, 5 and 10 wt.% were prepared using a green processing method, namely injection molding. The blends were characterized by thermal analyses and mechanical tests. DSC revealed a decrease in T_g of PLA blends with the addition of plasticizer while the dynamic-mechanical analyses showed that the PLA/plasticized blends presented lower storage modulus than neat PLA. Also, a depression of the reduced modulus and hardness were found in the case of PLA blends. The results showed that the synthesized plasticizer can enhance the PLA ductility.

Acknowledgements

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References:

1. Journal of Thermal Analysis and Calorimetry, 146 (***2021***), 131–141.
2. Cleaner Materials 2 (***2021***), 100022.

C.20 Proposal of Mechanical Recycling and Feasible Applications for Disposable Surgical Masks

Fulvia Cravero, Giulia Bernagozzi, Daniele Battegazzore, Alberto Frache

Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Alessandria site, Viale Teresa Michel 5, 15121 Alessandria, Italy

In a singular period, such as during a pandemic, the use of personal protective masks has become mandatory for all citizens in many countries worldwide. The most used devices are the disposable masks, that generate a substantial waste flow sent to incineration or landfill.
The characteristics of the constituent materials of the most common three-layered disposable masks have been studied through morphological, chemical, physical, and thermal analyses. Based on these investigations, mechanical recycling protocols with different approaches were proposed. The advantages and disadvantages of the different recycling solutions, along with the necessity of separation processes and other treatments have been analyzed.
The four solutions investigated lead to a recycling index from 78 to 91% of the starting disposable mask weight. The rheological, mechanical, and thermo-mechanical properties of the final materials obtained from the different recycling approaches were compared with each other and with solutions present on the market resulting in materials potentially industrially exploitable.
In particular, the study then focused on the development of an FDM 3D printable material with the aim of giving an added value to the recycled masks. Different percentages of talc were added to the pristine masks to confer specific rheological and thermal properties. However, this solution was not fully satisfactory, thus the masks were partially replaced by a first-use polypropylene copolymer. Two formulations with 35 and 50 wt.% of mask-material were selected as suitable for 3D printing applications.
In the further step, sanitized after use masks were used. The extruded pellets were processed to produce printing filament. Then, the mechanical properties and microstructure of the tensile specimens were characterized and compared with a commercial FDM material. For the first time was verified that a 3D printable material from disposable face masks can be obtained and shows comparable stiffness and strength to the commercial one.

C.21 Styrene-Free Biobased Thermosetting Resins with Tunable Properties

Adriano Vignali, Federica Zaccheria, Nicoletta Ravasio, Fabio Bertini

Istituto di Scienze e Tecnologie Chimiche (SCITEC) "Giulio Natta" – CNR

Research and application of biobased polymers is an ever increasing field due to both environmental and socio-economical reasons. Among the pursued ways, the use of vegetable oils as starting materials is certainly a convenient one. These feedstocks can be used as starting reagents for the preparation of traditional monomers or otherwise used as themselves via different kind of functionalization reactions. The latter possibility is the one used for the preparation of thermosetting resins.

In this work, oils with different unsaturation degree (soybean, hempseed and linseed oils) as starting materials for the preparation of acrylated monomers and their combination with terpenes (limonene, β-myrcene and α-pinene) as co-monomer, were used to obtain thermosetting resins according to the following procedure: the first step is the epoxidation of double bonds of vegetable oil, followed by addition of acrylic acid and by the curing process in the presence of co-monomer and radical initiator.

Thermal, mechanical and dynamic mechanical properties both of prepared materials and a reference styrene-based resin were studied. The characterization highlighted high thermal stability, good mechanical performance and glass transition temperatures between 40 and 80°C. The results showed not only the possibility of replacing the properties of the resin based on styrene, but even to overcome them. The choice of starting oil and co-monomer, in particular as function of their double bonds availability, allows obtaining thermosetting resins with tunable properties.

Moreover, a preliminary research focused on the design and preparation of sustainable composites based on the aforementioned resins and reinforced with natural fibers provides a feasible way to develop renewable fiber-polymer composites to satisfy sustainability demands.

C.22 A New Circular Economy Approach to the Production of EPDM-based Composites and Functionalized by-products of Forest Biomass Combustion

Marcin Marczak, Krzysztof Piotrowski, Piotr Sakiewicz, Grzegorz Matula, Mateusz Lis, Sylwester Kalisz

Silesian University of Technology

The Circular Economy approach poses new challenges for scientists and industry in the field of developing new formulations, including EPDM-based composites, as well as multi-criteria optimization of their properties. The technological approach presented in this paper is aimed at making it possible to replace some of the fossil raw material - $CaCO_3$, which is currently used filler, with materials derived from the energy management of the post-production residues (ashes) of forest biomass - by-products of combustion (BPC). The obtained formulations of polymer blends and composites are to be used ultimately for the production of granules constituting the basic component of the sport-area objects. The authors used two fractions (0.25 µm and 45 µm) of functionalized by-products of forest biomass combustion to produce newly developed, original composites. The paper describes the technological stages of the production process of composites based on ethylene-propylene-diene monomer (EPDM) terpolymer and coniferous ash. The obtained vulcanizates were tested for strength and tribological properties in conditions after conditioning and after the accelerated aging process (70h, 135oC). The paper describes also the influence of the thermally functionalized forest biomass-based ash fraction on the cross-linking characteristics and on the resulting strength and tribological properties of the EPDM composites. The research showed that replacing the chalk filler - $CaCO_3$ by BPC up to 10% by volume allows to obtain slightly better rheological properties of the mixtures. It was also found that the change of the BPC fraction in the composite formula influences the cross-linking density parameters (MH-ML, ts2 and t90). The colorimetric evaluation also showed, that the addition of the tested filler up to 4% by volume, in place of calcium carbonate, provides an acceptable total color difference dE * ab 2un.

C.23 Preparation and Carbonization of Glucose and Pyromellitic Dianhydride Crosslinked Polymers

Antonella Moramarco, Fabrizio Caldera, Federico Cesano, Anastasia Anceschi, Alessandro Damin, Marco Zanetti

University of Turin

In the last years there has been an increasing interest in cyclodextrins based nanosponges (CD-NSs). This kind of crosslinked polymers with nanoscale pores are produced from cyclodextrins (CDs) and bi- or polyfunctional chemicals, including dianhydrides, diisocyanates, active carbonyl compounds, carboxylic acids. CD-NSs are employed in several applications, from pharmaceutical field to the environmental one. CD-NSs can also be used in the production of microporous carbons through a pyrolysis treatment.
More recently, nanosponges synthesized using high amylose content maltodextrins as building blocks and PMDA as crosslinker have been shown to be excellent precursors for the production of porous carbons via pyrolytic process. The carbon thus obtained was completely comparable to that produced starting from CD-NSs, indicating that the pore size and the particularly narrow distribution observed probably derive from the glucopyranoside units present in both nanosponges.
Inspired by that, we first synthesized a new type of nanosponge based on D-glucose (GLU) and PMDA, then we pyrolyzed the nanosponges prepared to obtain porous carbons.
More in details, four nanosponges with different PMDA/GLU molar ratios (i.e. 1.5:1, 2:1, 2.5:1 and 3:1) were synthetized by reacting GLU with PMDA. FTIR analysis confirmed the expected chemical structure of the polymers, while TGA in N_2 atmosphere showed a multistep weight loss leading to a residue at 800 °C with a yield between 22 and 28 wt%.
The four nanosponges were then pyrolyzed at 800 °C. The prepared carbons showed similar properties, in particular no significant correlation was established between the formulation of the precursors and the porous structure and texture of the obtained carbons.
Overall, the results suggest that PMDA/GLU nanosponges are good candidates as precursors to obtain glassy carbons with a microporous texture and relatively high surface area. These hard carbons can be easily obtained and used to segregate relatively small molecules and contaminants. In this study pyrolyzed PMDA/GLU nanosponge having 1.5 molar ratio was studied as a sequestering agent of methylene blue (MB) from water solutions. The results suggest that commercial carbons exhibit better adsorption properties than Char1.5, due to their mesoporous structure.

C.24 Molecular Docking and DFT Calculations of Bio-based Aliphatic and Aromatic Polyesters

Anamaria Todea[1], Alessandro Pellis[2], Sara Fortuna[3], Danilo Di Stefano[4], Valerio Ferrario[1], Federico Zappaterra[1], Lucia Gardossi[1]

[1] Dipartimento di Scienze Chimiche e Farmaceutiche, Universita' degli Studi di Trieste, Piazzale Europa 1, 34127, Trieste, Italy
[2] Department of Chemistry and Industrial Chemistry, Universita' degli Studi di Genova, via Dodecaneso 31, 16146, Italy
[3] CONCEPT Lab, Istituto Italiano di Tecnologia (IIT), I-16152 Genova, Italy
[4] ESTECO SpA, Trieste, Italy

The bio-based polymers and additives synthesis has been a topic of interest for several groups due to the increasing demand for bio-plastic products. Among this arsenal of materials, the most promising one are polyesters due to their many unique properties suitable for development of novel manufacturing technologies[1]. Biocatalysis can boost such innovation, leveraging on enzymes that overcome the limitations of conventional chemical strategies by catalyzing, under highly selective and mild conditions, the targeted modification, synthesis or degradation of polymers as well as biobased polymers[2].

It must be underlined that enzymatically synthesized polyesters are in most cases fully biodegradable. For instance, lipases and cutinases catalyze the in vitro polycondensation of bio-based diacids and polyols, leading to biodegradable polyesters with controlled structures[3,4]. In biocatalysis, computational tools such as molecular modelling, multivariate statistics and chemometrics were successfully used but only applied to model simple and small ligand molecules.

The recent advances in computer science, together with advances in modelling tools for both polymer and enzymes and the availability of organized and accessible data, make nowadays possible to apply powerful analysis based on artificial intelligence and machine learning approaches[5] allowing to evaluate the environmental safety for new tailor-made biodegradable plastics design; however, such kind of applications to polymer science are still in infancy[6].

In this work, molecular docking simulations of aliphatic and aromatic bio-based oligoesters into the catalytic site of 6 different hydrolases were performed. For each considered substrate, computational Density Functional Theory (DFT) studies were performed and reactivity descriptors were calculated. The computational studies results were correlated with the available experimental data and suggesting that the ability of enzymes to hydrolyze or synthesize polyesters can rationally selected by integrating different computational tools.

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References

1. Todea A, Aparaschivei D, Badea V, Boeriu CG, Peter F. Biotechnol J. 2018, 13(6), 1-9
2. Guarneri A, Cutifani V, Cespugli M, Pellis A, Vassallo R, Asaro F, Ebert C., Gardossi L., Adv Synth Catal 2019;361:2559-73.
3. A Todea, DM Dreavă, IC Benea, I Bîtcan, F Peter, CG Boeriu, Processes, 2021, 9 (4), 646, 1-26.
4. Pellis A, Corici L, Sinigoi L., D'Amelio N., Fattor D., Ferrario V., Ebert C., Gardossi L., Green Chem., 2015, 17, 1756-1766.
5. Chen L., Pilania G., Batra R., HuanT. D., Kim C., Kuenneth C., Ramprasad R., Materials Science and Engineering: R: Reports, 144, 2021,100595.
6. Gartner T. E., Jayaraman A., Macromolecules 2019, 52, 3, 755-786.

C.25 Solution Blow Spinning of CA/PEO Nanofibers

Ana Kramar[1, 2], Thomas Luxbacher[3, 4], Javier González-Benito[1, 2]

[1] *Department of Materials Science and Engineering and Chemical engineering, Universidad Carlos III de Madrid, Avda. Universidad 30, 28911 Leganés, Spain*
[2] *Instituto Tecnológico de Química y Materiales "Álvaro Alonso Barba", Universidad Carlos III de Madrid, Avda. Universidad 30, 28911 Leganés, Spain*
[3] *Anton Paar GmbH, 8054 Graz, Austria*
[4] *Faculty of Chemistry and Chemical Engineering, University of Maribor, 2000 Maribor, Slovenia*

Solution blow spinning (SBS) is a versatile and robust method for nanofibers' production from polymer solutions [1]. As an alternative process to electrospinning, it enables high production yield and short processing time. In SBS, solution is pumped through the nozzle while high velocity pressurized air surrounds the nozzle, making a force for polymer jet expulsion and aids solvent removal during nanofibers formation [1]. Here we report the preparation of cellulose acetate (CA) nanofibers blended with polyethylene oxide (PEO). Nanofibers were spun using a home-made SBS device developed at UC3M [2]. After preparation of nonwoven mats, their morphology, structure, thermal properties and surface charge were investigated. Nonwoven mats were subjected to washing to remove water-soluble PEO, thus obtaining pure CA nanofibers. The procedure described in this work can be used to prepare nonwovens consisting of very fine cellulose-based nanofibers and have many potential applications, from biomedical to filtration or food packaging [3].

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References:

1. Medeiros, E.S.; Glenn, G.M.; Klamczynski, A.P.; Orts, W.J.; Mattoso, L.H.C. *J. Appl. Polym. Sci.* **2009**, *113*, 2322–2330.
2. Domínguez, J.E.; Olivos, E.; Vázquez, C.; Rivera, J.M.; Hernández-Cortes, R.; González-Benito, J. *HardwareX* **2021**, *10*, e00218.
3. Mokhena, T.C.; John, M.J. *Cellulose* **2020**, *27*, 1149–1194.

C.26 Novel Approaches for Creation of Polyelectrolytes (Poly(ionic liquid)s) with Improved Conductivity and Mechanical Performance

Alexander S. Shaplov[1], Elena I. Lozinskaya[2], Denis O. Ponkratov[2], Patrick Grysan[1], Pierre Verge[1], Gabriele Lingua[3, 4], Claudio Gerbaldi[3, 4]

[1] *Luxembourg Institute of Science and Technology (LIST)*
[2] *A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS)*
[3] *GAME Lab, Department of Applied Science and Technology (DISAT), Politecnico di Torino*
[4] *National Reference Center for Electrochemical Energy Storage (GISEL) – INSTM*

The global growth in the production of portable digital devices, drones and electric vehicles demands the development of low-cost, high-performance and reliable batteries and supercapacitors with improved cycle life. The need for safe and reliable electrochemical storage devices inspires the research on innovative polyelectrolyte materials.

Among promising candidates, a new class of polyelectrolytes, namely poly(ionic liquid)s (PILs), has recently gained significant attention. PILs can be considered as the macromolecular analogs of ionic liquids (ILs), in the best cases combining the advantages of polymers (viscoelasticity, processability, film-forming properties, etc.) and ILs (high thermal and electrochemical stabilities, enhanced ionic conductivity, etc.). In general, the ideal PIL for a solid-state battery or supercapacitor should have the ionic conductivity of a liquid (>10^{-5} S/cm at 25°C), the mechanical properties of a solid, and the formability of a commodity thermoplastic. However, the reciprocal association between high bulk ionic conductivity and low glass transition temperature (T_g) has limited the simultaneous realization of high toughness, flexibility and electrochemical performance in a single-component linear PIL. The suggested approach to overcome this problem consisted in the synthesis of ionic block copolymers, where the partial incompatibility between ionic and neutral blocks results in a microphase-separated morphology.

I. First family of materials represents anionic single-ion conducting block copolymers synthesized via a combination of the ring opening polymerization (ROP) of trimethylene carbonate (TMC) monomer and subsequent RAFT copolymerization of lithium 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethylsulfonyl)imide (LiM) and poly(ethylene glycol) methyl ether methacrylate (PEGM) [1]. The obtained poly[TMC_n-*b*-(LiM_m-*r*-$PEGM)_k$] block copolymers evolved in a quasi-hexagonally-packed cylinders morphology and demonstrated improved viscoelastic properties, good thermal stability (T_{onset} up to 155 °C), sufficient ionic conductivity (up to 3.7×10^{-6} S cm^{-1} at 70 °C), high lithium-ion transference number (0.91) along with an outstanding stability vs. anodic oxidation (exceeding 5 V vs. Li^+/Li at 70°C). Lab scale truly-solid-state Li/LFP and Li/NMC lithium-metal cells assembled with this PILs demonstrated reversible and very stable cycling at 70 °C delivering high specific capacity (up to 145 and 118 mAh g^{-1}, respectively, at C/20 rate) and proper operation even

at higher current regime.

II. Second family of PILs consists in anionic single-ion conducting A-B block copolymers, where A block represents a random copolymer of LiM and PEGM, while B block consists of poly(2-phenylethyl methacrylate) (poly(PhEtM)) [2]. Poly[(LiM_n-*r*-$PEGM_m$)-*b*-$PhEtM_k$] block copolymers were prepared solely by RAFT method, that allowed the manage not only the LiM:PEGM ratio, but also the molecular weights of both blocks, thus gaining the control over the microphase separation. Block copolymers having molecular weights in the range of 46 ÷ 63 kDa and any ratio of PEGM:LiM (from 3:1 to 7:1) tend to evolve in quasi-hexagonally-packed cylinders, while copolymers with higher molecular weights (M_n > 74 kDa) and the ratio of PEGM:LiM = 5:1 and MA/MB ≤ 2.0 show lamellar phase separation. The lamellar long-range ordering in poly[(LiM_{17}-*r*-$PEGM_{86}$)-*b*-$PhEtM_{131}$] and poly[(LiM_{17}-*r*-$PEGM_{86}$)-*b*-$PhEtM_{194}$] results not only in the improved viscoelastic (mechanical) performance compared to parent copolymer poly[LiM_{17}-*r*-$PEGM_{86}$] (complex viscosity = 2.5×10^8 mPa s and 8.7×10^4 mPa s at 25 °C, respectively), but also in the demonstration of sufficiently high ionic conductivity despite the decrease in Li^+ amount ($\sigma = 3.8\times10^{-7}$ and 4.1×10^{-7} S/cm at 25 °C, correspondingly). The selected poly[(LiM_{17}-*r*-$PEGM_{86}$)-*b*-$PhEtM_{131}$] further shows high t_{Li+} (0.96 at 70°C) and wide electrochemical stability (4.4 V vs. Li^+/Li at 70°C), which results in reversible and stable cycling at high specific capacities (up to 150 and 118 mAh g^{-1} at C/20 and C/5 rates, respectively) when assembled in lab-scale truly-solid-state Li metal cells with Li/copolymer/LiFePO4 configuration.

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References

[1] G. Lingua, P. Grysan, P.S. Vlasov, P. Verge, A.S. Shaplov, C. Gerbaldi, Unique Carbonate-Based Single Ion Conducting Block Copolymers Enabling High-Voltage, All-Solid-State Lithium Metal Batteries , *Macromolecules,* 54 (2021) 6911–6924.

[2] E.I. Lozinskaya, D.O. Ponkratov, I.A. Malyshkina, P. Grysan, G. Lingua, C. Gerbaldi, A.S. Shaplov, Y.S. Vygodskii, Self-assembly of Li single-ion-conducting block copolymers for improved conductivity and mechanical (rheological) performance, *Electrochim. Acta*, 2022, accepted for publication.

C.27 Characterization of Biodegradable PBAT-based Composites: Dynamic-Mechanical Analysis and Degradation Behaviour

Elena Togliatti[1, 2], Dainiel Milanese[1, 2], Diego Pugliese[2, 3], Corrado Sciancalepore[1, 2]

[1] Dipartimento di Ingegneria e Architettura, Università di Parma, Parco Area delle Scienze 181/A, 43124 Parma, Italia
[2] INSTM, Consorzio Interuniversitario Nazionale di Scienza e Tecnologia dei Materiali, Via G. Giusti 9, 50121 Firenze, Italia
[3] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italia

New biodegradable composite materials made of poly(butylene-adipate-*co*-terephthalate) (PBAT) filled with calcium-phosphate glass (CPG) microparticles were characterized by dynamic-mechanical analysis (DMA) and subjected to degradation tests though accelerated ageing and disintegration in composting condition. Realized composites at different concentration of 0, 4, 10, 20 and 40 %wt were employed to obtain standard 1BA specimens by injection molding and films by hot pressing. From DMA, an increase in Storage modulus (*E'*) as a function of CPG content was achieved, beside an approximately constant trend in the glass transition temperature (T_g). This behavior is sign of an effective reinforcement of the composites, with good interphase adhesion. The creep compliance (*J*) measured during deformation under constant stress decreased with increasing the concentration at each tested temperature, confirming the reinforcing effect obtained by the CPG addition to PBAT. Films that underwent accelerated ageing showed increased sensitivity to weathering agents, by an increment in color variation rate and in brittleness. The degradation degree, obtained after three months of fragmentation test, went from 38% for pristine PBAT up to 79% for PBAT + 40% CPG. Overall, the composites realized resulted to have enhanced stiffness, with possibility of modulation with the variation of filler content, and at the same time enhanced degradability both in weathering and composting condition, representing, therefore a promising and sustainable alternative to currently used traditional polymers.

C.28 Recyclability of Thermoplastic Organosheet Production Waste

Barbara Liedl, Christoph Burgstaller

Transfercenter für Kunststofftechnik GmbH

Continuous-fibre reinforced thermoplastics are attractive materials for automotive industry to fulfil their quest for weight reduction. Low density alongside with short cycle times and high mechanical properties offer these so-called organosheets a wide range of applications. [1]
During the production of moulded parts from semi-finished products, edge trimming after shaping produces waste, which cannot be directly used for any application again. Therefore, the aim of our work was to investigate the use of such production waste as reinforcement for thermoplastic composites after shredding and compounding. Polypropylene-glass fiber (PP-GF) consolidated composite laminate was shredded by a cutting mill to pieces of less than 2 mm in size. The shredded material was compounded at a share of 20 to 50 wt.% with PP in a co-rotating twin screw extruder. A adhesion modifier (PP functionalised with maleic anhydride) was used to enhance bonding between fibres and matrix. The determination of the average fiber length showed that the length of most fibres lies between 100 and 500 µm. Mechanical tests revealed that increasing fiber content goes along with increasing mechanical properties. As glass fibers increase stiffness of material, elongation at break of the compounds was reduced. The effect of the adhesion modifier was particularly evident in the impact strength of the compounds: Whereas impact strength in unnotched test specimen descreased with increasing fiber content, this trend could even be reversed by adding adhesion modifier. The results show that composite materials with appealing properties can be produced by recycling edge trims of organosheets, especially with the use of an adhesion modifier.

Acknowledgments
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References

[1] Stock, A.; Egger, P.: Hybridteilfertigung – Organobleche verlassen das Hochpreissegment. MM Composite World 2011/02, 12–15.

C.29 Dextrin-Based Polymers for The Removal of Salicylic Acid as An Emerging Pollutant from Aqueous Media

Claudio Cecone, Marco Ginepro, Francesco Trotta, Pierangiola Bracco

University of Turin

Dextrins are bio-derived materials which have attracted scientific and industrial attention in the past decade thanks to the possibility to be exploited in medical, pharmaceutical, and environmental applications.[1] However, their good water solubility limited their use in those applications in which certain mechanical properties were required, especially while working in aqueous media. For this reason, numerous attempts to cross-link water-soluble dextrins with the aim to obtain cross-linked polymers have been reported. Among the studied cross-linkers, water-soluble diglycidyl ethers displayed good performances in the productions of such products, avoiding the use of any organic solvent.[2] Emerging pollutants are chemicals and compounds that have recently been identified as dangerous to the environment and to the humans. They are defined as emerging because of the rising level of concern linked to them and because of the absence of any related national or international legislation. Used in many pharmaceutical, health care and cosmetic products, salicylic acid has become a global challenge due to its presence in wastewater effluents and potable waters, and for this reason considered as a contaminant. Unfortunately, traditional water purification techniques are not efficient for the removal of such pollutant.[3] In this work, dextrin-based polymers obtained via sustainable approach by crosslinking maltodextrins and beta-cyclodextrins with suitable diglycidyl ethers, were studied as adsorbents for the removal of salicylic acid from aqueous media.

References

[1] Y. Yu, M. Shen, Q. Song and J. Xie, Carbohydr. Polym., 2018, 183, 91–101.
[2] C. Cecone, G. Costamagna, M. Ginepro, F. Trotta, RSC Advances, 2021, 11, 7653 - 7662.
[3] M. Arshadi, F. Mousavinia, M.K. Abdolmaleki, M.J. Amiri, A. Khalafi-Nezhad, Journal of Colloid and Interface Science, 2017, 493, 138–149.

C.30 An open-loop recycling for textile waste: high-value carbon materials from PET-PU industrial scraps

Anastasia Anceschi *, Alessia Patrucco, Raffaella Mossotti

Consiglio Nazionale delle ricerca (CNR) – STIIMA

In the past few decades, global fiber consumption has been progressively increasing, leading to a higher amount of post-industrial and post-consumer fiber waste. Thus, an enormous amount of synthetic waste is generated, most of which is disposed of in landfills. Post-industrial waste is generated in the manufacturing process and, depending on the stage of manufacturing activities, it can be a single polymer or a complex multi-material system. Since a single polymer is easier to be recycled, a blend recycling process should be designed and projected. For companies, industrial blended scraps management is a very high challenge.
The most used textile fiber is polyester (PET), with an estimated production of 26 million tons per year. The PET is often blended with other polymers, mainly with polyurethane (PU), to improve the elastic characteristics of the final products. The PET-PU separation is not an easily manageable process, especially for industrial scraps. For this reason, in this work, the obtainment of a high-value carbon material from PET-PU industrial waste was investigated. The PET-PU scraps were subjected to a pyrolysis treatment at 800°C leading to an 18% of carbon yield. The carbon was thoroughly characterized with several techniques (FTIR spectroscopy, surface area analysis, SEM) and a comparison with PET and PU carbons was also performed. Moreover, the adsorbing properties were evaluated in simulated-wastewater treatment by measuring their adsorption performances in removing two dyes: Orange II and Methylene Blue. These tests showed that the PET-PU-derived carbon is able to remove more than 60% of the two selected dyes. Thus, these preliminary results underline that the PET-PU blend can be easily recycled in an open-loop system in which the synthetic scraps are efficiently transformed into a new high-added value product..

C.31 Covalent Adaptable Networks: Thermo-Reversible Crosslinked Rubber Prepared Via Melt Blending and Its Nanocomposites.

FRANCESCO CANTAMESSA[1], Giacomo Damonte[2], Orietta Monticelli[2], Rossella Arrigo[1], Alberto Fina[1]

[1] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Alessandria, Italy
[2] Dipartimento di Chimica e Chimica Industriale, Università di Genova, Genova, Italy

Covalent adaptable networks [1] represent an interesting route to solve the long-standing problem of thermosets non-reprocessability. Indeed, polymers containing reversible or exchangeable crosslinks may deliver mechanical and chemical stability while retaining reprocessability in the molten state. In this work, an ethylene-propylene-based rubber with a thermally reversible crosslinking, based on the well-known Diels-Alder reaction [2], was prepared for the first time via melt processing, thus without the use of solvent, paving the way to sustainable and industrially viable applications. The process was carried out in two melt blending steps. First, the commercial ethylene-propylene rubber grafted with maleic anhydride was functionalized with furan groups, as proven by FT-IR and ^{1}H NMR spectroscopy. Subsequently, the resulting furan grafted rubber was crosslinked with different amounts of bismaleimide in a lab scale extruder. Crosslinking was investigated by FT-IR spectroscopy and solubility tests at room temperature. Mechanical reinforcement of the rubber carried by crosslinking was investigated by tensile tests on hot-pressed films. The thermal reversibility character of the crosslinking was confirmed by solubilization test near retro-DA activation temperature, resulting in the full dissolution of the network, and further proved by multiple re-moulding via hot-pressing to obtain new fully homogenous films. In the second part of this research work, the rubber was added with two different amounts (5 and 10 wt%) of reduced graphene oxide (rGO) to prepare nanocomposites. SEM and rheology measures were addressed to evaluate the distribution and dispersion of the filler. Mechanical reinforcement was investigated by tensile tests, evidencing significantly higher stiffness and resistance. Furthermore, inclusion of dispersed rGO enhanced thermal conductivity, up to 125% increase at 10% rGO, thus opening for applications in the field of thermally efficient and highly flexible devices, including wearable and flexible electronics.

References

[1] Kloxin C.J. et al. Chemical Society reviews, **2013**.
[2] Polgar L.M. et al. Macromolecules, **2015**.

C.32 Synthesis of Phenothiazine-Based Low-Cost Transparent Polymers as HTMs for Perovskite Solar Cells via Buchwald–Hartwig Amination

Mohamed Magdy Hassan Desoky[1], Narges Yaghoobi Nia[2], Matteo Bonomo[1], Enrico Lamanna[2], Giuseppe Ferraro[1], Claudia Barolo[1, 3], Guido Viscardi[1], Pierluigi Quagliotto[1], Aldo Di Carlo[2, 4]

[1] Dipartimento di Chimica, Università degli Studi di Torino, via P. Giuria 7, Turin 10125, Italy; NIS Interdepartmental Centre and INSTM Reference Centre, Università degli Studi di Torino, Via G. Quarello 15A, Turin 10135, Italy

[2] CHOSE (Centre for Hybrid and Organic Solar Energy), University of Rome "Tor Vergata", via del Politecnico 1, Rome 00133, Italy

[3] ICxT Interdepartmental Centre, Università degli Studi di Torino, Via Lungo Dora Siena 100, Turin 10153, Italy

[4] Consiglio Nazionale delle Ricerche-Istituto di Struttura della Materia (CNR-ISM), Area di Ricerca di Tor Vergata, Via del Fosso del Cavaliere 100, Rome 00133, Italy

Among alternative energy sources, Perovskite Solar Cells (PSCs), raising in efficiency from 3.2% to 25% in only few years,[1,2] are the new frontier of the photovoltaic research. The polymeric Hole Transport Materials (HTMs) extract holes and protect perovskite from moisture degradation due to their superior sealant ability.[3] Recently we prepared some P3HT polymers to study the effect of the polymer structure on the PSC efficiency,[4] and approached the preparation of several small molecules and polymers, to search for correlations between structure and solar cell efficiency.

Here we report the synthesis of a few PTAA polymers based on phenothiazine as spacer. The polymers were prepared by polymerization of dibromo-substituted phenothiazine with differently substituted anilines, by the Buchwald Hartwig protocol using a Pd catalyst based on a NHC ligand,[5] obtaining polymers with short to medium molecular weight. Upon characterization, those polymers showed a very good stability (even >400°C), a generally good transparency in the visible spectrum and the estimation of energy levels showed that they can be compatible with the most common perovskites used in perovskite solar cells, even with the high band gap perovskites. Those polymers are promising candidates as HTMs for perovskite solar cells application and are now under test in this field.

References:

[1] Green M.; and Ho-Baillie, A. *ACS Lett.* 2017, *2*, 822-830.

[2] NREL https://www.nrel.gov/pv/cell-efficiency.html

[3] Zhou, W.; Wen, Z.; Gao, P. *Adv. Energy Mater.* 2018, *8*, 1702512.

[4] Yaghoobi Nia, N.; Bonomo, M.; Zendehdel M.; Lamanna, E.; Desoky, M. M. H.; Paci, B.; Zurlo, F.; Generosi, A.; Barolo, C.; Viscardi, G.; Quagliotto, P.; Di Carlo, A. *ACS Sustainable Chem. Eng.* 2021, *9*, 5061–5073.

[5] Sprick, R. S.; Hoyos, M.; Navarro, O.; Turner, M. L. *React. Funct. Polym.* 2012, *72*, 337-340.

C.33 Poly(acrylic acid)/ poly(diallyldimethylammonium chloride) (PDADMAC) Complexes Embedding Reduced Graphene Oxide

Tianhui Jiang, Alberto Fina, Federico Carosio

Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino. Sede di Alessandria V.le Teresa Michel, 515121 Alessandria, Italy

Recently, polyelectrolyte complexes (PECs) have attracted significant research attention. Mixed polycations and polyanions spontaneously form PECs via electrostatic interactions. It is also possible to make a responsive and smart material by tailoring the strength or texture based on the by inhibiting or promoting oppositely charged polyelectrolyte interactions. PECs could be useful in a number of applications including water treatment, papermaking, drug delivery, and tissue engineering, among others. In conventional polymers, the use of various nanomaterials is well known, to deliver electrical and thermal conductivity and controlled gas barrier, among others.
In this work, the strong polycationic poly(diallyldimethylammonium chloride) (PDADMAC) and the weak polyanionic poly(acrylic acid) (PAA) were complexed with the addition of reduced graphene oxide (rGO), to produce nanocomposites based on PEC rGO was introduced by sonicated in PAA solution and then grafted into PAA/PDAC during complexation together with PDAC. The influence of rGO and the preparation conditions (including the concentration of salt), were correlated with the microstructure, mechanical properties, and rheology properties of PEC composite films. In particular, rGO was found to enhance mechanical properties even with concentration below 1% wt.

C.34 Application of Agricultural Waste in the Technology of Elastomeric Materials.

Marcin Masłowski, Justyna Miedzianowska, Krzysztof Strzelec

Institute of Polymer and Dye Technology

Polymer composites are currently one of the most interesting research objects in the field of materials science, which is very popular both in terms of experimental research and the possibility of their subsequent applications. Strategies for introducing the principles of sustainable development to the production and modification of polymer composites require the search for new and environmentally friendly solutions.

In recent years, biocomposites have been playing an increasingly important role among many types of polymer composites. Due to their multifunctional and unique properties, they are one of the most rapidly developed materials both in research centers and in industry. They are used in many sectors of the economy, including automotive, aviation and construction mainly due to the huge demand from leading industries.

An interesting idea in the production of polymer biocomposites based on the addition of natural plant materials, widely available in Poland and Europe, is the use of cereal straw. Straw is ripe and dried stalks of cereals, legumes, rape and flax, of which the most numerous species is wheat straw. The chemical composition of straw is varied, determined by the species, harvest time, soil type and climatic conditions, but nevertheless, mainly it consists of cellulose, hemicellulose, lignin, proteins, carbohydrates, as well as minerals (calcium, magnesium, silicon compounds, phosphorus and potassium).

The application of straw and its use as a filler for polymer composites is an extremely interesting solution, especially taking into account the availability of raw materials and the low price. Additional advantages include a new, attractive way of agricultural waste management, in balance with environmental issues and pro-ecological policy. Above all, however, it is a material that positively influences a number of functional properties of the finished products filled with them. The use of straw as a bio-additive in elastomer technology has not been described and recognized. The selection of an appropriate polymer medium is crucial and has a significant impact on obtaining the appropriate performance properties. Undoubtedly, the use of cereal straw as a functional filler for composites of natural rubber is a scientific novelty as well as an interesting research direction.

C.35 Links among Microbial Communities, Soil Physicochemical Properties, and Soil Functions in Plastic-soil Systems: Are Fungi the Sole Player in the Degradation of Bio-based and Biodegradable Plastic?

Vusal Guliyev[1, 2], Benjawan Tanunchai[1], Witoon Purahong[1], Evgenia Blagodatskaya[1]

[1] *Helmholtz - Centre for Environmental Research*
[2] *Institute of Soil Science and Agro Chemistry, ANAS*

Due to uncompleted degradation of bio-based and biodegradable plastics (BBPs) in soils, they contribute to the plastic pollution in soil environments in different forms, including macro-, micro-and nano-plastics. Soil health remains under threat after plastic pollution and it could result in a problem in human health and food security. These plastics can interact with soil microorganisms that are important in governing soil ecosystem functions. This study aimed to study the effects of adding high load (6% w/w) of an important BBP (poly(butylene succinate-co-butylene adipate), PBSA) to soil systems with and without the addition of nitrogen fertilizer (ammonium sulfate, N) on soil physicochemical properties, fungal biomass and soil functions (soil enzyme activities) and the interaction of bacteria and fungi in BBPs degradation. We found that bacterial communities significantly correlated with all measured enzyme activities, including the plastic degrading enzyme (lipase) whereas the fungal community only correlated with chitinase and acid phosphatase. Soil physicochemical properties changed strongly in the treatment with both PBSA and N amendment (PSN treatment), whereas the same treatment without N amendment (PS treatment) only increased in soil C: N ratio. Fungal biomass significantly increased in PS and PSN treatment. PSN treatment significantly changed the relationships between soil physicochemical properties and microbial traits, however, the relationships between microbial traits and soil enzyme activities important for C and N acquisitions remained constant. In turn, PS treatment significantly altered the relationship between microbial traits and acid phosphatase. We demonstrate that although the soil functions related to nutrient cycling were not negatively affected in PSN treatment, soil health can be severely damaged by the enrichment of plant pathogens. Such pathogens serve also as saprotrophs and can thereby highly contribute to nutrient recycling as soil ecosystem functions. We conclude that fungi and bacteria are the key players in the BBP degradation process.

C.36 Enzymatic Depolymerization against Polymers Structure and Properties in the Perspective of Biochemical Recycling

Christina Gkountela[1], Efstratios Nikolaivits[2], George Taxeidis[2], Jasmina Nikodinovic-Runic[3], Evangelos Topakas[2], Stamatina Vouyiouka[1]

[1] Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Athens, Greece
[2] Industrial Biotechnology & Biocatalysis Group, Biotechnology Laboratory, School of Chemical Engineering, National Technical University of Athens, Athens, Greece
[3] Eco-Biotechnology & Drug Development Group, Laboratory for Microbial Molecular Genetics and Ecology, Institute of Molecular Genetics and Genetic Engineering, University of Belgrade, Belgrade, Serbia

Biochemical recycling *via* enzymatic depolymerization is an alternative, sustainable approach to produce oligomers or monomers for new polymers or other value-added products. It is a green process conducted under mild conditions not requiring the use of chemical catalysts. Even for the case of biodegradable polymers, enzymatic depolymerization as an upcycling approach becomes promising since their degradation kinetics in real environmental conditions is found slow and similar to conventional plastic waste. In this context, a psychrophilic esterase (MoPE) from the Antarctic bacterium *Moraxella* sp. was tested based on its ability to degrade *via* hydrolysis reactions a variety of semi-crystalline polymers (mass fraction crystallinity, x_c 11-64%) including polycaprolactone (PCL), poly(hydroxy butyrate) (PHB), poly(butylene succinate) (PBS), poly(lactic acid) (PLA) and polyurethane (PU). The efficiency of the process was evaluated based on number-average molecular weight decrease (ΔMn) and dry mass loss. The results were correlated with the initial polymer properties, including glass transition temperature (T_g), crystallinity and molecular weight. The initial T_g was found as the rate-determining factor for the induced hydrolysis: the water diffusion rate and segmental mobility in the amorphous regions are decreased in high-T_g matrices resulting in lower degradation rates. PCL presented high mass loss (33%) while keeping high molecular weight (ΔMn 10%) indicating end scission as the dominant hydrolysis mechanism. On the other hand, PLA, PHB, and PBS presented low or no mass loss (0 to 9%) but significant molecular weight reduction (up to 46%), attributed to the random scission hydrolysis mechanism. Finally, the alipharomatic, ether-based PU, which is considered non-biodegradable, was slightly degraded.
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C.37 Glass-filled Polylactic Acid Composites - Physical and Structural Properties

Luka Pavić[1], Teodoro Klaser[1], Željko Skoko[2], Ana Šantić[1]

[1] *Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia*
[2] *Department of physics, Faculty of science, Bijenička cesta 32, 10000 Zagreb, Croatia*

An effective solution to the negative environmental impact of synthetic polymers is their replacement with biopolymers (such as starch, cellulose, chitosan, zein or gelatin) derived from renewable resources. Biopolymers offer many advantages in terms of production and performance, but their unfavourable characteristic is mainly related to their poor mechanical properties. To overcome this drawback and produce an environmentally friendly polymer with superior properties, various composites with different combinations of matrix biopolymers and fillers have been developed in the last decade. One of the most studied types of biopolymers is polylactic acid (PLA), a versatile biodegradable material derived from natural resources. PLA has great potential to replace traditional petroleum-based polymers, but, its brittleness and low heat resistance still pose some limitations from an application perspective. A glass-filled polymer, on the other hand, is a mouldable composite material whose properties are enhanced by the addition of short glass fibres in a matrix of a polymer material. It is used to fabricate a wide range of structural components by injection or compression moulding.
In this work, PLA composites with different content and type of glasses (bioglass, phosphate-based glasses containing different modifiers and glass waste from Kelteks company) in a form of glass fibres (GF) and glass powder (PG) were prepared. The objective was to improve their thermal, structural, mechanical and electrical properties. The results of our thorough characterization of these materials using differential scanning calorimetry (DSC), X-ray diffraction, microscopy techniques, IR spectroscopy and impedance spectroscopy show that these novel PLA-GF and PLA-PG composites cover a wide range of physical properties and can be tuned in accordance to desire application.

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C.38 Morphological and Mechanical Properties of Multifilament Fibers Prepared by Melt Spinning Using Polymers Modified with Myrrh Extract

Evaldas Bolskis[1], Erika Adomavičiūtė[2], Egidijus Griškonis[3]

[1] Faculty of Mechanical Engineering and Design, Kaunas University of Technology, Studentu Str. 56, Kaunas, Lithuania
[2] Faculty of Mechanical Engineering and Design, Kaunas University of Technology, Studentu Str. 56, 51424 Kaunas, Lithuania
[3] Faculty of Chemical Technology, Kaunas University of Technology, Radvilenu pl. 19, Kaunas Lithuania

Nowadays exist many multifilament production methods. Three of them: dry, wet and melt spinning. Melt spinning is one of the most widely used processes to produce polymeric multifilaments from the method mentioned. It has advantages such as continuous processing, easy scalability, solvent-free fabrication, and fairly low production costs. Also in this process is not using organic solvents. It allow to use of formed fibres for biomedical application.
Many polymers can be used in melt-spinning processes. Petroleum-derived polyolefins in the melt spinning process are mainly used polypropylene (PP). This polymer is non-biodegradable, thermoplastic. Widely used in medicinal applications, for example, medical sutures. They noted good resistance, stability and low-tissue reaction.
The other polymer which is mostly used in the melt-spinning process is polylactide (PLA). It has unique bio-properties including biocompatibility and biodegradability. It is widely used for biomedical applications (such as musculoskeletal injuries, tissue engineering, and drug release systems).
In the melt-spinning process it is possible to use additives to form multicomponent yarns with various functionalities. It can be metal oxides, and they can be nanoparticles or minerals. Also, can be used natural compounds.
One of the natural compound which can be used in the melt spinning process as functional additives is Myrrh. It has long been used as a medicine and wound dressing. It has good antimicrobial effects against various bacteria such as Staphylococcus aureus, Salmonella enterica serovar typhimurium strains, etc. Compositionally, myrrh consists of alcohol-soluble resins (25–40%), volatile oils (3–8%) and a water-soluble gum (30–60%).
The aim of this research is to investigate the influence of formatting parameters on the PP and PLA yarns modified with myrrh extract morphological and mechanical properties.

C.39 Glycerol Trilevulinate: A Step Forward in the Transition from Plasticizers to Bioplasticizers

Luca Lenzi, Micaela Degli Esposti, Davide Morselli

Civil, Chemical, Environmental and Materials Engineering Department, University of Bologna

Traditional plasticizers such as phtalates are the most used additives for polymeric materials. In particular, phtalates arouse several concerns due to their biodegradability, renewability, cytotoxicity. The utilization of phtalates have been restricted and monitored worldwide, although they are still been used in innumerable consumer products due low their cost, attractive properties, and lack of valuable alternatives. In this work, we present a fully bio-based alternative plasticizer synthetized from Glycerol, which is a by-product of the biodiesel supply chains, and Levulinc Acid which is produced from lignocellulosic wastes. A mild-condition solvent-free esterification have been used to synthesized Glycerol Trilevulinate plasticizer (GT). The product has been characterized by FT-IR and NMR. Reaction parameters such as catalyst amount and the excess of Levulinc acid (reaction medium) have been optimized before testing the new additive with various polymers.

Poly(vinyl chloride) (PVC) is the most compounded polymer, which makes PVC the perfect model polymer for testing new additives and comparing them with the nowadays industrially used ones. GT has also been tested with several bio-based polymers, which typically lack of processability due to their highly crystallinity. Different ratios of GT have been tested with Poly(3-hydroxybutyrate), Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), Poly(lactic acid) and Poly(caprolactone). The additive miscibility in the different polymers have been investigated by migration tests and SEM imaging. DSC investigations showed a very high plasticization effect of GT in terms of glass transition temperature (Tg), melting temperature (Tm) and crystallinity reduction on all tested polymer, proving to be a promising and effective alternative plasticizer.

C.40 Polyhydroxyalkanoates/Tannins-based Films as Potential Material for Food Packaging Applications

Martina Ferri[1], Micaela Degli Esposti[1, 2], Ramona Iseppi[3], Davide Morselli[1, 2], Paola Fabbri[1, 2]

[1] *Department of Civil, Chemical, Environmental and Materials Engineering, University of Bologna*
[2] *Italian Consortium for Science and Technology of Materials INSTM*
[3] *Department of Life Sciences, University of Modena and Reggio Emilia*

The transition towards a circular plastic economy needs new strategies for the development of plastic materials, which completely fulfill the requirements of sustainability. Bio-based plastics offer multiple advantages in terms of potential replacement of traditional plastics, but their actual renewable carbon content is frequently much lower than expected due to the presence of non-renewable additives.

Tannins are eco-friendly, bio-sourced, highly reactive polyphenols and they are the fourth most abundant form of terrestrial biomass extracted compounds right after cellulose, hemicellulose, and lignin. They are well-known as natural preservatives and exibit high antioxidant activity. These prerequisites have made tannins interesting molecules as polymer additives to develop multifunctional materials suitable for a variety of applications, such as food conservation.

Biodegradable polyhydroxybutyrate-*co*-valerate (PHBV) and polyhydroxybutyrate (PHB) films with increasing concentration of tannins (1, 5, 10% w/w) have been prepared by solvent casting. Formic acid has been used to reach a good dispersion of tannins in the polymer matrix and as a greener alternative to common solvents such as chloroform. The gravimetric analysis performed after extraction in water (24h) has shown a complete retention of tannins in the films. Moreover, antioxidant properties have been evaluated by means of DPPH assay. Samples containing 10% of the bio-additive achieved 100% of scavenging in 10 minutes, revealing a strong radical scavenging activity (RSA). However, a significant antioxidant activity has been obtained also with the addition of 1% of tannin, reaching 60% of RSA in 7 hours. Furthermore, chemical and thermal properties, transparency and UV protection of the films have been assessed. Although 20-60% of transmittance was reached, samples demonstrated an extension of the wavelenght range absorbed compared to commercial packaging films. In addition, antimicrobial properties have been evaluated against Gram-positive and negative bacteria. Lastly, mechanical properties of the films have been compared to films available on the market.

C.41 Towards Hydrophobicity Tuning of the Diels-Alder Reaction Based Polymer Materials

Marina Eskova[1,2], Igor Nikovskiy[1], Alexander Polezhaev[1, 2], Elena Platonova[2], Sofia Morozova[2, 3]

[1] A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow 119334, Russia
[2] Department of Russian composites, N.E. Bauman Moscow State Technical University, Moscow 105005, Russia
[3] Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada

The introduction of dynamic bonds into the polymer structure, for example, using the Diels-Alder (DA) reaction, opens up new ways to control the functional properties of polymers and provides many applications based on self-healing, recycling materials and stimuli-responsive coatings. Of interest is the creation of brush-polymers in which the degree of crosslinking and the length of the side chains could be changed under the influence of an external stimulus. There are a few examples of dynamic polymer brushes, and most of them are based on the use of expensive organosilicon precursors. A new approach to solve this problem consists in using furan-containing polyurethanes that can reversibly react with maleimides by the DA reaction.
Ionic polyurethanes were chosen as the main polymer chain since varying monomer's nature allows controlling mechanical properties and solubility in a wide range. Introduction of N-alkyl maleimides (including fluorinated ones) to polymer chain via the Diels-Alder reaction provides reversibility and control of the frequency of side chains.
A synthetic route for the quaternization of polyurethane containing tertiary amine by the furan fragment was developed, as well as a scheme for the synthesis of an ionic monomer for further polymerization was optimized. In addition, a synthesis of maleimide derivatives for further introduction to the side chain was developed. Besides further control of the degree of modification could be realized through DA (20 - 40 ^{o}C) – retro-DA (80 – 150 ^{o}C) reactions. It has been shown that the degree of modification of polyurethanes by fluorinated fragments opens a way to control the contact angle with water for films based on them. The process is reversible, which makes it possible to change the wettability of the obtained coatings from hydrophilic to hydrophobic
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C.42 Design of A 3D Printing Eco-Friendly Lignin Acrylic Resin for Lcd Vat Polymerization

Goretti Arias-Ferreiro[1], Ana I. Ares-Pernas[1], Aurora Lasagabáster-Latorre[2], Silvia Lage-Rivera[3], Pablo Ligero[4], María S Dopico García[1], María J. Abad López[1]

[1] Universidade da Coruña, Campus Industrial de Ferrol, Grupo de Polímeros-CIT, Campus de Esteiro, 15403 Ferrol, Spain.
[2] Dpto Química Orgánica I, Facultad de Óptica, Universidad Complutense de Madrid, Arcos de Jalón 118, 28037 Madrid, Spain.
[3] Universidade da Coruña, Campus Industrial de Ferrol, Grupo de Polímeros-CIT, Campus de Esteiro, 15403 Ferrol, Spain
[4] Enxeñería Química Ambiental Group, Centro de Investigacións Científicas Avanzadas (CICA), Universidade da Coruña, 15071, A Coruña, Spain

Research into new materials suitable for 3D printing technologies is necessary to increase their range of applications. The design of novel environmentally friendly photocurable acrylic composites requires an appropriate balance between the relative concentration of the filler and the viscosity of the sample besides adjusting the polymerization conditions. Lignin is a sustainable complex aromatic heteropolymer; the second most abundant biopolymer on earth[1]. Its use as filler in additive manufacturing is an emerging field with only a few reports dealing with its use in stereolitography [2,3]. Furthermore, lignin has high potential in electronic applications, such as energy storage and conversion, as well as in other areas for instance pollutant removal.

This work pursues the development of polymer composites with enhanced properties based on unmodified lignin, suitable for additive manufacturing. The composites were formulated adding increasing amounts of lignin (0 to 4 wt.%) into an in-house photopolymerizable acrylic-resin compounded by Ethyleneglycolphenylether acrylate (EGPEA) as monomer, 1, 6-hexanediol diacrylate (HDODA) as crosslinker and diphenyl (2,4,6-tri- methylbenzoyl) phosphine oxide (TPO) as photoinitiator. The effect of the amount of lignin on the kinetics of photopolymerization was studied in situ using FTIR spectroscopy. The printability of the formulations was assessed by Liquid crystal display printing (LCD). Additionally, the obtained composites were characterized considering mechanical properties and morphology by SEM. The results show a limit on the lignin content, from which the resin becomes unsuitable for LCD printers.

References

Ebers, L. S., Arya, A., Bowland, C. C., Glasser, W. G., Chmely, S. C., Naskar, A. K., Laborie, M. P. *Biopolymers*, 2021, 112, 1–12.
Sutton, J. T., Rajan, K., Harper, D. P., Chmely, S. C. *ACS Appl. Mater. Interfaces*, 2018, 10, 36456–36463.
Zhang, S., Li, M., Hao, N., Ragauskas, A. J. *ACS Omega*, 2019, 4, 201


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