2025 PM16

Prague, Czech Republic

1–4 September 2025

16 POLYMER MEETING

INSTITUTE OF
MACROMOLECULAR
CHEMISTRY
CZECH ACADEMY OF SCIENCES

Book of Abstracts

Book of abstracts of the 16th Polymer Meeting 2025

1st edition, September 2025

PUBLISHED AND DISTRIBUTED BY
AMCA, spol. s r.o.
Vyšehradská 320/49
128 00 Prague 2
Czech Republic

The abstracts in this book have not been proofread for language, scientific or layout purposes. They are published as supplied by the authors of the contributions.

ISBN 978-80-88214-56-4

Date & venue

1 – 4 September 2025
Hotel Olšanka
Táboritská 23, Prague, Czechia

Organizer

INSTITUTE OF
MACROMOLECULAR
CHEMISTRY
CZECH ACADEMY OF SCIENCES

Organizing committee

PM16 Chair
Jiří Kotek
Institute of Macromolecular Chemistry, Czech Academy of Sciences
Prague, Czech Republic

Scientific committee
and at the same time international committee of the conference series:

Béla Iván (Hungarian Academy of Sciences, Budapest, Hungary)
Jiri Kotek (Czech Academy of Sciences, Czech Republic)
Peter Krajnc (University Maribor, Slovenia)
Igor Lacík (Slovak Academy of Sciences, Bratislava, Slovakia)
Robert Liska (Vienna University of Technology, Austria)
David Pahovnik (National Institute of Chemistry, Slovenia)
Christian Paulik (JKU Linz, Austria)
Christian Slugovc (Graz University of Technology, Austria)
Jaroslav Mosnáček (Slovak Academy of Sciences, Bratislava, Slovakia)
Gregor Trimmel (Graz University of Technology, Austria)
Ema Žagar (National Institute of Chemistry, Slovenia)

Local organizing committee

Hynek Beneš
Patrycja Magdalena Bober
Tomáš Etrych
Jiří Brus
Martin Hrubý
Jiří Kotek
Ognen Pop-Georgievski
Vladimír Proks
Vladimír Raus
Zdeněk Starý
Pavel Slabihoudek
Petr Štěpánek

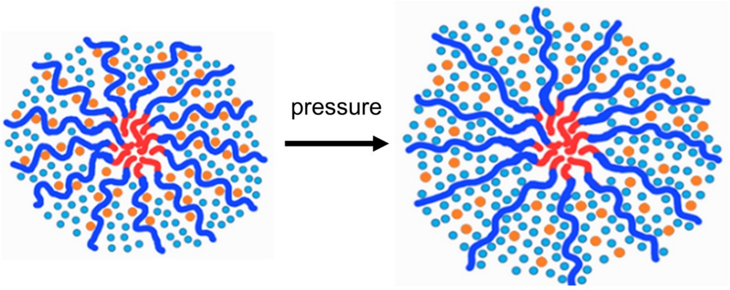
Plenary lectures

What high pressure can teach us about block copolymer micelles with a thermoresponsive shell

P. A. Alvarez Herrera[1], C.-H. Ko[1], C. Henschel[2],
A. Schulte[3], P. Müller-Buschbaum[1], A. Laschewsky[2,4], C. M. Papadakis[1*]

[1]*Technical University of Munich, TUM School of Natural Sciences, Garching, Germany*
[2]*Universität Potsdam, Institut für Chemie, Potsdam-Golm, Germany*
[3]*University of Central Florida, Department of Physics and College of Optics and Photonics, Orlando FL, U.S.A.*
[4]*Fraunhofer Institute forApplied Polymer Research, Potsdam-Golm, Germany*
[*]*papadakis@tum.de*

In dilute aqueous solution, thermoresponsive diblock copolymers with a hydrophobic and a thermoresponsive block self-assemble into core-shell micelles. Here, we investigate the self-assembly behavior of the model diblock copolymer PMMA-*b*-PNIPAM consisting of a short permanently hydrophobic poly(methyl methacrylate) and a long thermoresponsive poly(*N*-isopropylacrylamide) block. Synchrotron small-angle X-ray scattering reveals that, below the cloud point T_{CP}, spherical micelles are formed, having a PMMA core and a hydrated PNIPAM shell. Above T_{CP}, the micellar shell dehydrates, and the micelles contract and form aggregates.[1] Adding methanol as a cosolvent leads to strong changes of the micellar structure, which is due to the superposed co-nonsolvency effect of PNIPAM and the enhanced solvation of PMMA.[2] Applying pressure to an aqueous micellar solution of PMMA-*b*-PNIPAM is a tool to alter the hydration behavior of the PNIPAM block. In neat water, we find that not only the value of T_{cp}, but also the transition behavior depends on pressure.[3] In a water/methanol mixture, intricate behavior is found when pressure is varied, both below and above T_{cp}. The observed changes in this system can be traced back to the change of the solvation behavior of PNIPAM homopolymers under pressure, i.e. a replacement of adsorbed water on the PNIPAM segments by methanol molecules, as pressure is increased.[5,6] The pressure-induced alteration of the properties of the micellar shell and the correlation between the micelles allows investigating the relation between these effects.



Acknowledgments
We thank DFG for funding, EMBL@DESY, Hamburg, Germany, for beamtime and the CERIC-Eric Consortium for beamtime at ELETTRA, Bassovizza, Italy.

References

[1] Ko, C.-H., Papadakis, C. M. et al. Self-Assembled Micelles from Thermoresponsive Poly(methyl methacrylate)-*b*-poly(*N*-isopropylacrylamide) Diblock Copolymers in Aqueous Solution. *Macromolecules* **2021**, *54*, 384-397.
[2] Ko, C.-H., Papadakis, C. M. et al. Co-Nonsolvency Effect in Solutions of Poly(methyl methacrylate)-*b*-poly(*N*-isopropylacrylamide) Diblock Copolymers in Water/Methanol Mixtures. *Macromolecules* **2021**, *54*, 5825-5837.
[3] Alvarez Herrera, P. A. Papadakis, C. M. et al. Effect of Pressure on the Micellar Structure of PMMA-*b*-PNIPAM Diblock Copolymers in Aqueous Solution. *Macromolecules* **2024**, *57*, 10263-10274.
[4] Alvarez Herrera, P. A. Papadakis, C. M. et al.Effect of Pressure on the Micellar Structure and Aggregation Behavior of PMMA-*b*-PNIPAM Diblock Copolymers in a Water/Methanol Mixture. *Soft Matter* **2025**, *21*, 4681-4691.
[5] Niebuur, B.-J., Papadakis, C. M. et al. Pressure Dependence of Water Dynamics in Concentrated Aqueous Poly(*N*-isopropylacrylamide) Solutions with a Methanol Cosolvent. *Macromolecules* **2021**, *54*, 4387-4400.

[6] Papadakis, C. M.; Niebuur, B.-J., Schulte, A. Thermoresponsive Polymers under Pressure with a Focus on Poly(*N*-isopropylacrylamide) (PNIPAM). *Langmuir* **2024**, *40*, 1-20.

Poly(2-oxazoline)s: From an attractive alternative to PEG to an exotic speciality and back?

R. Luxenhofer[1]

[1]*Soft Matter Chemistry, Department of Chemistry, Faculty of Science, University of Helsinki, 00560 Helsinki, Finland*
**robert.luxenhofer@helsinki.fi*

Already in the earliest days of research into PEGylation, Poly(2-oxazoline)s (POx) have been investigated and established as attractive and efficient alternatives to PEG [1], but while PEG rapidly became the gold standard for hydrophilic biomedical polymers and PEGylation is one of the best known concepts in (bio)pharmaceutical technology, POx have long been living in relative obscurity, with all but a handful of researchers world-wide working with them.

Even though research around POx became more lively again in the late 2000s, the recent decade has been particularly interesting. Apart from drug [2,3], protein [4] and gene delivery systems [5], POx based thermoresponsive hydrogels have been developed for bioprinting. POx-based thermogels show interesting structure-property relationships [6][7][8] and rheological properties particularly suited for bioprinting, all in combination with excellent cytocompatibility.

This contribution will revisit the development of POx-based hydrogels for drug delivery and 3D printing, with a focus on biofabrication.

Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft (TRR225 - 326998133) and Business Finland (R2B project HydroXGel) is gratefully acknowledged.

References

[1] Zalipsky, S.; Hansen, C.B.; Oaks, J.M.; Allen, T.M., 1996. Evaluation of Blood Clearance Rates and Biodistribution of Poly(2-oxazoline)-Grafted Liposomes. *J. Pharm. Sci.* **1996**, *85*, 133–137.

[2] Luxenhofer, R.; Schulz, A.; Roques, C.; Li, S.; Bronich, T.K.; Batrakova, E.V.; Jordan, R.; Kabanov, A.V. Doubly amphiphilic poly (2-oxazoline) s as high-capacity delivery systems for hydrophobic drugs. *Biomaterials* **2010**, *31*, 4972–4979.

[3] Kierstead, P.H.; Okochi, H.; Venditto, V.J.; Chuong, T.C.; Kivimae, S.; Fréchet, J.M.J.; Szoka, F.C. The effect of polymer backbone chemistry on the induction of the accelerated blood clearance in polymer modified liposomes. *J. Control. Release* **2015**, *213*, 1–9.

[4] Tong, J.; Luxenhofer, R.; Yi, X.; Jordan, R.; Kabanov, A.V. Protein Modification with Amphiphilic Block Copoly(2-oxazoline)s as a New Platform for Enhanced Cellular Delivery. *Mol. Pharmaceutics* **2010** *7*, 984–992.

[5] Sanchez, A.J.D.S.; Loughrey, D.; Echeverri, E.S.; Huayamares, S.G.; Radmand, A.; Paunovska, K.; Hatit, M.; Tiegreen, K.E.; Santangelo, P.J.; Dahlman, J.E. Substituting Poly(ethylene glycol) Lipids with Poly(2-ethyl-2-oxazoline) Lipids Improves Lipid Nanoparticle Repeat Dosing. *Adv Healthcare Mat.* **2024**, *13*, 2304033.

[6] Hahn, L.; Karakaya, E.; Zorn, T.; Sochor, B.; Maier, M.; Stahlhut, P.; Forster, S.; Fischer, K.; Seiffert, S.; Pöppler, A.-C.; Detsch, R.; Luxenhofer, R., An Inverse Thermogelling Bioink Based on an ABA-Type Poly(2-oxazoline) Amphiphile. *Biomacromolecules* **2021**, *22*, 3017–3027

[7] Hahn, L.; Keßler, L.; Polzin, L.; Fritze, L.; Forster, S.; Helten, H.; Luxenhofer, R. ABA Type Amphiphiles with Poly(2-benzhydryl-2-oxazine) Moieties: Synthesis, Characterization and Inverse Thermogelation. *Macro Chem. Phys.* **2021**, *222*, 2100114

[8] Hahn, L.; Zorn, T.; Kehrein, J.; Kielholz, T.; Ziegler, A.-L.; Forster, S.; Sochor, B.; Lisitsyna, E.S.; Durandin, N.A.; Laaksonen, T.; Aseyev, V.; Sotriffer, C.; Saalwächter, K.; Windbergs, M.; Pöppler, A.-C.; Luxenhofer, R. Unraveling an Alternative Mechanism in Polymer Self-Assemblies: An Order–Order Transition with Unusual Molecular Interactions between Hydrophilic and Hydrophobic Polymer Blocks. *ACS Nano* **2023**, *17*, 6932–6942.

Ordered conjugated polymers for organic electronics

Tomasz Marszalek, Wojciech Pisula

Department of Molecular Physics, Faculty of Chemistry, Lodz University of Technology
Zeromskiego 116, 90-924 Lodz, Poland
Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
pisula@mpip-mainz.mpg.de

Solution processable conjugated polymers are promising for large area, lightweight, and flexible field-effect transistors. Control over their thin film microstructure and polymer organization is crucial for the charge carrier transport in transistors. Meniscus-guided coating covers techniques like zone-casting, blade-coating, dip-coating, and solution shearing, and is an efficient approach to solution process conjugated polymers into highly ordered thin films. Over the recent years, zone-casting has been further developed to precisely tune the crystallization of semiconducting polymers and to improve their charge carrier transport.

This presentation discusses the crystallization and film growth mechanism of conjugated polymers during zone-casting and dip-coating that are essential for the thin film deposition for field-effect transistors. An understanding of the alignment mechanism and fundamental principles of the fluid mechanics for the crystal growth has been developed. Relations between meniscus shape, fluid mechanical process and polymer crystallization during solution processing are provided. Homogeneous mono- and multilayers based on conjugated polymers have been fabricated for transistor applications through a careful control of the processing conditions [1].

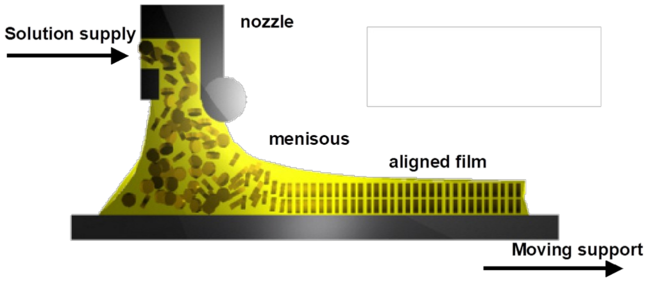


Figure 1: Illustration of the zone-casting process to control the organization of conjugated polymers in thin films.

Acknowledgments

This work was supported by the National Science Centre, Poland, through the grant UMO2023/49/B/ST11/02076.

References:

[1] O. Yildiz, Z. Wang, M. Borkowski, S. Wang, Z. Li, J. J. Michels, P. W. M. Blom, W. Pisula, T. Marszalek, *Adv. Funct. Mater.* **2024**, *34*, 2314131; O. Yildiz, Z. Wang, M. Borkowski, G. Fytas, P. W. M. Blom, J. J. Michels, W. Pisula, T. Marszalek, *Adv. Funct. Mater.* **2022**, *32*, 2107976; K. Zhang, M. Borkowski, P. Wucher, P. M. Beaujuge, J. J. Michels, P. W. M. Blom, T. Marszalek, W. Pisula, *Adv. Electron. Mater.* **2021**, *7*, 2100397; J. J. Michels, K. Zhang, P. Wucher, P. M. Beaujuge, W. Pisula, T. Marszalek, *Nat. Mater.* **2021**, *20*, 68; O. Yildiz, Z. Wang, M. Borkowski, G. Fytas, P. Blom, J. J. Michels, W. Pisula, T. Marszalek, *Adv. Funct. Mater.* **2021**, *32*, 2107976; K. Zhang, Z. Wang, T. Marszalek, M. Borkowski, G. Fytas, P. Blom, W. Pisula, *Mater. Horiz.* **2020**, *7*, 1631; K. Zhang, T. Marszalek, P. Wucher, Z. Wang, L. Veith, H. Lu, H. J. Räder, P. M. Beaujuge, P. Blom, W. Pisula, *Adv. Funct. Mater.* **2018**, *28*, 1805594; M. M. Li, D. K. Mangalore, J. B. Zhao, J. H. Carpenter, H. P. Yan, H. Ade, H. Yan, K. Müllen, P. W. M. Blom, W. Pisula, D. M. de Leeuw, K. Asadi, *Nat. Commun.* **2018**, *9*, 451.

(De)Activating Bond Exchange Reactions in Dynamic Polymer Networks

D. Reisinger[1], S. Schlögl[1,2*]

[1]*Polymer Competence Center Leoben GmbH, Leoben, Austria*
[2]*Institute of Chemistry of Polymeric Materials, Technical University of Leoben, Leoben, Austria*
[*]*sandra.schloegl@pccl.at*

Latent catalysts are a versatile strategy to temporally and locally control the rate of bond exchange reactions (and the related material flow) in dynamic polymer networks.[1-4] Herein, we explored novel families of reversibly switchable catalysts, which undergo a distinctive shift in their pKa values due to an external trigger (either light or a change in temperature).
In a first step, the reversible activation/deactivation of a photoswitchable nitrogen superbase undergoing light-induced isomerization of dithienylethene groups was studied in thiol-ene photopolymers.[5] Depending on the color of light used (visible versus UV light), a substantial difference in the pKa value was observed, which was exploited to kinetically control the base-catalyzed bond exchange between thioester and thiol groups. The reversibility and local control of the isomerization reaction (and the related bond exchange kinetics) was demonstrated by stress relaxation, reshaping, micro imprint and tensile testing experiments.
In a further approach, photochromic merocyanine-based photoacids were synthetized and applied as reversibly switchable catalysts for acid-driven dynamic polymer networks.[6] Upon visible light exposure, the catalyst was activated by undergoing a spirocyclization, while the deactivation reaction took place under dark conditions at elevated temperature. The photoacid was placed in a thiol-ene photopolymer comprising ample -OH and ester moieties and a reversible control of the transesterification kinetics was demonstrated by stress relaxation studies. The fast isomerization kinetics and fatigue resistance were used to generate gradients of active photoacid in a spatially resolved manner at the micrometer level. The resulting gradient in relaxation properties was applied for mold-free reshaping of dynamic photopolymers.

Acknowledgments

The research work was carried out within the COMET-Module project "Repairtecture" (project-no.: 904927) at the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the COMET-program of the Federal Ministry for Innovation, Mobility and Infrastructure and the Federal Ministry of Economy, Energy and Tourism. The COMET-Module is funded by the Austrian Government and the State Governments of Styria and Upper Austria.
A part of the research work has received funding from the European Union's Horizon2020 research and innovation program under the Marie Skłodowska-Curie grant agreement, No 101085759 (SURE-Poly).

References

[1] Reisinger, D., Kaiser, S., Rossegger, E., Alabiso, W., Rieger, B., Schlögl, S. Introduction of photolatent bases for locally controlling dynamic exchange reactions in thermo-activated vitrimers. *Angewandte Chemie* **2021**, *60*, 14302-14306.
[2] Dertnig, C., Guedes de la Cruz, G., Neshchadin, D., Schlögl, S., Griesser, T. Blocked Phosphates as Photolatent Catalysts for Dynamic Photopolymer Networks. *Angewandte Chemie* **2022**, *135*, e202215525.
[3] Rossegger, E., Shaukat, U., Moazzen, K., Fleisch, M., Berer, M., Schlögl, S. The role of photolatent catalysts on the exchange kinetics of dual-wavelength 3D printable and photopatternable thiol-click vitrimers. *Polymer Chemistry* **2023**, *14*, 2640-2651.
[4] Reisinger, D., Kriehuber, M. U., Bender, M., Bautista-Anguís, D., Rieger, B., Schlögl, S. Thermally Latent Bases in Dynamic Covalent Polymer Networks and their Emerging Applications. *Advanced Materials* **2023**, *35*, 2300830.
[5] Reisinger, D., Sietmann, A., Das, A., Plutzar, S., Korotkov, R., Rossegger, E., Walluch, M., Holler-Stangl, S., Hofer, T. S., Dielmann, F., Glorius, F., Schlögl, S. Light-Driven, Reversible Spatiotemporal Control of Dynamic Covalent Polymers. *Advanced Materials* **2024**, *36*, 2411307.
[6] Reisinger, D., Wimberger, L., Korotkov, R., Scott, T.F., Cameron, N.R., Boyer, C., Schlögl, S. Reversible On-Demand Activation of Acid-Catalyzed Dynamic Polymers for Gradient-Driven Reshaping. *Advanced Materials* **2025**, submitted.

Unleashing the potential of enzymes for green furan-based polymer synthesis

Katja Loos
Macromolecular Chemistry and New Polymeric Materials
Zernike Institute for Advanced Materials / University of Groningen
Nijenborgh 3 / 9747 AG Groningen / The Netherlands
email: k.u.loos@rug.nl

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

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

References

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

Aqueous phase propagation kinetics in radical polymerization

I. Lacík

Polymer Institute of the Slovak Academy of Sciences, Bratislava, Slovakia
igor.lacik@savba.sk

The availability of individual rate coefficients in radical polymerization is a prerequisite for understanding the polymerization kinetics and mechanism. Among all the rate coefficients, the propagation rate coefficient, k_p, is of special interest since it determines the rate of polymer chain growth, and, additionally, its availability is required to estimate termination and a transfer rate coefficients. The method of choice for determination of accurate k_p values is the pulsed-laser polymerization combined with size-exclusion chromatography, pioneered by Olaj et al. [1]. This method has been used in the last decades for determination of k_p values for a number of monomers polymerized in organic [2] and aqueous [3] solutions.

This contribution will focus on k_p behavior for various monomers in aqueous solutions, including non-ionized and ionized monomers, and sparingly water-soluble monomers. The presence of functional groups in the monomer structure gives rise to intra and intermolecular interactions that are amplified by hydrogen bonding interactions with water molecules used as a solvent.

For non-ionized monomers (i.e., acrylic acid, methacrylic acid, acrylamide, *N*-vinyl pyrrolidone), water molecules accelerate the propagation step in going from bulk polymerization to dilute systems predominantly due to lowering the barrier to the internal rotational mobility within the transition state structure for propagation. This phenomenon is generally observed for all non-ionized monomers. In case of ionized monomers (i.e, anionically charged sodium acrylate, sodium methacrylate, and cationically charged methacrylate and methacrylamide monomers), the kinetics is dominated by electrostatic interactions with k_p values being reduced compared to those for non-ionized monomers due to repulsive interactions between equally charged monomer and radical chain-end. Repulsion interactions can be shielded by counterions to the charged groups, originated either from charged monomer or from salts added to the polymerization system. The radical polymerization of sparingly water-soluble monomers (i.e., methyl acrylate, methoxyethyl acrylate, methyl methacrylate) represents an interesting situation given by a limited solubility of monomers and insolubility of formed polymers in an aqueous environment. The k_p values for these monomers significantly increase in water compared to bulk polymerization.

Keywords: PLP-SEC, propagation rate coefficient, aqueous phase polymerization

Acknowledgments

This work was supported by the Slovak Scientific Grant Agency VEGA 2/0143/23.

References

[1] Olaj, O. F.; Bitai, I.; Hinkelmann, F. The laser-flash-initiated polymerization as a tool of evaluating (individual) kinetic constants of free-radical polymerization, 2. The direct determination of the rate of constant of chain propagation. *Die Makromolekulare Chemie* **1987**, *188 (7)*, 1689-1702.
[2] Beuermann, S.; Buback, M. Rate coefficients of free-radical polymerization deduced from pulsed laser experiments. *Progress in Polymer Science* **2002,** *27 (2)*, 191-254.
[3] Buback, M.; Hutchinson, R. A.; Lacík, I. Radical polymerization kinetics of water-soluble monomers. *Progress in Polymer Science* **2023,** *138*, 101645.

Safety and Sustainability Challenges Facing Phenolic Resins: Advances and Substitutions

J.F. Gérard[1*], J. Duchet-Rumeau[1], N. Chaussoy[1,2], L. Dentzer[1], D. Brandt[2]

[1]*UMR 5223 CNRS Ingénierie des Matériaux Polymères/INSA Lyon, Villeurbanne, France*
[2]*CEA-DAM Centre du Ripault, Monts, France*
[*]*jean-francois.gerard@insa-lyon.fr*

The synthesis of the phenolic resin was discovered by Baekeland a century ago adhesive and their excellent environmental resistance, adhesive capabilities, and fire high performances make them ones of the main wood adhesives but also in automobile, aerospace, composite materials, and other sectors. Phenolic resins are still widely used today with a global production of about 12 million tons/year. Usually, these resins contain residual free formaldehyde, which is highly toxic and carcinogenic and will soon be banned by the the REACh regulation. Consequently, phenolic resins must be revisited and/or substituted. Commonly, urea is added to phenolic resins as formaldehyde scavenger but urea is not relevant for high-temperature applications. Thus, an easy-to-implement method was developed with an aminophenol, giving access to a noncarcinogenic resin while maintaining the thermomechanical properties. The chemistry and the reaction mechanism of aminophenols with formaldehyde is described. The interest of this additive is multiple 1/ for trapping of formaldehyde to fit the REACh regulation, *i.e.* < 0.1 wt. %free formaldehyde) and 2/ maintaining the thermostability of the modified phenolic network ($T_{d5\%}$ = 395 °C and char yield = 63%). This method which is applicable on an industrial scale, uses mild reaction conditions and limits volatile organic compound emissions, *i.e.* two ways to improve durability and reduce toxicity of the resin.

The other route investigated is the design of "phenolic"-like resins without phenol or formaldehyde by substitution with "simple" molecules. The substitution of formaldehyde with aromatic aldehydes is a relevant way to ensure that the cured resin has degradation properties comparable to phenol/formaldehyde resins. In particular, terephthalaldehyde (TPA) appeared to be the most relevant candidate leading to thermostability properties similar to conventional phenolic resins but have too poor mechanical properties to be used as matrices in composite materials. The substitution of phenol with other phenolic compounds (including biosourced ones) was considered in order to increase the mechanical properties of the cured resin, but also to limit the toxicity of the unreacted liquid resins. Several compounds such as hydroxymethylphenols (HMP), resorcinol, 3-methoxyphenol, orcinol, 3-methylcatechol, hydroquinone, phloroglucinol, or 3,5-dimethoxyphenol were considered. All the results showed that the substitution of the phenol by a non-functionalized phenolic compound decreased the degradation behavior, except resorcinol, and did not afford materials with acceptable mechanical properties. Nevertheless, 2-HMP and 4-HMP (incl. without an alkali base), allow for obtaining materials with very interesting thermostability and thermomechanical properties. In addition, 2-HMP and TPA are non-toxic and the synthesis of this type of resin would be easily scalable. These compounds could be sustainable, 2-HMP could be produced by the reduction of salicylaldehyde (bio-renewable resource from lignin), and TPA could be produced by the reduction of terephthalic acid (potentially biosourced). Thus, these types of resins would be suitable candidates to replace conventional phenolic resins.

Keywords: phenolic resin, polyaddition, formaldehyde-free, biobased

Acknowledgments

The authors thanks Michelin Co. and CEA-DAM/DGA for financial supports.

References

[1] Xu, Y., Guo, L., Zhang, H., Zhai, H., and Hao, R. Research status, industrial application demand and prospects of phenolic resin. *RSC Adv.*, **2019**, 9, 28924

[2] Basafa, M., Hawboldt, K. A review on sources and extraction of phenolic compounds as precursors for bio-based phenolic resins. *Biomass Conversion and Biorefinery*, **2021**, https://doi.org/10.1007/s13399-021-01408-x

[3] Chaussoy, N., Brandt, D., Gérard, J.F. Formaldehyde-Free and Phenol-Free Non-toxic Phenolic Resins with High Thermostability. *ACS Appl. Polym. Mater.,* **2023***,* 5, 7, 5630–5640

[4] Chaussoy, N., Brandt, D., Gérard, J.F. Versatile Method To Reduce the Free Formaldehyde Content in Phenolic Resins for High-Temperature Applications. *ACS Appl. Polym. Mater.*, **2022**, 4, 6, 4454–4463

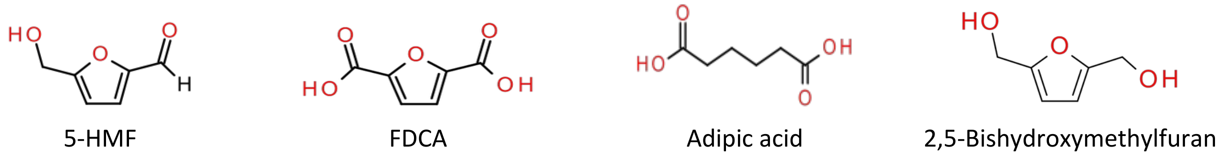
Can biobased polymers replace their fossil analogues?

Søren Hvilsted[1*], Rajni Hatti-Kaul[2]

[1]Hvilsted Consult, Hørsholm, Denmark,
[2] Division of Biotechnology and Applied Microbiology, Lund University, Lund, Sweden
[*]soren@hvilstedconsult.dk

The worldwide production of plastics is growing with ever increasing speed. The reason is simple: plastic is fantastic. However, it comes with a price: the plastic waste is also increasing with unwanted effects like accumulation in the marine environment and in nature. Furthermore, incineration of waste plastic results in carbon loss caused by the CO_2 emission, where the latter contributes to undesirable climate change. Recycling and reuse of waste plastic seams in general not to be economically viable although small locally based recycling schemes exist. However, a real change gamer will be legislative demands on more recycling.

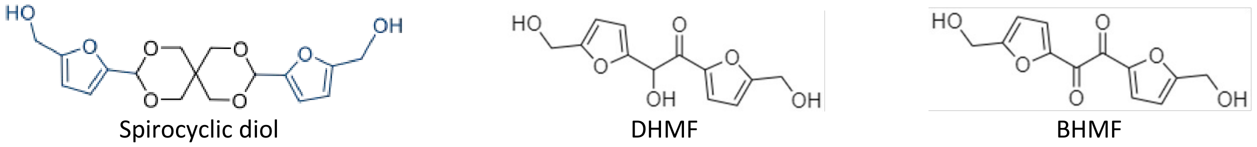
Another alternative is the biobased polymers. A few companies have expressed the desire to be fossil free in the near future. One example is the toy company LEGO that already since 2018 uses biobased PE flexible elements, where it doesn't compromise the critical mechanical demands on the building bricks. Biobased monomers (BM) like the sugar cane-based PE are all considerably more expensive than the fossil-based originals. Scale-up of other interesting BMs are in progress although the industrial involvement is sluggish. One example is the 5-hydroxymethyl furfural (5-MHF, Fig. 1), that can be produced in one step from fructose [1]. To minimize crosslinking of HMF molecules under acidic conditions and at high temperatures, a reactor has been designed and is being tested for scaling up the process. 5-HMF can be the source of a number of high value base chemicals [2] useful e.g. for polyesters, polyamides and polyurethanes. One particularly important example is furan dicarboxylic acid (FDCA, Fig. 1) that can be prepared enzymatically from 5-HMF via whole cell catalysis [3]. FDCA is the cornerstone in poly(ethylene furanoate) (PEF).



5-HMF FDCA Adipic acid 2,5-Bishydroxymethylfuran

Fig. 1 Key building blocks and monomers for biobased polyesters, polyamides and polyurethanes.

The rigid spirocyclic diol (Fig. 2) based on 5-HMF and pentaerythritol has enabled the production of sustainable rigid polyurethane coatings and foams. Another new biobased building block is 5,5'-bis(hydroxymethyl)furion (DHMF, Fig. 2) prepared by carboligation of two 5-HMF molecules using chemical catalysts or enzymes. Oxidation of DHMF results in 5,5'-bis(hydroxymethyl)furil (BHMF, Fig. 2). DHMF and BHMF are currently investigated as cross-linkers for polyurethane binders with application in floor coatings.



Spirocyclic diol DHMF BHMF

Fig. 2 Novel biobased building blocks for polyesters and polyurethanes

The future of biobased polymers seems to rely on the availability of biobased monomers and polymers in addition to the companies' willingness to pay the higher production cost of both monomers and polymers.

Acknowledgments

The Swedish Foundation for Strategic Environmental Research (MISTRA) is acknowledged for funding the research programme Sustainable Plastics and Transition Pathways (STEPS).

References

[1] Sayed, M.; Warlin, N.; Hulteberg, C.; Munslow, I.; Lundmark, S.; Pajalic, O.; Tunå, P.; Zhang, B.; Pyo, S-H.; Hatti-Kaul, R. 5-Hydroxymethylfurfural from Fructose: An Efficient Continuous Process in a Water-Dimethyl Carbonate Biphasic System with High Yield Product Recovery. *Green Chemistry* **2020**, *22*, 5402-5413.

[2] Van Putten, R-J.; van der Waal, J.C.; deJong, E.; Rasrendra, C.B.; Heeres, H.J.; de Vries, J.G. Hydroxymethylfurfural, A Versatile Platform Chemical Made from Renewable Resources. *Chemical Reviews* **2013**, *113*, 1499-1597.

[3] Sayed, M.; Gaber, Y.; Junghus, F.; Martin, E.V.; Pyo, S-H.; Hatti-Kaul, R. Oxidation of 5-hydroxymethylfurfural with a Novel Aryl Alcohol Oxidase from Mycobacterium sp. MS1601. *Microbial Biotechnology,* **2022**, *8,* 2176-2190.

Invited lectures

Morphology alterations within emulsion templated macroporous polymers

Peter Krajnc

PolyOrgLab, University of Maribor, Slovenia

peter.krajnc@um.si

Emulsions with high volume fractions of the droplet phase (frequently termed high internal phase emulsions-HIPEs) can be a useful template for the preparation of highly porous monolithic polymer structures with either oil-soluble or water soluble monomers. While the typical polymerized high internal phase emulsion topology resembles interconnected cellular foam-like structure, the lecture will discuss the possibilities of significant morphology alterations by several methods like phase inversion induction and combinations with other templating methods.

Novel Functional Polymers From Renewable Monomers

J. Mosnáček*, M. Gurská, A. Eckstein, G. Zain, S. Lenka, J. Kollár, M. M. Puzhakkalakath, M. Danko, K. Mosnáčková, F. Pippig

[1]*Polymer Institute of the Slovak Academy of Sciences, 845 41 Bratislava, Slovakia*
* *jaroslav.mosnacek@savba.sk*

In recent years, there is increasing demand for polymer materials from renewable sources, i.e. biomass. It is related to the high global consumption of materials based on fossil resources, which are non-renewable, their quantity is limited and they are not environmentally friendly. One of the effective alternatives for creating new polymer materials is the use of renewable raw materials. The biomass is a source of a wide range of compounds that are either themselves suitable monomers or their derivatives are potential monomers for polymer chain formation. Some of the polymers can possess convenient chemical-mechanical properties, thanks to which they can able to replace synthetic polymers from fossil sources. One group of the potential monomers are furan-based compounds that contain a suitable functional group for polymerization. The most frequently used are furfural and 5-hydroxymethylfurfural. The advantage of furfural is its preparation from agricultural and forest waste, which consists in the acid-catalyzed dehydration reaction of aldoses or ketosis.[1] α-Methylene-γ-butyrolactone (MBL), known also as a Tulipalin A is an additional type of renewable monomer, and has already successfully been polymerized by various polymerizations.[2]

One part of our work deals with the preparation of three furan derivatives, which have potential to be used in the synthesis of functional polymers. These compounds represent monomers obtained from biomass as a result of the derivatization of 5-(hydroxymethyl)-furfural. Two polymerization techniques were chosen for the polymerization of these derivatives, atom transfer polymerization, ATRP, and nitroxide mediated polymerization, NMP. The derivatives containing vinyl or (meth)acrylate groups were homopolymerized or copolymerized using these polymerization techniques with the aim to prepare functional polymer with controlled molar mass and narrow distribution of molar masses (low dispersity). Second part of our work deals with the synthesis of various functional polymers from Tulipalin A and its derivatives. Thus, superabsorbent hydrogels, polymeric particles, amphiphilic polymers, polyesters as well as polyamidoamines were prepared. In addition, the amine groups at the polyamidoamines chain ends can be extended by reaction with 2,5-furandicarboxaldehyde.

Acknowledgments

The authors thank for support to FUR4Sustain project, Grant Agency VEGA through project VEGA 2/0137/23 and SRDA grant agency through project APVV-23-0534.

References

[1] Gandini A., Lacerda T.M., Polymers From Renewable Resources **2016**, 1–42, ISBN 0471238961.

[2] (a) Zain G., Bondarev D., Doháňošová J., Mosnáček J. *ChemPhotoChem*. **2019**, 3, 1138–1145; (b) Kollár J., Mrlík M., Moravčíková D., Kroneková Z., Liptaj T., Lacík I., Mosnáček J. *Macromolecules* **2016**, 49, 4047-4056; (c) Danko M., Basko M., Ďurkáčová S., Duda A., Mosnáček J. *Macromolecules*, **2018**, 51, 3582-3596; (d) Ismael I., Mrlík M., Vykydalová A., Annušová A., Halahovets Y., Mosnáček J., Danko M. *Polym. Adv. Techn.*, **2024**, 35 (4), e6404.

High Rate Uniaxial and Cyclic Multiaxial Testing of Polymer Lattice Structures

Z. Major[1*], Anna Hössinger Kalteis1 and Michael Lackner1

[1]*Institute of Polymer Product Engineering, Linz, Austria*
Johannes Kepler University Linz
[*]*Corresponding Author zoltan.major@jku.at*

Abstract. A wide variety of lattice structures can be designed and fabricated by additive manufacturing of polymeric materials. Complex components with sufficient stiffness, strength and surface quality can be manufactured by selective laser sintering using PA12 and TPU grades. To cope with design challenges of polymeric lattice structures a comprehensive test program was developed and implemented in a Horizon research a project (MOAMMM, FET Open, 2021-2024). The main parts of this test program are sown in figure 1.

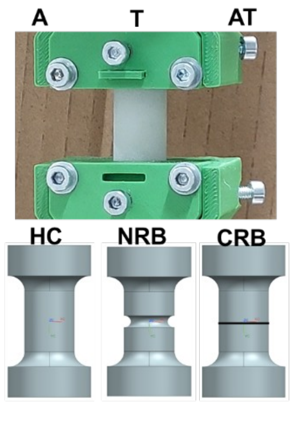
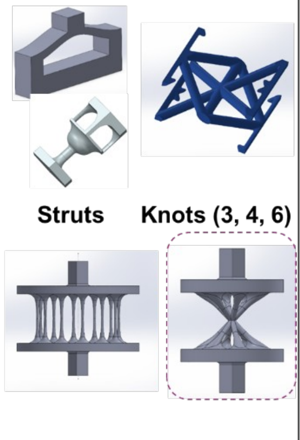
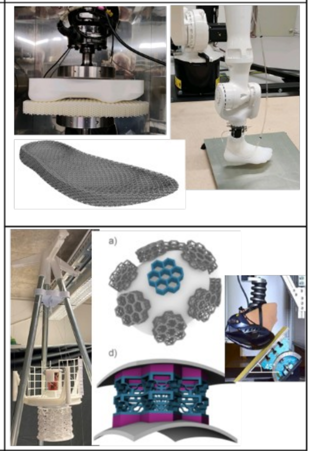
Material tests Laboratory Specimens • Cylindrical specimens with/without notch, printing orientation • Multiaxial loading	Processing tests Struts, knots, single cells	Performance tests • Model component • Lattice cells in cylindrical specimens	Component tests • Helmet – impact • Shoe sole – pulse, cyclic
			

Fig. 1: Overview of the specimen configurations and test methods

The two main highlights of the material testing are:

- Uniaxial compression tests were performed over a wide loading rate range (up to about 30°m/s) to characterize the loading rate dependent yield and post-yield behavior .
- The combined effect of anisotropy and multiaxial loading (axial, torsional and combined axial/torsional) was characterized under both monotonic and cyclic loading conditions. A multiaxial strength/fatigue-map was designed and plotted for the materials investigated.

Acknowledgments

These experiments have been performed in the Multi-scale optimisation for additive manufacturing of fatigue resistant shock-absorbing MetaMaterials (MOAMMM) project. This project has received funding from the European Union's Horizon 2020 research programme under grant agreement No 862015.

References

[1] Z. Major, M. Lackner, A. Hössinger-Kalteis, and T. Lück. « Characterization of the Fatigue Behavior of SLS Thermoplastics. » Procedia Structural Integrity 34 (2021): 191-198.

[2] D.A. Hun, M. Haddad, I. Doghri, M. Lackner, Z. Major, L. Doppelbauer, S. Haouala. "A Computationally Efficient Hybrid Formulation for Viscoelastic-Viscoplastic Polymer Solids and Structures Under Large Numbers of Loading Cycles" International Journal of Solids and Structures, 314, (2025): 113290.

GRADIENT COPOLYMERIZATION-INDUCED SELF-ASSEMBLY: FROM MONOMERS TO NANOPARTICLES IN A SINGLE STEP

Ondrej Sedlacek[1]
[1]Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, 128 40
Prague 2, Czech Republic-Email: sedlacek@natur.cuni.cz

Polymerization-induced self-assembly (PISA) has established itself as a versatile strategy for the one-pot fabrication of polymer nanoparticles, enabling high solid contents and minimizing the need for extensive post-polymerization processing.[1] Through the in situ generation of amphiphilic copolymers, PISA efficiently produces stable nanostructures with controllable morphologies and tailored properties.

In this work, we explore the integration of PISA with gradient copolymerization to achieve the single-step synthesis of amphiphilic nanoparticles. Leveraging monomers with contrasting reactivities and solubility profiles, we steer the formation of gradient copolymer architectures that spontaneously assemble into stable nanoparticle dispersions. Three systems are highlighted. First, an aqueous gradient PISA approach yields highly responsive ^{19}F MRI nanotracers from *N,N*-(2,2,2-trifluoroethyl)acrylamide and hydrophilic poly(ethylene glycol) methyl ether methacrylate, exhibiting enhanced relaxivity and strong potential for diagnostic imaging.[2] Second, a RAFT/MADIX-mediated statistical emulsion copolymerization of *N,N*-dimethylacrylamide and vinyl acetate results in surfactant-free latex nanoparticles, where the emulsion conditions significantly boost polymerization rates and impact morphology, leading to block-like structures despite a gradient-feed strategy. Finally, cationic ring-opening polymerization in dodecane enables the synthesis of poly(2-oxazoline) nanoparticles across both block and gradient configurations.[3] This CROPISA method also facilitates formulations suitable for applications such as Pickering emulsion stabilization. Collectively, these examples showcase the versatility of gradient copolymerization-induced self-assembly, offering efficient pathways to sophisticated polymer nanomaterials for a wide range of applications.

References:

d'Agosto, F., Rieger, J., and Lansalot, M., RAFT-mediated polymerization-induced self-assembly. *Angew.Chem. Int. Ed.* **2020**, *59*(22), 8368-8392.

[2] Panakkal, V. M., Havlicek, D., Pavlova, E., Jirakova, K., Jirak, D., and Sedlacek, O., Single-Step Synthesis of Highly Sensitive ^{19}F MRI Tracers by Gradient Copolymerization-Induced Self-Assembly. *Biomacromolecules* **2024**, *25*(12), 7685-7694.

[3] Lusiani, N., Pavlova, E., Hoogenboom, R., and Sedlacek, O., Cationic ring-opening polymerization-induced self-assembly (CROPISA) of 2-oxazolines: From block copolymers to one-step gradient copolymer nanoparticles. *Angew. Chem. Int. Ed.* **2024**, e202416106.

Bicontinuous nanophasic amphiphilic conetworks as intelligent drug release matrices and nanoreactors for novel nanohybrids

Béla Iván[1]*, Áron Bajcsi[1], Eszter Budai[1], Csaba Fodor[1], Márton Haraszti[1], Dániel Kalocsai[1],
György Kasza[1], Péter Mezey[1], Anna Petróczy[1], Tímea Stumphauser[1], Yi Thomann[2],
Ralf Thomann[2], Rolf Mülhaupt[2]

[1]Polymer Chemistry and Physics Research Group, Institute of Materials and Environmental Chemistry,
HUN-REN Research Centre for Natural Sciences, H-1117 Budapest, Magyar tudosok krt. 2, Hungary
[2]Freiburg Material Research Center, Institute for Macromolecular Chemistry and Freiburg Center for
Interactive Materials and Bioinspired Technologies (FIT), University of Freiburg,
Stefan Meier Str. 31, D-79104 Freiburg, Germany
*****Corresponding Author's E-mail address: *ivan.bela@ttk.hu*

Undoubtedly, multicomponent polymer architectures have gained significant interest over the years due to their special properties and to the large variety of application possibilities. Among such macromolecular materials, polymer conetworks, especially amphiphilic conetworks (APCNs), composed of chemically (covalently) bonded hydrophilic and hydrophobic polymer chains, belong to a special class of rapidly emerging nanostructured materials with various unique structural features and characteristics (see e.g. Refs. 1-7 and references therein). Because of the immiscibility of the components, the synthesis of such macromolecular assemblies is quite challenging. Several successful synthetic routes have recently been developed by us, including various protection-deprotection schemes. Unique bicontinuous (cocontinuous) nanophase separated morphology exists in APCNs in a broad composition window with domain sizes in the range of ~2-30 nm. This provides unprecedented possibilities to obtain various new specialty intelligent (smart, responsive) and organic solvent selective superabsorbent poly(ionic liquid) conetwork gels, and catalytically active organic-inorganic nanohybrids by applying one of the nanophases as nanoreactor. The resulting novel materials have a variety of high value-added potential applications from intelligent drug delivery to antibacterial biomaterials, nanocatalysis, photonics, energy and environment protection related materials, sensors, and specialty superabsorbents etc.

Acknowledgments. Support by the National Research, Development and Innovation Office, Hungary (NN116252, NN129366, K135946, PD139162) and the European Research Area ERA-Chemistry program is acknowledged.

References

[1] Petróczy, A.; Szanka, I.; Wacha, A.; Varga, Z.; Thomann, Y.; Thomann, R.; Mülhaupt, R.; Bereczki, L.; Hegyesi, N.; Iván, B. *Gels* **2025**, *11*, 318.
[2] Stumphauser, T.; Kasza, Gy.; Domján, A.; Wacha, A.; Varga, Z.; Thomann, Y.; Thomann, R.; Pásztói, B.; Trötschler, T.; Kerscher, B.; Mülhaupt, R.; Iván, B. *Polymers* **2020**, *12*, 2292.
[3] Pásztor, Sz.; Kali, G.; Iván, B. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, 55, 1818-1821.
[4] Fodor, Cs., Kali, G.; Thomann, R.; Thomann, Y.; Iván, B.; Mülhaupt, R. *RSC Adv.* **2017**, *7*, 6827-6837.
[5] Pásztor, Sz.; Kali, G.; Iván, B. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, 55, 1818-1821.
[6] Kali, G.; Iván, B. *Eur. Polym. J.* **2016**, *84*, 668-674.
[7] Kali, G.; Vavra, Sz.; László, K.; Iván, B. *Macromolecules* **2013**, *46*, 5337-5344.

Entropy diluent in polymer crystals and blends

J. H. Sim[1*], Y. Kang[2*]

[1] *Research Institute for Convergence of Basic Science, Hanyang University, Seoul 04763, Republic of Korea*
[2] *Department of Chemistry, Hanyang University, Seoul 04763, Republic of Korea*
[*] *jhsim@hanyang.ac.kr; youngjkang@hanyang.ac.kr*

Over the pase century, significant progress has been made in understanding the properties of polymers and this progress has been driven by innovative synthetic techniques, precise experimentation, and profound physical insight. However, despite the widespread approaches with enthalpic perspective, such as tailoring chemical structures and controlling molecular interactions, there has been little active effort to exploit polymer properties by manipulating entropy.

In this presentation, we will explore the role and importance of entropy control in various studies of polymer properties, such as crystallization, blending, and phase transition with the case of the novel concept named "entropy diluent" substantially decrease the conformation entropy of polymer chains. For example, atatactic poly(methyl methacrylate) (PMMA) was successfully crystallized into 1D hypo-crystals whose polymer chains are laterally oriented and closely packed in one direction perpenticular to the molecular axis. Also, straightforward prepartion method suppressing phase separation of incompatible polymer blends, such as polystyrene (PS)/PMMA, to the level of indistinguishable dynamic heterogeneity.

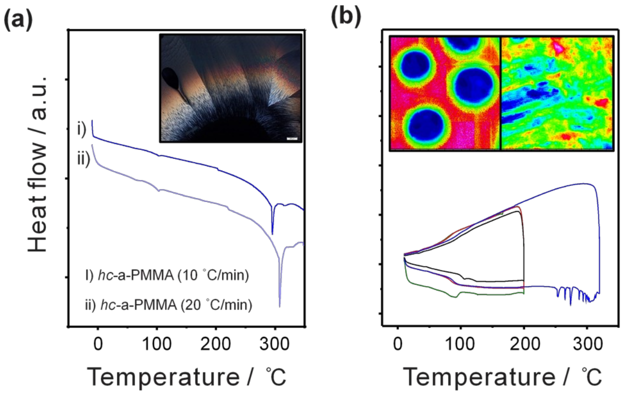


Figure 1. DSC thermograms of (a) 1D hc-PMMA and (b) PS/PMMA_{BA}: inset in panel (a) shows polarized optical microscopy image of 1D hc-PMMA film and in panel (b) represents polarized FT-IR mapping images of PS/PMMA (left image) and PS/PMMA_{BA} (right image).

Keywords: entropy diluent, 1D hypo-crystals, polymer blends

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) and Korea Basic Science Institute (National Research Facilities and Equipment Center) grant funded by the Ministry of Education (2020R1A6A1A06046728 and 2022R1A6C101A779).

References

[1] Sim, J. H.; Kwon, Y.; Eom, S.; Hwang, M.; Park, S.; Choi, H.; Chung, H.; Sohn, D.; Kang, Y. 1D Hypo-Crystals of Stereo-Irregular PMMA via Spray-Induced Rapid Solidification of Aqueous Solutions. *Macromolecules* **2022**, *55*, 1700-1708.
[2] Sim, J. H.; Eom, S.; Lee, S.; Oh, C.; Lee, M.; Kim, S.; Lee, W. B.; Ryu, J.; Sohn, D.; Chung, H.; Hyon, J.; Park, C.; Thomas, E. L.; Kang, Y. 1D hypo-crystals: A novel concept for the crystallization of stereo-irregular polymers. *Materials Today.* **2020**, *40*, 26-37.

Effect of epoxy-metal interphase development on debonding kinetics of advanced laminates

Gernot Wallner, Gary Säckl, Gabriel Riedl, David Stifter

Institute of Polymeric Materials and Testing – Christian Doppler Laboratory for Superimposed Mechanical-Environmental Ageing of Polymeric Hybrid Laminates, University of Linz, Austria
**gernot.wallner@jku.at*

Hybrid metal laminates are of high relevance for renewable energy technologies such as wind power generators, electric engines or transformers. Especially for electrical steel stacks, waterborne epoxy coatings cured with the latent curing agent dicyandiamide (DICY) are well-established. As evidenced in previous studies for electrical steel laminates, chemical interactions take place already during coating of waterborne epoxy varnishes onto the metal substrate. The main objective of this study was to evaluate waterborne epoxy/metal interactions on a fundamental and more comprehensive level. Pure metals such as Sn, Ti, Fe, Al, Zn or Mg with oxide or hydroxide passsivation layers differing in their isoelectric point (IEP) were considered. While Sn is chracterized by a rather acidic oxide, MgOH is classified as alkaline. First, the pure metal sheets were immersed in a boiling solution of DICY in water. The lower the IEP, the higher was the amount of protonated amine at the surface. Vice versa, high IEP metals revealed an pronounced formation of imine species. Second, epoxy coated metal sheets were investigated. The coated metal was cryo-ultra-low-angle-microtomed (cryo-ULAM) and characterized by XPS. At the epoxy/metal interface, reaction products were detected which were in agreement with the immersion test. Moreover, it was confirmed that especially alkaline metal oxides are prone to release metal ions migrating into the epoxy coating. Metal complexes were discrnible within the bulk, but also on the surface of the few microns thin epoxy coating. Finally, the effect of the IEP of the substrate on the crack growth kinetics of bonded laminates was assessed by cyclic fatigue tests on double cantilever beam specimen. The higher the IEP of the metal substrate, the slower was the crack growth rate in the stable crack growth regime and the higher was the strain energy release rate in the threshold regime. Overall, this study clearly confirmed that chemical interactions are taking place during manufacturing of waterborne epoxy/metal laminates, which have a significant impact on the adherence and the crack growth resistance [1].

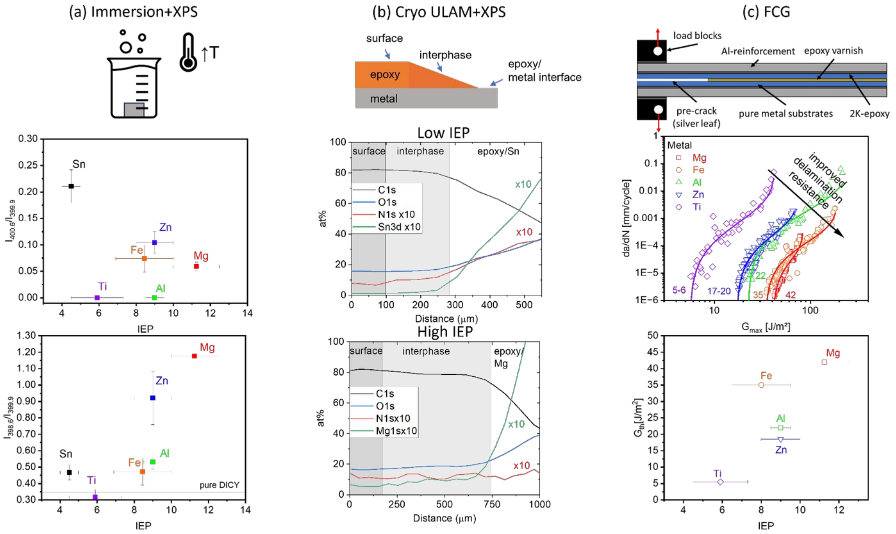

(a) Immersion+XPS (b) Cryo ULAM+XPS (c) FCG

Fig. 1: **Effect of the isoelectric point of a metal oxide on the formation of DICY reaction products (a) after immersion in a solution of DICY in water, and (b) in epoxy coatings on metal substrates, and (c) on the fatigue debonding kinetics of epxy/metal laminates.**

Acknowledgments

The financial support by the Austrian Federal Ministry for Digital and Economic Affairs, the National Foundation for Research, Technology and Development and the Christian Doppler Research Association is gratefully acknowledged.

Reference

[1] Säckl, G., Riedl, G., Duchoslav, J., Marchfelder, C., Aufray, M., Stifter, D., Wallner, G.M., (2025). Metal laminates based on waterborne epoxy varnishes - chemical inter-actions and effect on fatigue crack growth kinetics, Progress in Organic Coatings, 200, 109104.

Crystallization and Recrystallization of PB-1: Impact of Sorbitol-Based Nucleating Agent

J. Navrátilová[1*], L. Gajzlerová[1], M. Polášková[1,2], R. Čermák[1]

[1] *Department of Polymer Engineering, Faculty of Technology, Tomas Bata University in Zlin, Vavreckova 5669, 760 01 Zlin, Czech Republic*
[2] *The Centre of Polymer Systems, Tomas Bata University in Zlin, trida Tomase Bati 5678, 760 01 Zlin, Czech Republic*
**j1navratilova@utb.cz*

Polybut-1-ene (PB-1) is semicrystalline polymer interesting for its polymorphic nature, undergoing phase transitions between different crystalline forms over time. Initially, PB-1 crystallizes into a kinetically preferred tetragonal phase (phase II), which gradually transforms into the thermodynamically stable hexagonal phase (phase I), especially under ambient conditions [e.g. 1]. This transition is of great interest due to its impact on material properties, e.g. mechanical strength or long-term stability. A deeper understanding of the crystallization and recrystallization kinetics of PB-1 is thus essential for optimizing processing conditions and enhancing their performance in practical applications.

The work is focused on crystallization and recrystallization of PB-1 homopolymer and random PB-1 copolymer with low content of ethylene. The effect of the addition of nucleating agent (NA) 1,2,3,4-bis(3,4-dimethylbenzylidene) sorbitol, commercial clarifying agent designed primarily for polypropylene (PP), Millad 3988, on the crystallization and subsequent recrystallization is studied, particularly in relation to the kinetics of the process [2]. The NA was applied in two common concentrations 0.2 and 0.6 wt. %. The recrystallization from tetragonal phase II into hexagonal phase I in defined times of ageing at room temperature was characterized by spectrophotometry, wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC). The structure was also obserd via polarized light and scannning electron microscopes.

It was found, that NA Millad 3988 is effective, particularly for the copolymer. The addition of 0.2 wt. % significantly increases the crystallization temperature, and, at the same time, narrows the crystallization peak. On the other hand, the haze increased dramatically in PB-1/NA systems. Thus, the NA used does not act as a clarifying agent and a two-phase system is formed. Under the given sample preparation conditions, NA did not form an organogel leading to a decrease in transparency as is commonly done in PP. It was found that at a concentration of 0.2 wt.% dissolution of NA in PB-1 does occur, but the melting temperature is crucial. As the temperature increases, the solubility also increases. The dissolved nucleating agent, however, was found to form rod-shaped crystals with a diameter of about 1 μm on cooling. These cause nucleation of PB-1. WAXS analysis revealed that NA accelerates recrystallization from phase II to I in homopolymer. In the case of the copolymer, the effect of NA is not as pronounced, however, it also interferes with the recrystallization process.

According to results, it can be confirmed that the addition of commercial NA Millad 3988 has a significant effect on the crystallization and recrystallization behavior of both the PB-1 homopolymer and the PB-1 copolymer, even at a concentration of 0.2 wt.%. Millad 3988 very significantly increases the rate of crystallization in copolymer while it considerably accelerates the recrystallization of homopolymer. However, the crystallization process may be affected by the solubility of NA in PB-1 melt at high processing (melt) temperatures at such low concentrations.

Keywords: polybut-1-ene, crystallization, recrystallization, nucleation

References

[1] Miller, R.L.; Holland, V.F. On Transformations in Isotactic Polybutene-1. *Journal of Polymer Science Part B: Polymer Letters* **1964**, *2(5)*, 519-521.

[2] Horvath, Z.; Gyarmati, B.; Menyhard, A.; Doshev, P.; Gahleitner, M.; Varga, J.; Pukanszky, B. The Role of Solubility and Critical Temperatures for the Efficiency of Sorbitol Clarifiers in Polypropylene. *RSC Advances* **2014**, *4(38)*, 19737-19745.

Sustainable PFAS-free Binder for High-Energy Lithium-Ion Batteries

K. Bretterbauer*

Johannes Kepler University Linz, Institute for Chemical Technology of Organic Materials, Linz, Austria
**klaus.bretterbauer@jku.at*

Climate change and the energy transition require a sustainable energy supply. Besides the green generation of energy, its storage is crucial for economic and social development. Research and industry demonstrate that high-energy lithium-ion batteries (LIB) represent the key technology toward a sustainable future.

The LIB constitutes a very complex system due to the interaction of many materials working together to create a well-working device. Considering the cathode, it consists of a current collector made from aluminum foil coated with a mixture of the active lithium transition metal oxide (Ni, Mn, Co) and electrically conducting carbon black. This cathode is soaked in electrolyte and is connected to a polyethylene foil that serves as the separator (Figure 1a). This composite electrode is held together by a polymeric binder that ensures intensive contact between all components and maintains mechanical integrity. Currently, fluorinated polymers are used as binders in lithium-ion batteries, which require hazardous per- and polyfluorinated chemicals (PFAS) and toxic solvents as processing aids.

Herein, a sustainable approach to the energy storage sector is presented, encompassing a holistic view of the value chain, achieved with polymeric surfactants derived from 11-acrylamidoundecanoic acid [1]. The materials developed facilitate the production of PFAS-free batteries, with the primary raw material sourced from the renewable resource, castor oil (Figure 1b). Enhanced adhesion and flexibility result in a longer battery service life, and the salt character provides the polymer with ionic conductivity, along with the option to process the cathodes in water and utilize a water-based recycling process. Thus, elements with limited availability, such as Li, Ni, Mn, and Co, can be recovered in an energy-efficient and environmentally friendly manner. Due to the pH-dependent solubility of the polymers, it can be recovered as well. The binder was also shown to work with other battery systems based on sodium or potassium.

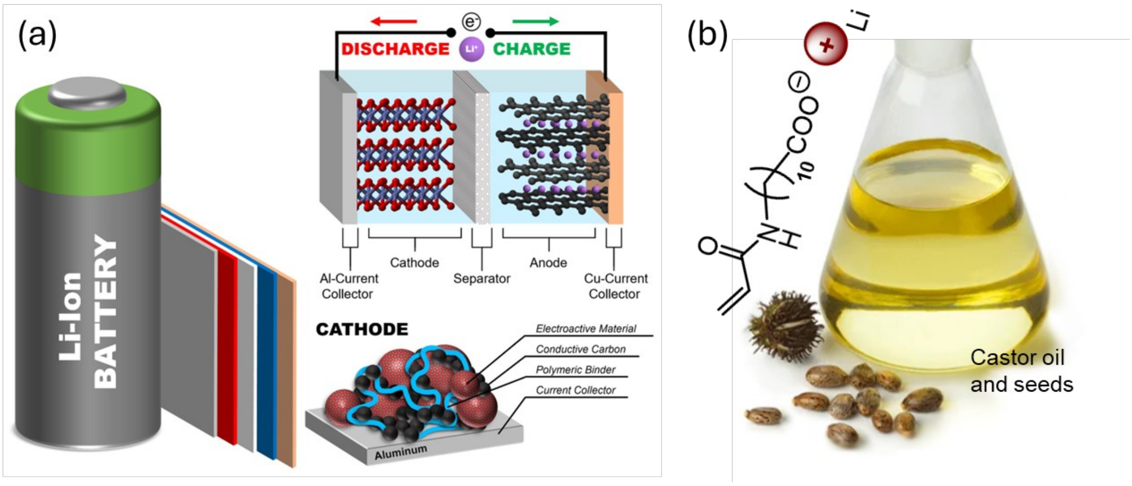


Figure 1. Schematic representation of the components and operating principle of a lithium-ion battery (a) and the castor oil-related monomer as the basis of the sustainable polymeric binder (b).

Keywords: PFAS-free, sustainable energy materials, polymeric surfactant, polyelectrolyte

References

[1] Leibetseder, F.; Xie, J.; Leeb, E.; Hesser, G.; Pettinger, K.-H.; Bretterbauer K. Recyclable Fluorine-Free Water-Borne Binders for High-Energy Lithium-Ion Battery Cathodes. *Advanced Energy Materials* **2024**, *14*(27), 2401074.

Ionic Liquids: A powerful Toolbox for the design of multifonctional polymer materials

Sébastien Livi[1]*, Léa Simonnet[1], Jean-François Gerard[1], Jannick Duchet-Rumeau[1]

[1] *Universite Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, CNRS UMR 5223, Ingénierie des Matériaux Polymères, F-69621 Villeurbanne Cédex, France*
**sebastien.livi@insa-lyon.fr*

Nowadays, advanced polymer materials are at the forefront of tackling global challenges such as environmental issues while pursuing research into high-performance materials. Thus, the development of new synthetic methods is critical for designing innovative polymer materials and proposing sustainable solutions to meet the requirements of the circular economy, *i.e.* to be sustainable, reusable, and recyclable. Scientists must thus propose through a *'Functional materials by design'* approach to develop molecular brick platforms or additives allowing the integration at the molecular scale of the required functions in the initial synthesis steps. Simultaneously, scientists must think to the End-of-Life of these functional materials by the concept *'design to recycle' or 'design to degrade'* , to be reused in a closed loop supply chain. In fact, the unique properties of ionic liquids (ILs), such as their high thermal stability, low vapor pressure, non-flammability, and hydrophobic behaviour make them promising candidates for the development of a new generation of polymer materials with enhanced properties [1-4] as well as solvents greening the chemical recycling of thermoplastics. Recently, our laboratory has designed a new generation of more environmentally friendly, i.e. reusable and/or degradable epoxy-amine and epoxy-anhydride networks by using ILs leading to networks with Tg included between 60 °C to 200 °C combining good thermomechanical and mechanical properties. In other side, ionic liquid and a deep eutectic solvent (DES) were used to compatibilize polymer blends based on PBSA/PHB (80/20). Thus, we have demonstrated that the addition of a small amount of these interfacial agents simultaneously led to a considerable improvement in the mechanical performances of the blends. In terms of thermal stability, the use of ILs and DES stabilized the PBSA/PHB blend and retarded its thermal degradation (+ 100 °C), Moreover, the oxygen and water permeability were also investigated confirming that the synergistic effect of these additives with the PHB inducing a significant reduction in permeability and increasing the degradability of the corresponding polymer blends. In summary, Ionic Liquids are a promising additives to design fnctional polymer materials with high performances.

Keywords: Ionic Lquids, Degradable networks, Polymer blends, Chemical recycling

Acknowledgments

Ce travail a bénéficié d'une aide de l'Etat gérée par l'Agence Nationale de la Recherche au titre de France 2030 portant la référence ANR-22-PERE-0005 du projet RECYCOMP de l'Axe Matériaux Composites. This work benefited from State aid managed by the National Research Agency under France 2030 bearing the reference ANR-22-PERE-0005 of the RECYCOMP project of the Composite Materials Axis.

References

[1] S Livi, J Baudoux, J Duchet-Rumeau, JF Gérard, Ionic Liquids : A Versatile Platform for the Design of a Multifunctional Epoxy Networks 2.0 Generation, Progress in Polymer Science, 132, 101581 (2022).

[2] G. Perli, C.Y. Okada, J-F. Gerard, J. Duchet-Rumeau, S. Livi, Design for disassembly of composites and thermoset by using cleavable ionic liquid monomers as molecular building blocks, Composites Part B: Engineering, 264, 110899 (2023).

[3] Z Bensalem, H Chabane, HS Ababsa, A Mekki, S Livi, Ionic Liquids versus Deep Eutectic Solvent: A Tunable Platform for the Design of Biopolymer Blends, ACS Sustainable Chem. Eng. 2024, 12, 3, 1309–1319, (2024).

[4] H. Chabane, Z Bensalem, HS Ababsa, A Mekki, S Livi, Polyhedral Oligomeric Silsesquioxane-Supported Ionic Liquid as Platform for Designing Sustainable PBSA Nanocomposites, ACS Sustainable Chem. Eng. 2024, 12, 40, 14784–14794 (2024).

Advanced Erbium-Polyaniline Quantum Dots Composites for Next-Generation Energy Storage

Elena Tomsik*, Marwa Ennouri

Institute of Macromolecular Chemistry CAS, Heyrovského nám. 2, 162 00 Prague, Czech Republic
**Corresponding Author's E-mail address tomsik@imc.cas.cz*

Simultaneous harvesting of sunlight and storing its energy in optoelectronic devices is a scientific challenge. The current work pursues two main goals: 1) to understand the interaction of erbium ions with stable PANI quantum dots (8 nm), obtained by acid-assisted polymerization method, and 2) to investigate the potential application of Er-PANI:PSS composite as a next-generation energy storage system. Stable PANI quantum dots of 8 nm size are obtained by the acid-assisted polymerization method for the first time. These nanoparticles were further stabilized by PSS and decorated with erbium ions. FTIR and XPS analyses confirm that no direct erbium-PANI coordination is observed; nevertheless, PANI is likely present in the second coordination sphere of the erbium complex, potentially enabling energy transfer between the PANI π-system and Er3+ ions. CV and LSV measurements show that the incorporation of Er^{3+} ions into the composite leads to a marked improvement in electrochemical performance. A further enhancement in areal current was achieved under light irradiation, particularly when using a 655 nm LED, which corresponds to one of the most intense regions of the solar spectrum. This enhancement in electrochemical performance directly translates to a significant increase in specific capacitance; the pristine PANI:PSS suspension exhibited an areal capacitance of 47.2 mF/cm², which increased to 183 mF/cm² upon Erbium addition and reached 299 mF/cm² under light irradiation of the composite suspension (Figure 1).[1]

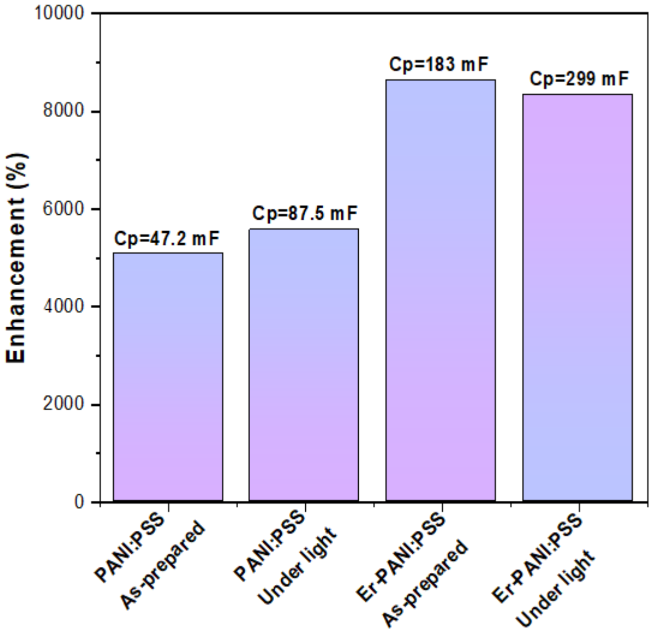


Figure 1. Areal capacitance of different systems, calculated from CV.

Keywords: Polyaniline Quantum Dots, Energy Materials, Erbium Ions.

References

[1] Ennour,i M.; Svoboda, J.; Morávková, Z.; Hromádková, J.; Tomsik, E. Harnessing Light in Tandem: Advanced Erbium-Polyaniline QD Composites for Next-Generation Energy Storage, *Nanoscale*, submitted.

Chemical recycling of polyurethane foams

E. Žagar,* E. Koša, D. Pahovnik

Department of Polymer Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia
**ema.zagar@ki.si*

The global production of plastics has risen sharply from two million tonnes in 1950 to 450 million tonnes today, because plastic is a light, cheap and versatile material and is therefore used in many areas, from construction and household to medicine, packaging, etc. At present, not all plastic waste can be recycled, incinerated or landfilled, so more and more of it ends up in the environment, which has become a problem of our society. For this reason, there is a strong focus on improving the recycling rate of plastic waste. So far, mechanical recycling of plastic waste is the most developed, but it is not suitable for all types of plastic. An alternative to mechanical recycling is chemical recycling, which enables the production of raw materials that can be used as substitutes for petrochemicals.

The presentation will focuse on the chemical recycling of polyurethane (PU) foams, which have a cross-linked structure and are therefore not suitable for mechanical recycling. PU foams can be chemically degraded by different metods (glycolysis, hydrolysis, aminolysis, hydrogenolysis, amonolysis) to recover polyether polyols [1–3]. In this presentation we will discuss the advantages and disadvantages of the individual recycling methods for PU foams.

References

[1] M. Grdadolnik, A. Drinčič, A. Oreški, Ö. Can Önder, P. Utroša, D. Pahovnik, E. Žagar. Insight into chemical recycling of flexible polyurethane foams by acidolysis. ACS Sustainable Chemistry & Engineering 2022, 10, 1323-1332.
[4] B. Zdovc, M. Grdadolnik, D. Pahovnik, E. Žagar. Determination of end-group functionality of propylene oxide-based polyether polyols recovered from polyurethane foams by chemical recycling. Macromolecules 2023, 56, 3374–3382.
[3] M. Grdadolnik, B. Zdovc, A. Drinčič, Ö. Can Önder, P. Utroša, S. Garcia Ramos, E. Dominguez Ramos, D. Pahovnik, E. Žagar. Chemical recycling of flexible polyurethane foams by aminolysis to recover high-quality polyols. ACS Sustainable Chemistry & Engineering 2023, 11, 10864-10873.

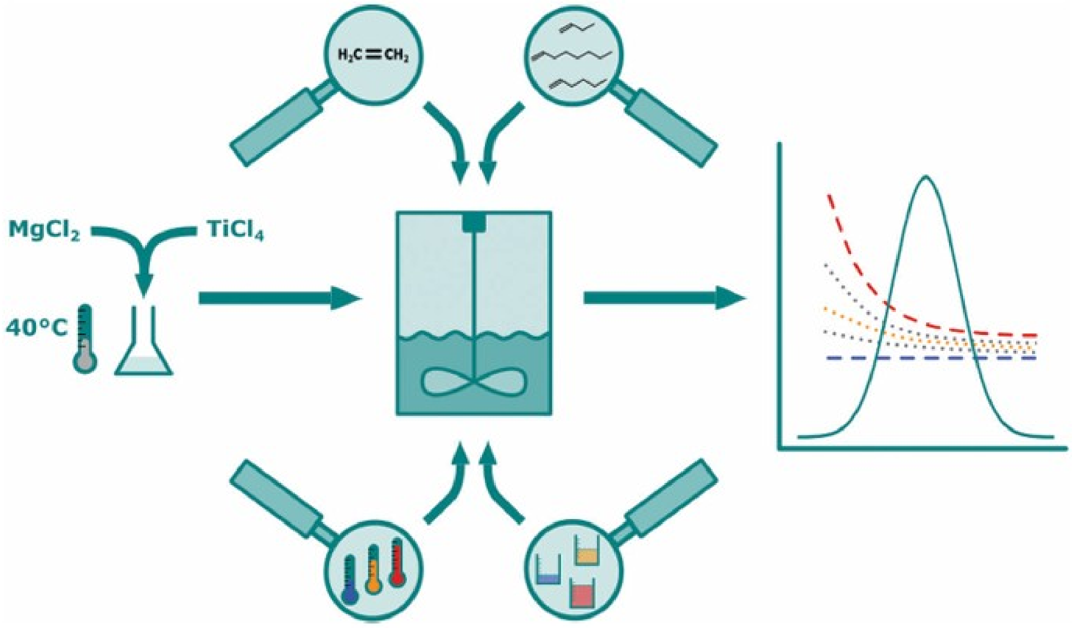
Tuning the properties of Polyethylene by catalyst and comonomer design

C. Paulik[1*], L. Göpperl[1]

[1]*Institute for Chemical Technology of Organic Materials, Johannes Kepler University, Linz, Austria*
[*] christian.paulik@jku.at

Ziegler-Natta (ZN) based co-polymerization processes for the production of linear low-density polyethylene (LLDPE) generally give rise to a non-uniform incorporation distribution of the comonomer. The comonomer is incorporated predominantly in lower molecular weight fractions, while the incorporation of the comonomer decreases towards higher molecular weight fractions. This puts ZN based LLDPE polymers at a disadvantage compared to polymers made by metallocene catalysts, which have a much more uniform incorporation distribution.

By adjusting the synthesis protocol of ZN catalyst peparation, e.g. by lowering the titanation temperature during, the comonomer incorporation behavior can be adjusted. However, polymerization process parameters also affect the resulting incorporation distribution. A targeted selection of the process conditions polymerization temperature, type and amount of comonomer can be used to influence the properties of the later LLDPE. [1, 2]



Keywords: Polymerization, Polyethylene, Ziegler-Natta catalysis

References

[1] Göpperl L., Pernusch D., Schwarz J. Paulik C., Impact of polymerization process parameters on improved comonomer incorporation behavior in Ziegler-Natta catalysis. *Macromol. React. Eng.* **2022**, 16, 2100042.

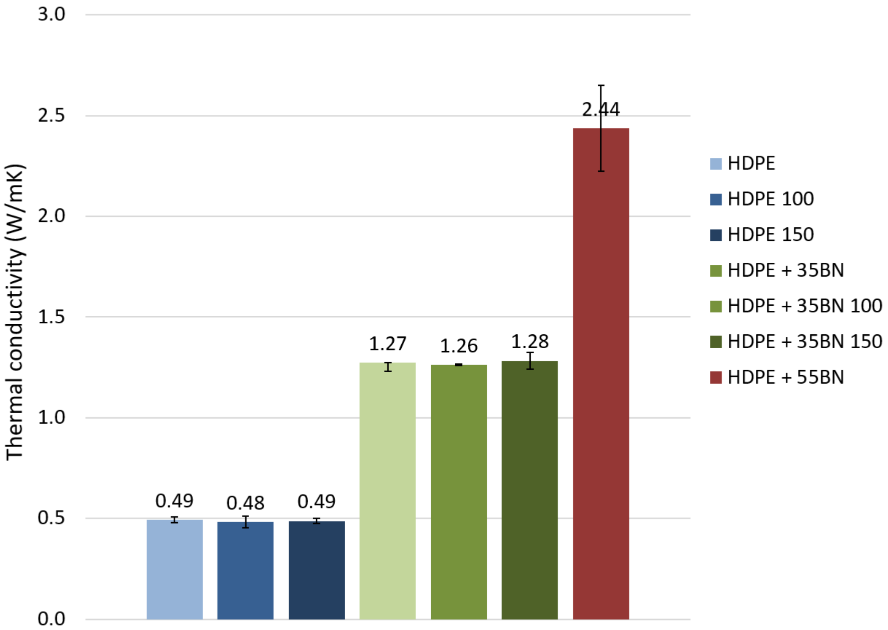
[2] Göpperl L., Cipullo R., Schwarzinger C., Paulik C., Branched Comonomers in LLDPE-Influence of Short Chain Branch Shape on Crystallinity. *Macromol. React. Eng.* **2023**, 17, 2300035.

Thermally Conductive Shape Memory Polymer Composites Filled with Boron Nitride for Heat Management in Electrical Insulation

Andrzej Rybak

ABB Corporate Technology Center, Krakow, Poland
**andrzej.rybak@pl.abb.com*

The evaluation of a possible application of functional shrinkable materials in thermally conductive electrical insulation elements was investigated. The effectiveness of an electron beam and gamma radiation on the crosslinking of a selected high density polyethylene grade was analyzed, both qualitatively and quantitatively. The crosslinked polymer composites filled with ceramic particles were successfully fabricated and tested. On the basis of the performed investigation, it was concluded that the selected filler, namely a boron nitride powder, is suitable for the preparation of the crosslinked polymer composites with enhanced thermal conductivity. The shape memory effect was fully observed in the crosslinked samples with a recovery factor reaching nearly 99% [1]. There was no significant influence of the crosslinking, stretching, and recovery of the polymer composite during shape memory phenomenon on the value of thermal conductivity. The proposed boron nitride filled polyethylene composite subjected to crosslinking is a promising candidate for fabrication of thermally shrinkable material with enhanced heat dissipation functionality for application as electrically insulating components.



Thermal conductivity values measured perpendicularly to injection molding direction for samples with different content of the BN filler: 0, 35, and 55 wt.%. Results are shown for reference pristine samples and samples after testing shape memory effect. Bars with standard deviation are indicated for each type of specimen.

Keywords: shape memory; polymer composites; thermally shrinkable materials; thermal conductivity; electrical insulation

Acknowledgments

The Author would like to thank Agnieszka Adamus-Wlodarczyk and Piotr Ulanski from Faculty of Chemistry, Institute of Applied Radiation Chemistry at Lodz University of Technology for their help with the research.

References

[1] Rybak, A.; Malinowski, L.; Adamus-Wlodarczyk, A.; Ulanski, P. Thermally Conductive Shape Memory Polymer Composites Filled with Boron Nitride for Heat Management in Electrical Insulation. *Polymers* **2021**, *13*, 2191.

Polypeptide-Based Hybrid Block Copolymer Synthesis by Ring-Opening Polymerization

D. Pahovnik,* U. Češarek, E. Žagar

Department of Polymer Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia
**david.pahovnik@ki.si*

Ring-opening polymerization (ROP) of heterocyclic monomers such as lactones, lactides, epoxides and α-amino acid *N*-carboxyanhydrides (NCAs) is an invaluable tool for the preparation of biocompatible and (bio)degradable polymers in a controlled manner. Since polyesters/polyethers prepared by ROP propagate through hydroxyl group, which is a slow initiating group for ROP of NCAs, the synthesis of polypeptide-based hybrid block copolymers usually requires multi-step reactions. To overcome the issue of slow NCA initiation by the hydroxyl group, we separated the slow initiation from the fast propagation and performed them sequentially instead. The developed method has been successfully applied for the synthesis of block copolymers using hydroxyl-terminated macroinitiators [1] and for the one-pot sequential ROP of cyclic esters or carbonates and NCA, which differ not only in their reactivity but also in the type of the propagating species [2]. While the developed synthetic approach enables the preparation of linear hybrid block copolymers, the synthesis of more complex polymer architectures such as miktoarm stars still requires the use of protecting groups, as the coexistence of different functional groups is unavoidable. We have developed synthetic approaches for the preparation of amphiphilic miktoarm star block copolymers to investigate how the architecture of the block copolymers influences their self-assembly. We have prepared AB_2-type amphiphilic miktoarm stars consisting of one hydrophilic arm (A) and two hydrophobic arms (B) to mimic the structure of lipids. We used a heterofunctional core as a multifunctional initiator to prepare the miktoarm stars. The hydroxyl group of the initiator was used to initiate the ring-opening polymerization (ROP) of trimethylene carbonate (TMC) or propylene oxide (PO) to form the hydrophobic arms B, while the hydrophilic block A was prepared by ROP of sarcosine NCA using the amine group for ROP initiation. To selectively initiate ROP, the amine group of the heterofunctional core was protected with a suitable protecting group. While carbamate-based protecting groups such as Boc and Cbz are compatible with the catalytic systems used for TMC polymerization, the incorporation of primary amine functionality into polyethers is more challenging due to the harsher conditions usually employed for ROP of epoxides. To overcome this challenge, we used a two-component Lewis acid-excess organocatalytic system that triggers efficient anionic ROP of epoxides while preserving the integrity of carbamate protection [3]. Despite the higher intrinsic acidity of the carbamate group compared to the hydroxyl group, it is not competitive in both deprotonation and ring-opening steps. This is due to the acidity-reversing effect of the catalyst, which allows site-specific ethoxylation to proceed exclusively from the hydroxyl group.

References

[1] Gradišar Š., Žagar E., Pahovnik D. Ring-Opening Polymerization of *N*-Carboxyanhydrides Initiated by a Hydroxyl Group. *ACS Macro. Lett.* **2017**, *6*, 637.

[2] Gradišar Š., Žagar E., Pahovnik D. Hybrid block copolymers of polyesters/polycarbonates and polypeptides synthesized via one-pot sequential ring-opening polymerization. *Polym. Chem.* **2018**, *9*, 4764.

[3] Češarek, U.; Liu, L.; Chen, Q.; Wen, T.; Žagar, E.; Zhao, J.; Pahovnik, D. Acidity Reversal Enables Site-Specific Ring-Opening Polymerization of Epoxides from Biprotonic Compounds. *J. Am. Chem. Soc.* **2025**, *6*, 5189-5196.

New avenues for multi-material 3D printing in light-based additive manufacturing

Katharina Ehrmann

Additive Manufacturing Team at TU Wien, Wien, Austria

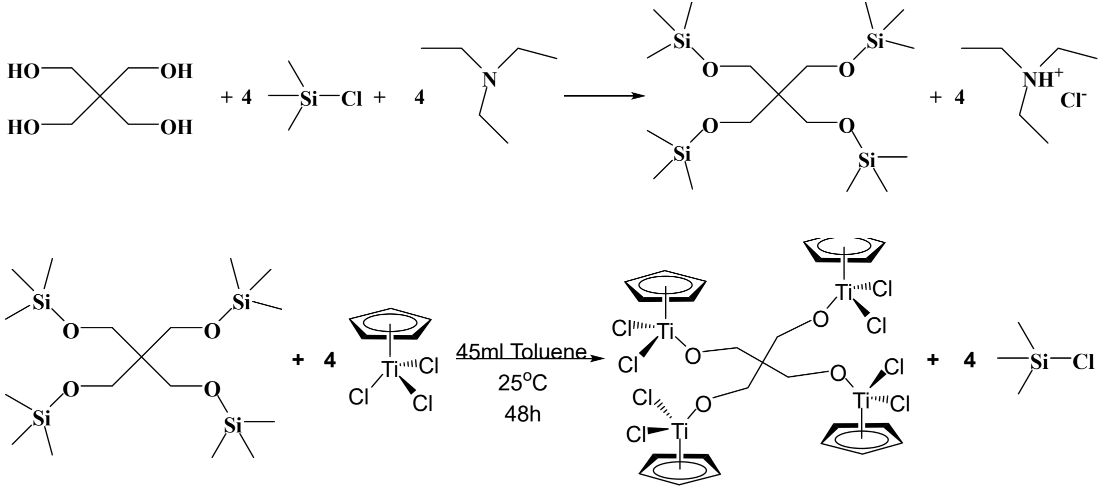
Light-based additive manufacturing (3D printing) typically relies on radical photopolymerization utilizing (meth)acrylates or thiol-ene monomers. Thus, printing of functional polymers is usually based on mimicking conventional functional polymers. In contrast to this mimicry approach, we utilize the largely untapped potential of diversifying the printing parameters such as temperature, light intensity and light colour to. This allows unprecedented diversity in the chemistries utilized for 3D printing and even unlocks multi-material 3D printing within one step, for which first examples will be presented.

Synthesis of star-shaped poly(n-hexyl isocyanate) homopolymers via coordination polymerization and core-first methodology using half-titanocene alkoxy complexes

Evangelos Apostolakis, Marinos Pitsikalis*

National and Kapodistrian University of Athens, Chemistry Department, Panepistimiopolis Zografou, 15771
** pitsikalis@chem.uoa.gr*

In this work, the synthesis and characterization of star-shaped poly(n-hexyl isocyanate), PHIC, homopolymers with three, four, six, and eight arms are presented. The polymers were synthesized via the core-first methodology, utilizing tri-, tetra-, hexa-, and octa-functional half-titanocene alkoxy complexes as coordination polymerization multifunctional initiators. These complexes served as the cores, from which the PHIC chains were grown, leading to the formation of star-shaped structures with precise arm numbers. The following scheme shows the synthesis of the tetra-functional half-titanocene complex employed for the preparation of the 4-arm PHIC stars. A significant challenge was the synthesis of the multi-functional half-titanocene alkoxy complexes, as severe solubility issues emerged between the ligands and the primary complex $[(\eta^5\text{-}C_5H_5)TiCl_3]$. Overcoming these solubility problems between these various ligands and the primary complex required extensive optimization of the experimental parameters, making the synthesis of the initiators particularly demanding. The resulting star-shaped PHIC homopolymers were thoroughly characterized using various techniques. Size exclusion chromatography (SEC), was employed for the study of their molecular characteristics, NMR spectroscopy to verify their star-structure as well as the purity of the half-titanocene alkoxy complexes. Additionally, viscosity measurements were performed to determine the intrinsic viscosity of the polymers. This information, in combination with the average molecular weight of the star homopolymers from static light scattering (SLS) measurements, provided valuable data leading to the calculation of the number of branches of the star-shaped polymers.



Scheme. Synthesis of the tetra-functional half-titanocene complex employed for the preparation of 4-arm PHIC stars

References

1) Patten, T.E.; Novak, B. M. Living Organotitanium(IV)-Catalyzed Polymerizations of Isocyanates *J. Am. Chem. Soc.* **1996**, *118*, 1906- 1916
2) Yoshio, I.; Keikichi U.; Norio, K. Polymerization of isocyanates. V. Thermal degradation of polyisocyanates *J. Polym. Sci: Part A-1.* **1968**, *6*, 2611-2620
3) Touris, A,; Kostakis, K.; Mourmouris, S.; Kotzabasakis, V.; Pitsikalis, M.; Hadjichristidis, N. Complex macromolecular architectures based on *n*-hexyl isocyanate and ε-caprolactone using titanium-mediated coordination polymerization *Macromolecules* **2008**, *41*, 2426-2438.

Stability of Organic Solar Cells

Gregor Trimmel

Graz University of Technology, Institute for Chemistry and Technology of Materials, Graz, Austria
*gregor.trimme@tugraz.at

Organic solar cells can be manufactured in efficient and low cost roll-to-roll processes and have reached power conversion efficiencies above 20%. Especially the development of non-fullerene acceptors has led to remarkable improvements of the OPV efficiencies. The last essential issue to be solved before the technology can be commercialized on a GW scale, is the still moderate stability of OPV limiting the lifetime to a few years. Thus, within this work, we summarize our investigations on polymer/non-fullerene acceptor organic solar cells (OSCs).

OSCs consists of a combination of two organic semiconductors, an electron-donating semiconductor (donor) and an electron-accepting semiconductor (acceptor) with shifted HOMO-LUMO values, arranged either in a bilayer heterojunction or in a bulk heterojunction (inter-penetrating network). The active layer is thereby contacted by selective transport layers and subsequent electrodes. Upon absorption of a photon, excitons (electron-hole pairs) are formed, separated into free charge carriers at the interface via electron transfer (redox-reaction) and the free charge carriers are extracted via the transport layers and electrodes.

Stability issues may arise from the intrinsic (photo and photoelectrical) stability of the materials, the interactions between the materials as well as impurities.

In this contribution, we summarize the current status of organic solar cells and discuss our investigations on different aspects on the OSC´s stability.

The first issue is the photostability of the organic semiconductor as well as the charge transport layers, which can be improved by a careful design of the materials. Secondly, we will discuss the incompatibilty of several materials combinations, e.g. fluorinaated aryl compounds with aluminium electrodes, as this can lead to a dehalogenation reaction and enrichment of fluoride at the interface to the electrode.

Finally we will discuss the purity of organic semiconductors. Whereas purity is of utmost importance in inorganic semiconductor industry, the type and amount of impurities are often not known at all in solution processed OSCs. Thus we carried out a pyrolysis-gas chromatography - mass spectrometric (GC-MS) study on one of the most investigated OSC system PM6-Y6.

The potential of non-porous polymer membranes in downstream separation processes

Pavel Izák

Institute of Chemical Process Fundamentals of the AS CR, Rozvojová 135, 165 02 Prague 6, Czech Republic,
izak@icpf.cas.cz

This talk summarizes results and also the potential of separation of fluids through nonporous membranes. Two aproaches were selected for this stuidy ionic liquids membranes and thin film composite (TFC) membranes. TFC have molecular-level sieving structures consisting of multiple layers of polymeric materials. The three-layer film configuration has the proper mechanical stability and high selectivity of undesired materials to generate a high filtration rate [1]. The first (top) layer serves as a dense selective barrier with a thickness of around 1 µm, which is made of polyamide that swells in water and make perm-selective membrane [2]. Two other layers are thicker to ensure mechanical rigidity with higher porosity than the top layer. A water-swollen spiral-wound membrane filter was used to separate CH_4 from two types of feed streams: a synthetic binary mixture of CH_4 and CO_2 and raw agro-biogas. At a pressure of 3 bar of the synthetic biogas, CH_4 content increased from 52 vol% of the feed stream up to 98 vol% of the retentate stream. Two filters aligned in parallel increased the recovery ratio by 8.5% from the single filter operation, which is ascribed to doubling the biogas retention time in the parallel filters by bisecting the feed stream. The water-swollen membrane technology developed in this study proved efficient in producing high-quality biomethane and desulfurizing feed biogas. The retentate streams had a biomethane concentration of 95-98 vol% of pure CH_4 and a low concentration of H_2S of an order of 10 ppmv [3]. Experimental controlling factors may include but are not limited to the feed flow rate, pressure, membrane properties, and module configuration. More extensive experimental research, to be supported by theoretical analysis, is required to further improve biomethane production using water-swollen membrane technology.

Keywords: non-porous membranes, ionic liquids, thin film composite membranes, flue gas, bio gas

Acknowledgments

Financial support obtained from the Czech Science Foundation, projects 24-10288S, is gratefully acknowledged.

References

[1] P. Stanovský, M. Benkocká, Z. Kolská, M. Šimčík, P. Slepička, V. Švorčík, K. Friess, M.C. Ruzicka, P. Izak, 2022. Permeability enhancement of chemically modified and grafted polyamide layer of thin-film composite membranes for biogas upgrading. J. Membr. Sci. 641.

[2] M. Simcik, M.C. Ruzicka, M. Karaszova, Z. Sedlakova, J. Vejrazka, M. Vesely, P. Capek, K. Friess, P. Izak, Polyamide thin-film composite membranes for potential raw biogas purification: Experiments and modelling, Sep. Purif. Technol. 167 (2016) 163-173.

[3] P. Wojnarova, J. Rusin, P. Basinas, M. Kostejn, P. Stanovsky, A.S. Kim, P. Izák, Unveiling the potential of composite water-swollen spiral wound membrane for design of low-cost raw biogas purification, Separation and Purification Technology, 326 (2023) 124783.

Outstanding PFAS Removal from Water Using Tailored Porous Polymers

M. Yu[1,2], A. Fabisikova[3], P. Schweng[1], M. Zehl[3], Y. Liao[2], R. T. Woodward[1,*]

[1] *Institute of Materials Chemistry and Research, Faculty of Chemistry, University of Vienna, Austria*
[2] *State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai, China*
3 Institute of Analytical Chemistry, Faculty of Chemistry, University of Vienna, Austria
[*]*robert.woodward@univie.ac.at*

The persistence and toxicity of per- and polyfluoroalkyl substances (PFAS) in water systems remain a critical environmental challenge, with increasing regulatory scrutiny and global efforts to phase out their use.[1] Conventional adsorbents often fall short in balancing uptake capacity, kinetics, and reusability—parameters essential for meaningful remediation.

In this work, we present a new class of hypercrosslinked polymer networks engineered to address these limitations. The materials exhibit a maximum uptake capacity exceeding 1500 mg g^{-1} for perfluorooctanoic acid (PFOA, **Figure 1**), with complete adsorption achieved within one hour at low concentrations. They are readily synthesised from inexpensive precursors, display excellent structural and thermal stability, and maintain performance over multiple regeneration cycles. Our findings offer a promising platform for scalable water purification technologies and contribute to the broader effort of designing practical materials for persistent pollutant removal.

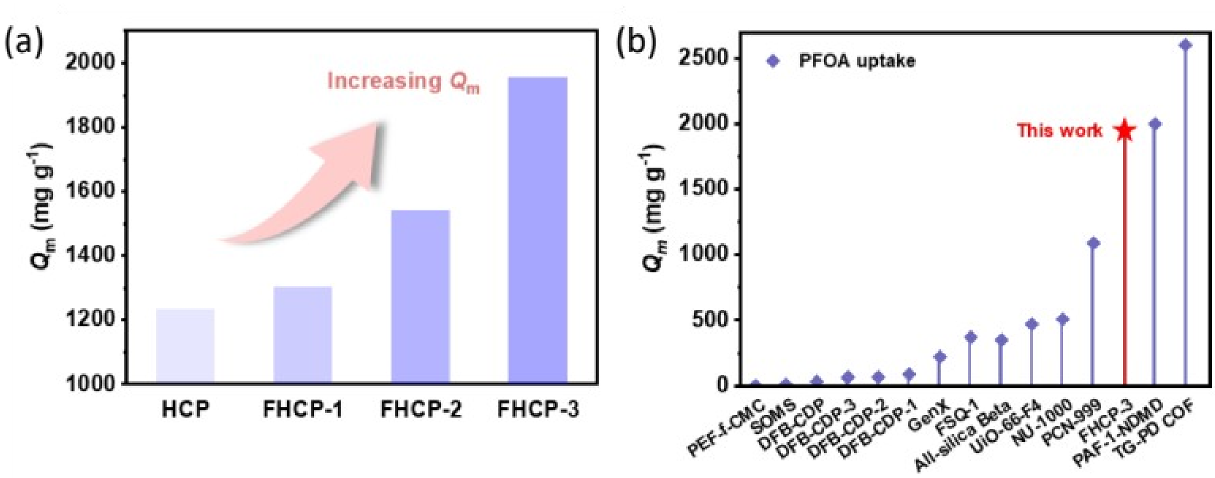


Figure 1. (a) Maximum adsorption capacities, Qm, of our HCP adsorbents for PFOA. (e) PFOA adsorption capacity of our best-performing polymer (red) compared with reported adsorbents from the literature (purple)

Keywords: PFAS remediation; adsorption; porous organic polymers; water purification; persistent pollutants

References

---

[1] Lim X.; Could the world go PFAS-free? Proposal to ban 'forever chemicals' fuels debate. *Nature* **2023**, 620, 24

Turning Liquids Solid: High Internal Phase Emulsions for Production of Micromixers and Microreactors

Sebastian Hummer, Hande Barkan-Öztürk, Julia Jüstel, Robert Woodward, Angelika Menner, Alexander Bismarck*

Polymer & Composite Engineering (PaCE) Group, Institute of Materials Chemistry, Faculty of Chemistry, University of Vienna, Währinger Strasse 42, 1090 Vienna, Austria.
*alexander.bismarck@univie.ac.at

Emulsion templating – the use of W/O emulsions whose oil phase comprises monomers – has been known as a technique for creating macroporous polymers for over 60 years but only received significantly more attention in the past 25 years. Advantages of emulsion templated macroporous polymers include significant permeability, simple control of porosity and ease of functionalisation. Little research has been carried out on the effect of polyHIPE structures on the fluids passing through it; this is important if polyHIPEs are to find applications such as chemical reactors. In order to assess the potential of polyHIPEs for micromixing of fluids, we synthesised model poly(styrene-co-DVB)HIPEs, which were post-functionalised by hypercrosslinking to serve as catalyst support for the continuous flow synthesis of paracetamol. The post-functionalised polyHIPEs baring organophosphorus moieties had surface areas of up to 500 m²/g. The phosphorus moieties act as catalyst anchor sites for the subsequent loading of Pd. We demonstrate that Pd-loaded polyHIPEs are effective in reducing 4-nitrophenol to 4-aminophenol, achieving turnover numbers of ∼2,000. Such functionalised divinylbenzene-based polyHIPEs can be processed into flow-cells and used for the creation of Plant-on-a-Bench as microreactor/mixer and extraction units for continuous flow synthesis.

Self-Assembly strucutres from block copolymers mediated by hydrogen bonding interaction

Shiao-Wei Kuo
Department of Materials and Optoelectronic Science. National Sun Yat Sen University, Kaohsiung, Taiwan
E-mail: kuosw@faculty.nsysu.edu.tw

Soft materials based on block copolymers that exhibit Archimedean tiling patterns have attracted significant interest due to their potential applications in nanopatterning, nanocomposites, and shape selectivity. Additionally, researchers have widely investigated the corresponding mesoporous materials with Archimedean tiling from block copolymers as templates with high surface area and pore volume, or tunable porosity with different length scales, in separation, energy storage, drug delivery, photo-catalysis, photovoltaic solar cells, and chemical sensing. We highlight recent progress in constructing Archimedean tiling patterns based on the creation of ordered structures from block copolymers by self-assembly through hydrogen bonding interaction

Keywords: Self-Assembly, Block Copolymer, Hydrogen Bonding Interaction

Acknowledgments
This study was supported financially by the National Science and Technology Council, Taiwan, under contracts NSTC 113-2223-E-110-001

References

[1] Chou, T.C.; Kuo, S.W. Miktoarm star polymers as templates for mesoporous phenolic materials: Enhancing microphase separation and expanding phase diagrams. *Giant* **2025**, *22*, 100355.
[2] Chou, T.C.; Kuo, S.W. Controllable Wet-Brush Blending of Linear Diblock Copolymers with Phenolic/DDSQ Hybrids toward Mesoporous Structure Phase Diagram, *Macromolecules* **2024**, *57*, 5958-5970.
[3] Kuo, S.W. Construction Archimedean tiling patterns based on soft materials from block copolymers and covalent organic frameworks. *Giant* **2023**, *15*, 100170.

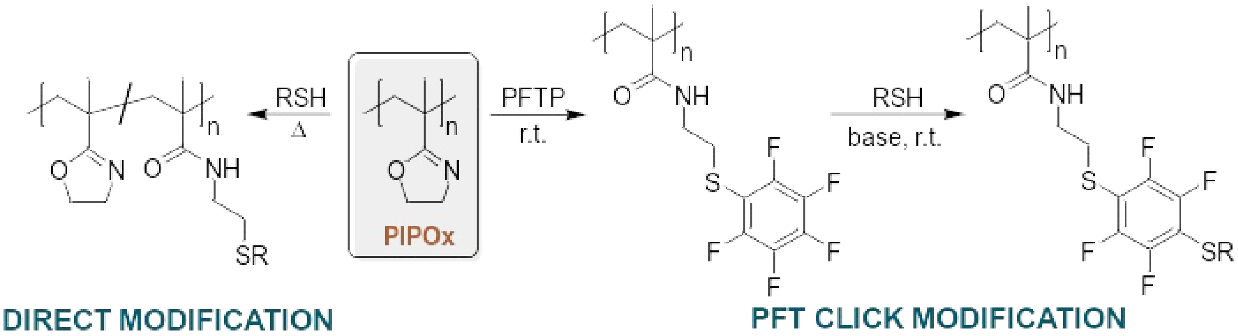
Synthesis of Functional (Co)Polymers Through the Post-Polymerization Modification of Poly(2-Isopropenyl-2-Oxazoline) with Thiols

S. Gupta, M. Janata, A. Mahun, V. Raus*

Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, 162 00, Prague 6, Czech Republic
*raus@imc.cas.cz

The great potential of poly(2-isopropenyl-2-oxazoline) (PIPOx) as a versatile platform for post-polymerization modifications has been recently realized.[1,2] Well-defined PIPOx can be prepared via different polymerization methods from a commercial monomer,[3] and the polymer features many favorable characteristics, including solubility in both water and organic solvents, thermal and hydrolytic stability, non-cytotoxicity, biocompatibility, and immunomodulation and non-fouling properties. Importantly, PIPOx provides catalyst- and byproduct-free, orthogonal ring-opening addition reactions, yielding functional poly(methacrylamide)s that find important applications, particularly in the biomedical field.[2] However, until recently, only relatively sluggish PIPOx reactions with carboxylic acids have been routinely exploited.

In this contribution, we will present the significant extension of the PIPOx post-polymerization modification platform in two directions. Firstly, we will summarize the results of our very recent comprehensive investigation of PIPOx reactivity with aliphatic and aromatic thiols, revealing that these reactions are dramatically accelerated in water, affording high degrees of modification faster and/or under milder reaction conditions than in organic solvents.[4] Secondly, we will demonstrate for the first time that the clean and rapid reaction with 2,3,4,5,6-pentafluorothiophenol transforms PIPOx into a highly reactive precursor for efficient *para*-fluoro-thiol (PFT) click reactions.[5] Within both these directions, we evaluated in detail the reactivity of a wide range of commercially available thiols, showing that numerous useful functionalities (e.g. charged groups, fluorescent tags, polymers, amino acids, peptides...) can be easily introduced into the polymeric precursor in an orthogonal fashion while maintaining a high degree of stoichiometric control over the composition of the final functional (co)polymer. These developments make the PIPOx platform an ideal tool for precision synthesis of large functional (co)polymer libraries.



Scheme 1. Synthesis of functional poly(methacrylamides) via PIPOx modification with thiols.

References

[1] Kopka, B.; Kost, B.; Basko, M. Poly(2-isopropenyl-2-oxazoline) as a reactive polymer for materials development. *Polym. Chem.* **2022**, *13 (33)*, 4736-4746.

[2] Kronek, J.; Minarčíková, A.; Kroneková, Z.; Majerčíková, M.; Strasser, P.; Teasdale, I. Poly(2-isopropenyl-2-oxazoline) as a Versatile Functional Polymer for Biomedical Applications. *Polymers* **2024**, *16 (12)*, 1708.

[3] Raus, V.; Hološ, A.; Kronek, J.; Mosnáček, J. Well-Defined Linear and Grafted Poly(2-isopropenyl-2-oxazoline)s Prepared via Copper-Mediated Reversible-Deactivation Radical Polymerization Methods. *Macromolecules* **2020**, *53 (6)*, 2077-2087.

[4] Gupta, S.; Janata, M.; Raus, V. Postpolymerization Modification of Poly(2-isopropenyl-2-oxazoline) with Thiols: Scope and Solvent Effects. *Macromolecules* **2025**, 58 (4), 2125–2134.

[5] Gupta, S.; Mahun, A.; Janata, M.; Raus, V. *Manuscript in preparation.*

Polymer-linked planet–satellite-type supracolloids: a versatile form of responsive soft matter

S. Jancke, C. Rossner[1,2*]

[1]*Leibniz Institute of Polymer Research Dresden, Germany*
[2]*Univeristy of Chemistry and Technology Prague, Czech Republic*
[*]*rossner@ipfdd.de*, *rossnerc@vscht.cz*

Planet–satellite-type supracolloids represent a form of soft matter in which coupling interactions can be engineered by adjusting interparticle spacing.[1] For many applications, a high number of strong coupling interactions and hence many interacting particles with short spacings are sought. This is the case for, e.g., plasmon−plasmon coupling interactions that create local "hot spots" with high electric field enhancement. Thus, applications that are near-field promoted, such as surface-enhanced Raman scattering, provide an example. However, such coupling scenarios are typically realized by particle linkers that form a dense surface layer and may impede access of molecules of interest – be they reactants or analytes – into the hot-spot sites. This presentation will highlight the usefulness of end-grafted polymer-molecule linkers in planet–satellite-type structures. These linking entities form a ligand layer that is not dense in a good solvent environment, thereby ensuring hot-spot accessibility; whereas the stimulus-responsive properties of that linker can be employed to actuate interparticle distances, thereby switching on the desired coupling effect, Figure 1 [2].

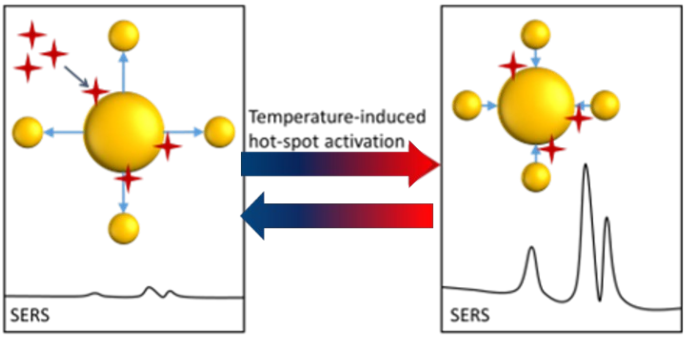


Figure 1: Temperature-moderated hot-spot activation in polymer-linked gold/gold planet–satellite nanostructures (figure is adapted from [2]).

Keywords: surface-grafted polymers, hybrid polymer/inorganic nanomaterials, responsive soft matter

Acknowledgments
Funding by Deutsche Forschungsgemeinschaft under grant 466182523 is gratefully acknowledged.

References

[1] Rossner, C. Polymer-Grafted Gold Colloids and Supracolloids: From Mechanisms of Formation to Dynamic Soft Matter. *Macromol. Rapid Commun.* **2025,** *46,* 2400851.
[2] Jancke, S.; Liu, C.; Wang, R.; Sarkar, S.; Besford, Q. A.; König, T. A. F.; Popp, J.; Cialla-May D.; Rossner, C. Turning on hotspots: supracolloidal SERS probes made brilliant by an external activation mechanism. *Nanoscale* **2023,** *15,* 18687.

Standard oral lectures

Pulsed Field Gradient NMR for Polymer Molecular Weight and Functionalization Analysis with benchtop NMR

Hélène Freichels, Jürgen Kolz*, Federico Casanova

Magritek GmbH, Philippstr. 8, 52068 Aachen, Germany
**Juergen@magritek.com*

The strength of Pulsed Field Gradient Nuclear Magnetic Resonance (PFG-NMR) lies in its ability to separate molecules by hydrodynamic radius while simultaneously resolving chemical structures. The latest generation of benchtop NMR systems offers these capabilities in a compact, user-friendly, and cost-effective manner, making the technique a viable alternative to established methods like size exclusion chromatography.

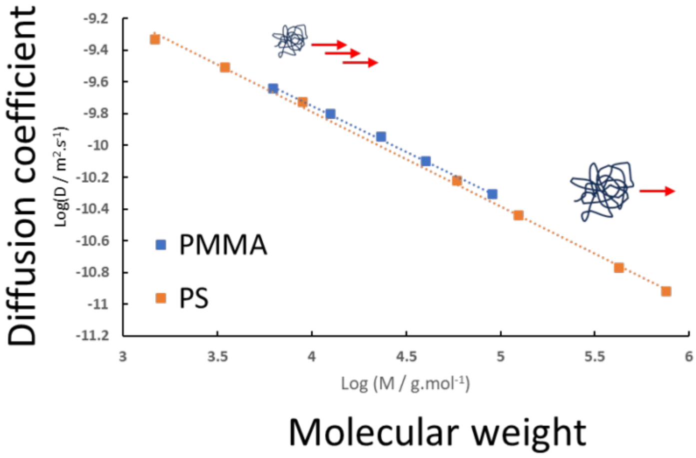
In this study, benchtop PFG-NMR was employed for molecular weight (MW) determination using Diffusion-Ordered Spectroscopy (DOSY) at 80 MHz. Self-diffusion coefficients (D) of polystyrene and polymethyl methacrylate standards in deuterated chloroform were measured and correlated with MW, achieving measurement times below 10 minutes—significantly improving throughput compared to Size-Exclusion Chromatography (SEC).

To assess accuracy, DOSY-derived MW values were validated against end-group analysis for polyphenylsulfone, demonstrating strong concordance. A similar validation for polysiloxanes further confirmed DOSY’s robustness for MW determination. Additionally, DOSY analysis of lignin revealed a well-defined D-MW correlation, highlighting its applicability to both synthetic and natural polymers. Preliminary investigations on chitosan further support its relevance for biopolymer analysis.

Beyond MW determination, PFG-NMR was used to monitor end-group functionalization of poly(ε-caprolactone) (PCL) via the Pulsed Field Gradient-Stimulated Echo (PGSTE) method. This approach effectively resolved reactants and functionalized polymer species, even in cases of spectral overlap, eliminating the need for extensive purification.

Benchtop PFG-NMR provides a compact, cryogen-free platform for rapid, solvent-flexible polymer characterization, offering a viable alternative to high-field NMR for both synthetic and natural macromolecules.

Keywords: benchtop NMR, Pulsed Field Gradient



Plot of log(D) vs log(M) for PMMA (blue) and PS (orange)

Dynamic light scattering from polymers: Fine tuning of the method

Petr Štěpánek
Institute of Macromolecular Chemistry CAS, Prague, Czech Republic

Dynamic light scattering (DLS) has become a routine characterization technique used mostly for the size determination of various objects in liquid dispersions. This contribution shall address various difficulties and challenges encouneterd during measurement of more complex polymer systems, in particular:

1. Handling of "difficult" samples such as systems containing dust or large particles, systems exhibiting multiple light scattering, superimposed diffusive and relaxation behavior of decay rate, systems with a combination of weakly and strongly scattering objects, systems with multiple relaxation modes. The techniques used are the software- and hardware-based dust filtering, subtraction method, multiangle data analysis, 3-dimensional analysis of DLS correlation functions.

2. Applications of DLS to various complex systems such as internal dynamics of block copolymers in solutions, collective diffusion in concentrated polymer solutions, DLS from polymers under zero-average contrast conditions, critical behavior and correlation lengths in polymer blends and in bicontinuous microemulsions, density fluctuations in polymer melts, and detection of undulation modes in polymer systems with lamellar morphology.

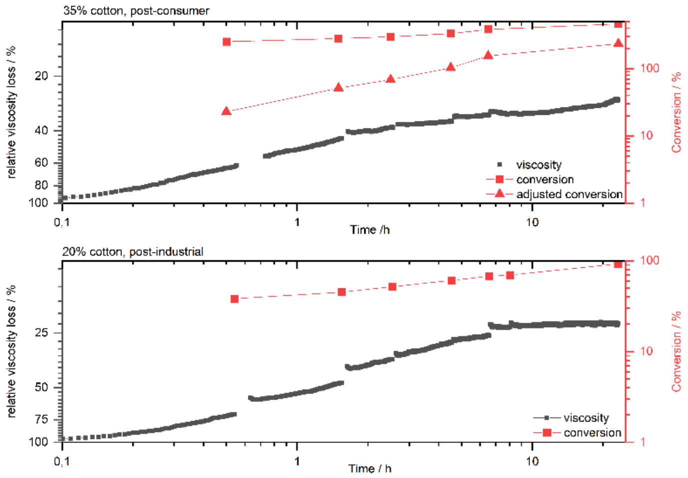
Acknowledgments
This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic (grant no. LM2023053).

Online rheometry for monitoring polyester-cotton waste hydrolysis

D.Ostner-Kaineder[1*], M. W. Hlawitschka, C.Burgstaller[2]

[1]*University of Applied Science Upper Austria, Wels, Austria*
[2]*Transfercenter für Kunststofftechnik GmbH, Wels, Austria*
[3]*Johannes Kepler University, Linz, Austria*
[*]*doris.ostner-kaineder@tckt.at*

Polyester-cotton blends are a subfraction of textile waste that is difficult to recycle via traditional methods for the singular components. Biocatalytic degradation of the cotton offers a chance to regain pure polyester while providing glucose as a useful secondary product [1]. Reaction progress can be monitored using refractive index (RI) or spectroscopic measurements of the glucose concentration. However, these methods are influenced by the presence of contaminants [2,3] . The aim of this work is to investigate the flow resistance of the suspension as an alternate process monitoring method that is independent of present contaminants. Therefore, viscosity of the suspension was measured continuously while RI samples were taken at fixed intervals. Viscosity decreases and RI increases over time, following power law behavior and reaching a plateau after 24h. RI was used successfully to assess reaction progress for post-industrial (homogenous) materials. However, for mixed post-consumer materials incorrect conversion results appear even after adjusting for increased starting RI values. Viscosity measurements therefore offer a promising alternative, which may also be implemented cost-effectively at larger scale by monitoring of impeller torque.



Monitoring of viscosity and conversion (via glucose concentration) the hydrolysis of post-industrial and post-consumer textile waste

Keywords: reaction monitoring, online measurement, flow behavior

Acknowledgments

We would like to thank the Austrian research promotion agency (FFG) and EU Horizon Programme. This research was performed in the course of and funded by the projects TexPET (FFG) and Plastice (EU).

ADDIN CitaviBibliographyReferences

[1] Vera, R. E.; Zambrano, F.; Suarez, A.; Pifano, A.; Marquez, R.; Farrell, M.; Ankeny, M.; Jameel, H.; Gonzalez, R. Transforming textile wastes into biobased building blocks via enzymatic hydrolysis: A review of key challenges and opportunities. *Cleaner and Circular Bioeconomy* **2022,** *3*, 100026. DOI: 10.1016/j.clcb.2022.100026.

[2] Shehadeh, A.; Evangelou, A.; Kechagia, D.; Tataridis, P.; Chatzilazarou, A.; Shehadeh, F. Effect of ethanol, glycerol, glucose/fructose and tartaric acid on the refractive index of model aqueous solutions and wine samples. *Food chemistry* **2020,** *329*, 127085. DOI: 10.1016/j.foodchem.2020.127085.

[3] Shih, C.-J.; Smith, E. A. Determination of glucose and ethanol after enzymatic hydrolysis and fermentation of biomass using Raman spectroscopy. *Analytica chimica acta* **2009,** *653* (2), 200–206. DOI: 10.1016/j.aca.2009.09.012.

[4] Wiman, M.; Palmqvist, B.; Tornberg, E.; Lidén, G. Rheological characterization of dilute acid pretreated softwood. *Biotechnology and bioengineering* **2011,** *108* (5), 1031–1041. DOI: 10.1002/bit.23020.

Biodegradable and bio-based aliphatic polyurethane foams

O. Gotkiewicz[1], K. Skleničková[1], V. Pokorný[1], P. Parcheta-Szwindowska[2], Olga Kočková[1], H. Beneš[1]

[1]*Institute of Macromolecular Chemistry of the Czech Academy of Sciences, Prague 6, Czech Republic*
[2]*Department of Polymer Technology, Faculty of Chemistry, Gdansk University of Technology, Gdansk, Poland*
**benesh@imc.cas.cz*

Polyurethane (PUR) foams are, due to their high tunability and versatility, unambiguously the most globally produced thermosets. However, conventional / commercial PUR foams based on aromatic polyisocyanate have relatively low resistance to abiotic photo-degradation. As a result, these materials are unsuitable for outdoor applications, where their mechanical disintegration occurs relatively easily with the formation of microplastics, or the production of toxic degradation products. For this reason, in recent years, there have been works that aim to prepare more environmentally friendly PUR foams that would be easier to recycle or willing to biodegrade without the formation of toxic decomposition products.

In past, we have developed fully aliphatic PUR foams that show biodegradable behaviour in various environments [1,2]. Such kind of foams may find a number of applications, e.g. as matrices for biofiltration [3] or as porous carriers in wastewater treatment plants [4].

This contribution shows the influence of chemical composition, supramolecular arrangement and macroscopic properties (cell morphology and mechanical properties) on the degradation behaviour of fully aliphatic PUR foams. It is shown that to ensure sufficiently fast degradability and recycling via solvolysis of the PUR foams, it is necessary, in addition to choosing the appropriate structure of the starting monomers, to control the development of the supramolecular arrangement of the PUR network. The replacement of petrochemical raw materials with bio-based feedstocks and their influence on the final properties of PUR foams, their (bio)degradation behaviour and solvolysis are also discussed.

Keywords: polyurethane foam, biobased feedstock, biodegradation

Acknowledgments

This work was financially supported by the Lead Agency bilateral Czech-Polish project provided by the Czech Science Foundation (24–10651K) and National Science Center Poland (UMO-2023/05/Y/ST8/00076).

References

[1] Skleničková, K.; Suchopárová, E.; Abbrent, S.; Pokorný, V.; Kočková, O.; Nevoralová, M.; Cajthaml, T.; Strejček, M.; Uhlík, O.; Halecký, M.; Beneš, H. Biodegradation of Aliphatic Polyurethane Foams in Soil: Influence of Amide Linkages and Supramolecular Structure. *Sci. Total Environ*. **2024**, *912*, 169062.

[2] Skleničková, K.; Vlčková, V.; Abbrent, S.; Bujok, S.; Paruzel, A.; Kanizsová, L.; Trhlíková, O.; Říhová Ambrožová, J.; Halecký, M.; Beneš, H. Open-Cell Aliphatic Polyurethane Foams with High Content of Polysaccharides: Structure, Degradation, and Ecotoxicity. *ACS Sustain. Chem. Eng*. **2021**, *9*, 6023–6032.

[3] Beneš, H.; Vlčková, V.; Paruzel, A.; Trhlíková, O.; Chalupa, J.; Kanizsová, L.; Skleničková, K.; Halecký, M. Multifunctional and Fully Aliphatic Biodegradable Polyurethane Foam as Porous Biomass Carrier for Biofiltration. *Polym. Degrad. Stab*. **2020**, *176*, 109156.

[4] Skleničková, K.; Pečenka, M.; Říhová Ambrožová, J.; Abbrent, S.; Vlčková, V.; Beneš, H.; Halecký, M. Influence of Biodegradable Polyurethane Foam on Biocoenosis and Sludge Activity in Reactors Simulating Low-load Wastewater Treatments. *Journal of Water Process Engineering*, **2021**, *44*, 102455

Formation and Characterization of Biobased Nanofibers from poly(Tulipalin A) prepared by Photomediated ATRP

G. Zain[1*], Aziza Hussien[2], Gomaa F Elfawal[1], A. Kleinová[1], J. Mosnáček[1]

[1]Polymer Institute SAS, 84541 Bratislava, Slovakia
[2]Proteinic and Man-made Fibers Department, Textile Research Institute, National Research Centre, 12622 Giza, Egypt

*upolgaza@savba.sk

The development of polymers from renewable resources is becoming a prominent area of interest for industry and academia. One of the most attracting renewable monomers is Tulipalin A - namely α-methylene-γ butyrolactone (MBL) which is a fully renewable vinyl monomer found in tulips. MBL consists of a five-member ring with an oxygen and carbonyl group, possesses structural features similar to those of methyl methacrylate (MMA). MBL was already reported for preparation of thermoplastic elastomers[1], hydrogels[2], polyester with pendant double bonds[3]. Its functional groups have been also used for surface functionalization which open a new window for imparting new properties for different surfaces. Here, we show the transformation of PMBL to nanofibers by electrospinning technique. PMBL with different molar masses was first synthesized by photomediated atom transfer radical polymerization according to our reported study[4], then the obtained polymers were tested for electrospinning. PMBL with 55000 g/mole and Đ of 1.2 was found to form nanofibers in 40% DMF. PMBL of low molar mass was also found to form nanofibers when it was mixed with poly(caprolactone). The obtained fibers were characterized by FTIR and SEM. The mechanical properties and other analyses will be tested as well.

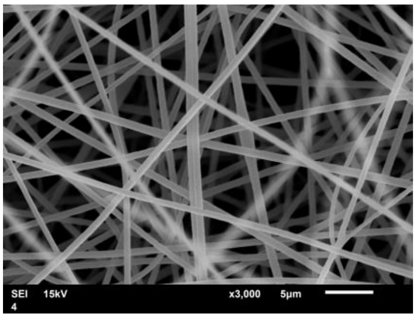


Figure 1. PMBL nanofibers.

Acknowledgments

We thank the following projects for enabling the research: POO-09I03-03-V04-00241 (34%), funded by the EU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V04-00241., VEGA 2/0137/23 (33%), and APVV-23-0534 (33%).

References

[1] Mosnáček, J.; Yoon, JA.; Juhari, A.; Koynov, K.; Matyjaszewski, K. Synthesis, morphology and mechanical properties of linear triblock copolymers based on poly(α-methylene-γ-butyrolactone). Polymer (Guildf) **2009**, 50, 2087–94.

[2] Kollár, J.; Mrlík, M.; Moravčíková, D.; Kroneková, Z.; Liptaj, T.; Lacík, I. Tulips: A Renewable Source of Monomer for Superabsorbent Hydrogels. Macromolecules **2016**, 49, 4047–56.

[3] Danko, M.; Basko, M.; Ďurkáčová, S.; Duda, A.; Mosnáček, J. Functional Polyesters with Pendant Double Bonds Prepared by Coordination–Insertion and Cationic Ring-Opening Copolymerizations of ε-Caprolactone with Renewable Tulipalin A. Macromolecules **2018**, 51, 3582–96.

[4] Zain, G.; Bondarev, D.; Doháňošová, J.; Mosnáček, J. Oxygen-Tolerant Photochemically Induced Atom Transfer Radical Polymerization of the Renewable Monomer Tulipalin A. ChemPhotoChem **2019**, 3, 1138–45.

Towards Sustainable Functional Polyester Materials

K. M. Saller*, A. Kruglhuber, C. Bernhard

[1]*Institute for Chemical Technology of Organic Materials, Johannes Kepler University, Linz, Austria*
**klara.saller@jku.at*

Why are polyesters so important for a sustainable future? Availability of bio-based monomers, mechanical and chemical recyclability, as well as biodegradability are promising features in terms of sustainability. But what can we do with polyesters? Since polyesters can be synthesized from numerous different monomers their physical, mechanical, and thermal properties strongly vary and can be finetuned to fulfill certain material requirements. Adding multifunctional monomers to the polyester structure allows crosslinking, modifying hydrophilicity, or introducing chelating ligands. Due to their promising properties and versatility, polyesters from mutlifunctional monomers are increasingly investigated although synthetic and analytical challenges need to be tackled.

Research on the trifunctional monomer dimethylolpropionic acid (Fig. 1) revealed that mostly linear polyesters with pendant COOH groups are formed when choosing the right reaction partners [1]. Monomer reactivities and miscibility in melt are crucial factors to identify successful synthesis procedures and obtain materials with desired properties. A reactivity study on a series of monomers was carried out to facilitate systematic investigations on multifunctional building blocks. Matching of suitable reaction components and conditions becomes significantly easier by developing a powerful toolbox of analytical methods focussing on NMR spectroscopy and MALDI mass spectrometry which fundamentally enhances the understanding of newly investigated functional polyesters.

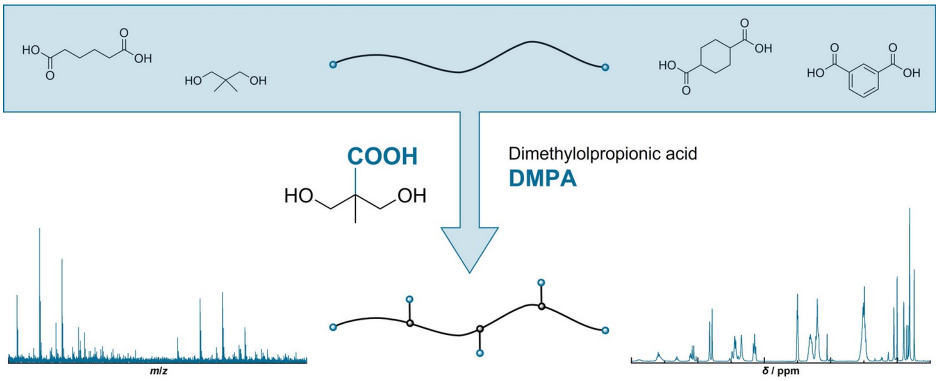


Figure 1: Polyesters with pendant carboxylic acid groups are synthesized using dimethylolpropionic acid [1].

Keywords: functional polyesters, sustainable materials, polymer spectroscopy

References

[1] Saller, K.M.; Hubner, G; Schwarzinger, C. Introducing free carboxylic acid groups along polyester chains using dimethylolpropionic acid as diol component *Eur. Polym. J.* **2023**, 198, 112442.

Non-Isothermal Curing Kinetics of EVA, POE, and EPE Encapsulants for PV Applications

Gabriel Riedl, Martin Tiefenthaler, Gernot M. Wallner

Institute of Polymeric Materials and Testing – Christian Doppler Laboratory for Superimposed Mechanical-Environmental Ageing of Polymeric Hybrid Laminates, University of Linz, Austria
**gabriel.riedl@jku.at*

This work presents a method to determine the non-isothermal curing kinetics of peroxide-crosslinking ethylene vinyl acetate copolymer (EVA), polyolefin elastomer (POE) and coextruded multilayer EVA/POE/EVA (EPE) encapsulants. The curing kinetics were derived from dynamic mechanical analysis (DMA) in plate-plate configuration under isothermal conditions, following ICTAC recommendations [1]. DMA was performed from 125 to 150°C for EVA and POE, and from 140 to 160°C for EPE due to its higher curing onset. Measurements were performed in 5°C increments. Conversion curves were obtained from viscosity changes, and curing rates by numerical differentiation (s. Fig. 1, left). The kinetics were modelled using a temperature dependent Arrhenius rate coefficient (s. Fig. 1, middle) and a rate model based on a form of the Sestak-Berggren equation (s. Fig. 1, right). To evaluate the accuracy of the model, the initial isothermal DMA data was fitted and a non-isothermal validation routine was performed. The curing model showed a very high accuracy under both conditions. Using an integration-by-summation approach, the non-isothermal curing process can be calculated by solely tracking temperature (Eq. 1).

All encapsulants followed a similar reaction model, with peak curing rates near 30% conversion. While activation energies were comparable, pre-exponential factors varied notably. EVA cured fastest, POE slowest and EPE was intermediate. Additionally, the model was further applied to predict the crosslinking homogeneity in mini PV modules. Therefore, temperature was monitored at seven positions during vacuum lamination. The fastest crosslinking was observed at the bottom glass, which was in direct contact with the heated plate of the laminator. Interestingly, the slowest conversion was observed in the module center and not at the topside glass. Presumably, this was related to the heat flux through the silicone membrane.

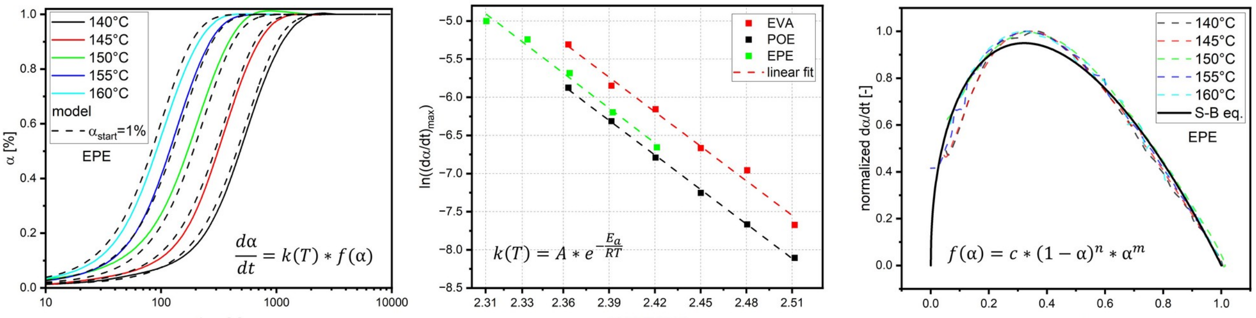


Fig. 1: **Conversion curves at and model fit at different temperatures (left), Fit of the Arrhenius rate model for EVA, POE and EPE (middle) and the fitted reaction model (right)**

$$\alpha_n = \alpha_0 + \sum_{k=1}^{n} \dot{\alpha}\,(T_k, \alpha_{k-1}) * \Delta t_k \qquad (1)$$

Acknowledgments

The financial support by the Austrian Federal Ministry for Digital and Economic Affairs, the National Foundation for Research, Technology and Development and the Christian Doppler Research Association is gratefully acknowledged.

References

[1] S. Vyazovkin, A.K. Burnham, L. Favergeon, N. Koga, E. Moukhina, L.A. Pérez-Maqueda, N. Sbirrazzuoli, ICTAC Kinetics Committee recommendations for analysis of multi-step kinetics. Thermochimica Acta **2020**, 689, 178597

RTM6 Epoxy resin: An In-Situ Rheo-Raman Study of Curing Kinetics and Dynamic Mechanical Analysis (DMA) of the Cured Material

J. Rodriguez [1]*, M. Walluch [2]*

[1]Anton Paar Germany GmbH, Stuttgart, Germany
[2]Anton Paar GmbH – Business Area Rheometry, Graz, Austria
*Corresponding author: e-mail: matthias.walluch@anton-paar.com

The kinetics of an RMT 6 epoxy resin and the thermo-mechanical properties of the finally cross-linked product were experimentally studied using an Anton Paar MCR 702 MultiDrive rheometer. In order to gain insights in the evolution of macroscopic rheological properties induced by chemical reactions within the sample material, the rheological measurements were coupled with in-situ Raman spectroscopy. The gelation-kinetics was further evaluated with a so-called Multiwave rheometry test. Accordingly, the WINTER-CHAMBON criterion was used to determine the sol/gel transition point [1]. For dynamic mechanical analysis of the cured component a linear drive module was added to the instrument. The combination of linear drive and rotational drive in one device allowed the characterization of thermal transitions using dynamic mechanical analysis (DMA) in two different deformation modes (torsion and bending). Two thermal events could be detected from the DMA test: the main glass transition temperature and a sub-glass transition of the material [2]. Additionally, this unique experimental setup allows determining the complex Young's modulus as well as shear modulus using a single specimen in a continuous measurement run over a wide temperature and frequency range. The instrument frame and air bearings are designed to provide outstandingly low radial and axial compliance at the same time, thus enabling the measurement of accurate modulus values in all testing modes.

Keywords: DMA, Epoxy, Curing, Kinetics, Dynamic Mechanical Analysis

References

[1] Chambon F and Winter H H (Linear viscoelasticity at the Gel Point of a Crosslinking PDMS with Imbalanced Stoichiometry. Journal of Rheology, 1987.

[2] Terekhina S, Fouvrya S, Salviaa M, Bulanov I. An indirect method based on fretting tests to characterize the elastic properties of materials: application to an epoxy resin RTM6 under varia-ble temperature conditions. Wear, 2010.

From Theory to Devices: DFT-Driven Insights into Polyfullerene for Designing Efficient Organic Photovoltaics Materials

Bruno H. Barboza[1], Orisson P. Gomes[2*], Marco Antônio G. B. Gomes[2],
Augusto Batagin-Neto[3], Roger C. Hiorns[2], Didier Bégué[2],

[1] *Sao Paulo State University (UNESP), School of Sciences, POSMAT, Campus of Bauru, Brazil*
[2] *Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux (IPREM), University of Pau and the Adour Region, Pau, France*
[3]*Sao Paulo State University (UNESP), Campus of Itapeva, Brazil*
[*]*orisson.ponce-gomes@univ-pau.fr*

The potential for organic photovoltaics (OPV) to become a key energy solution relies on its economic viability, which is closely tied to efficiency, manufacturing costs, weight, scalability, and—critically—device lifetime. In this sense, polyfullerenes (PFs) have emerged as promising materials in this field due to their unique ability to simultaneously improve efficiency, stability, and mechanical robustness in photovoltaic devices [1]. However, to fully unlock their potential, a deep understanding of their electronic structure is essential. In this work, we employ density functional theory (DFT) in combination with condensed-to-atoms Fukui indexes (CAFI) to provide a comprehensive analysis of poly(fullerene) systems. While conventional DFT provides valuable insights into the electronic structure, the CAFI approach offers an additional layer by highlighting nucleophilic (f^+) and electrophilic (f^-) regions, thus pinpointing the molecular sites most susceptible to electron donation or acceptance [2]. Identifying these key sites enables the prediction of favorable charge transfer pathways, both between fullerene units and in interactions with electron donor species.

By integrating this analysis with molecular electrostatic potential (MEP) mapping, we investigate both "soft-soft" interactions (linked to frontier orbital deformations) and "hard-hard" interactions (related to electrostatic behavior) [2]. This dual methodology allows us to predict reactivity patterns with potential donor or acceptor species, identify favorable molecular orientations for charge transfer, and elucidate key structure-property relationships essential for material design. The interplay between orbital-driven and electrostatic-driven interactions provides a detailed understanding of how the poly(fullerene)s participate in charge transfer. Finally, this study establishes a robust framework for the rational design of advanced OPV materials, demonstrating how targeted computational strategies can accelerate the development of more efficient and durable organic photovoltaic-based devices.

Keywords: Polyfullerenes, Organic Photovoltaic Devices, Density Funcional Theory, Condensed-To-Atoms Fukui Indexes.

Acknowledgments

The work leading to this presentation has received funding from the European Horizon program under grant agreement HORIZON-CL5-2024-D3-01-02-EFFECTOR-10117280. Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Proc. 88887.933010/2024-00.

References

[1] Batagianni, E.; Doat, O.; Elissalt, N.; Bouassa, D. E. M.; Bittencourt, J. C.; Goncalves, G. C.; Moreno, V. F.; Lima, J. V. M.; Nogueira, G. L.; Affonço, L. J.; Paulin, J. V.; Fernandes, S. L.; Ferranti, R.; Khoukh, A.; Silva Filho, L. C.; Agostini, D. L. S.; Olivati, C. A.; Campana, P. T.; Graeff, C. F. O.; Bégué, D.; Hiorns, R. C. Radical and environmentally friendly route to poly(fullerene)s incorporating C_{60}, C_{70}, and PCBM. *Macromolecules* **2025**, *58,* 1686–1704.

[2] Gomes, O.P.; Rheinheimer, J.P.C; Dias, L.F.G; Batagin-Neto, A.; Lisboa-Filho, P.N. Revisiting the hydroxylation phenomenon of SiO_2: a study through “hard-hard” and “soft–soft” interactions. *Journal of Molecular Modeling* **2022**, *28:115*, 1-10.

A bio-sourced tool kit to defuse the Cr(VI) threat in wastewater

Philip Verdross[2], Hande Barkan Öztürk[1], Alexander Bismarck[*]

[1,2,]University of Vienna, Vienna, Austria*
[*]alexander.bismarck@univie.ac.at

The presence of chromium in waterbodies is a risk for human health and the environment. Especially in tannery operations chromium is still in use in relevant quantities. Polymeric adsorbents that can be used for the adsorption of heavy metal ions from industrial effluents are often not biogenic. We investigated how to produce porous lignin-based thermosets for the adsorption of heavy metal ions (chromium in our case) from water as a greener alternative. Amino-functionalised (triethylenetetramine) porous lignin monoliths were produced by polymerizing an emulsion template containing untreated kraft black liquor (as industrially produced) with oxirane-crosslinkers (green poxy and epichloro hydrin). The adsorbents bare inherent chemical functionality for the adsorption/chemical binding of transition metal ions due to the use of triethylenetetramine. We tested our material for removal of Cr(VI) ions from water and simulated waste water. We found good adsorption of chromium ions, as well as the reduction of dangerous Cr(VI) to harmless Cr(III) upon adsorption. The monoliths were tested in static and continuous adsorption experiments and chromium removal from water and synthetic wastewater was quantified. The materials that we made incorporate mostly bio-carbon due to the use of bio-sourced oxiranes together with lignin contained in black liquor. Only the amine crosslinker is not biogenic.

Keywords: Lignin, water purification, wastewater

Acknowledgments
We thank the FWF for funding our work via the award BIOMAMA.

References

[1] Hande Barkan-Öztürk, Philip Verdross, Alexander Bismarck, Macroporous lignin adsorbents: A bio-sourced tool kit to defuse the Cr(VI) threat in wastewater, Journal of Environmental Chemical Engineering, Volume 12, Issue 5, 2024

Characterisation of poly(lactic acid) self-reinforcement and its influence on material morphology, crystallinity and properties

I. Trofin[1*], M. Borůvka[2], D. Kaineder[1,3], S. Hild[1]

[1] *Institute of Polymer Science, Johannes Kepler University, Linz, Austria*
[2]*Faculty of Mechanical Engineering, Technical University of Liberec, Liberec, Czech Republic*
[3]*Competence Center CHASE GmbH, Linz, Austria*
[*]*ingrid.trofin@jku.at*

Poly(lactic acid) (PLA) is a bio-based, biodegradable material that has shown great potential as an alternative to fossil-based polymers. PLA is biocompatible and has favourable physico-chemical properties (e.g., optical, mechanical, barrier) that are comparable to those of synthetic, commercially-available polymers, with PLA already being used in biomedical, industrial and commercial applications. However, its low thermal stability and low impact strength are disadvantageous for further technical applications [1].

The current study proposed a solvent-free methodology, using the PLA stereocomplex (PLA-SC) between enantiomeric poly(D-lactic acid) (PDLA) and poly(L-lactic acid) (PLLA) to achieve material self-reinforcement. The stereocomplexation is driven by the intermolecular hydrogen-bonding established between the $-CH_3$ and O=C groups of the single components. Due to the resulting compact domains, the stereocomplex has a greater thermal stability than the PLA homopolymers [2]. The PLA-SC was produced in a 1:1 D/L ratio, post-annealed, then incorporated in low amounts (1, 3, 5 wt.%) into PLA matrices of different optical purities, i.e., D-isomer content. This compounding was done at three PLA-SC threshold melting temperatures, in order to alter the strength of the internal hydrogen-bonding within the stereocomplex crystallites by partially melting them.

The influence of PLA-SC on crystallinity and morphology was investigated, in relation to mechanical and rheological properties. An increase in crystallinity with the addition of PLA-SC was indicated by differential scanning calorimetry (DSC) and confirmed by Raman spectroscopy for both matrices (PLLA and poly(D,L-lactic acid) (PDLLA)). The self-nucleation effect of the stereocomplex was remarked under the thermo-optical microscope (POM), where the pellets were isothermally crystallised at 120 °C. An increase in the percentage of PLA-SC resulted in a notable rise in the number of nuclei and an initial formation of bigger semi-crystalline structures. Atomic force microscopy (AFM) measurements, further performed on the thin-films so-obtained via POM, revealed two distinct morphologies correlated to the crystallinity trends recorded, namely spherulites and shish-kebabs, the latter being known as flow-induced, oriented semi-crystalline conformations. Rheology measurements showcased the effect of the stereocomplex stability on the PLA behaviour under deformation, while mechanical tests showcased its effect on the PLA behaviour under stress. The heat deflection temperatures (HDT) also registered an increase for both PDLLA and PLLA, proving that the HDT values of the PLA materials were governed by their crystallinities and that the low dimensional thermal stability of PLA could be overcome.

The incorporation of low amounts of PLA stereocomplex into PLA matrices of different optical purities under industrial processing conditions led to the self-reinforcement of PLA and the concomitant improvement of material properties, without compromising its positive life cycle assessment.

Acknowledgments

This work was partially conducted within the COMET Centre CHASE, funded within the COMET – Competence Centers for Excellent Technologies programme by the BMK, the BMDW and the Federal States of Upper Austria and Vienna (grant 901897), managed by the Austrian Research Promotion Agency (FFG).

References

[1] Castro-Agguire, E., et.al. Poly(lactic acid)—Mass production, processing, industrial applications, and end of life. *Advanced Drug Delivery Reviews* **2016**, *107*, 333-366.

[2] Brizzolara, D., et.al. Mechanism of the Stereocomplex Formation between Enantiomeric Poly(lactide)s. *Macromolecules* **1996**, 29, 191-197.

Polyurethane Networks Designed for Fast Depolymerisation

Olga Gotkiewicz[1*], Sébastien Livi[2], Hynek Beneš[1]

[1]Institute of Macromolecular Chemistry of the Czech Academy of Sciences, Heyrovského nám. 2, Prague 6 162 00, Czech Republic
[2]Université de Lyon, CNRS, Université Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, UMR 5223, Ingenierie des Matériaux Polymères, CédexF-69621, France
[*]gotkiewicz@imc.cas.cz

Polyurethane (PUR) foams, the most widely produced thermosetting plastics, significantly contribute to the global plastic waste crisis. Conventional disposal methods, such as landfilling and incineration, pose environmental challenges and hinder progress toward a circular economy. A more sustainable approach begins with the design of PUR foams that can facilitate depolymerisation and promote easier chemical recycling.
In this study, we present a novel strategy for enhancing the degradability of PUR foams by incorporating moieties that facilitate cleavage into their structure. The modified foams are based on bio-sourced raw materials and maintain excellent mechanical and thermal properties while enabling more efficient breakdown. Furthermore, the solvolysis of the foams yields a recycled polyol, which can replace up to 50 wt% of virgin polyol in the production of bio-based rigid PUR foams. The resulting materials exhibit stable mechanical performance, a highly closed-cell structure, and enhanced thermal insulation properties, advancing the development of more sustainable PUR-based products.

Keywords: polyurethane, recycling, solvolysis, sustainability

Acknowledgments
This work was financially supported by the Lead Agency bilateral Czech-Polish project provided by the Czech Science Foundation (24–10651K) and National Science Center Poland (UMO-2023/05/Y/ST8/00076) and by the Czech Academy of Sciences and Centre National de la Recherche Scientifique - Mobility Plus Project No. CNRS-24-09.

References

[1] O. Gotkiewicz, M. Kirpluks, Z. Walterová, O. Kočková, S. Abbrent, P. Parcheta-Szwindowska, U. Cabulis and H. Beneš, ACS Sustain Chem Eng, 2024, 12, 1605–1615..

Combining electrospinning and glass-coated magnetic microwires for the development of responsive hybrid nanofibrous devices

L. Vignau[1], V. Zhukova[2], A. Zhukov[2,3], A. Eceiza[1], N. Gabilondo[1]

[1] "Materials + Technologies" Group (GMT), Chemistry and Environmental Engineering Department, Faculty of Engineering of Gipuzkoa, University of the Basque Country (UPV/EHU), Donostia - San Sebastian, Spain
[2]Department of Polymers and Advanced Materials: Physics, Chemistry and Technology, Faculty of Engineering of Gipuzkoa, University of the Basque Country (UPV/EHU), Donostia -San Sebastian, Spain
[3]IKERBASQUE, Basque Foundation of Science, Bilbao, Spain
laura.vignau@ehu.eus

Electrospinning is an adaptable method for the production of polymeric nanofibers [1] with enormous potential for their use in biomedical applications, mainly in wound dressing and drug delivery. In the search of materials for this field of application, chitosan (Cs) is one of the most commonly used polymers, thanks to its biocompatible and antimicrobial character [2]. Moreover, recently, in the biomedical field, potential uses of amorphous glass-coated magnetic microwires in hyperthermia are investigated [3]. In this context, the main objective of this research was to produce and characterize magnetically responsive membranes composed of glass-coated magnetic microwires in between two of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) layers and an inner curcumin loaded Cs/polyether oxide (PEO) bioactive layer. The good spinnability, mechanical resistance and surface properties of PHBV conferred stability to the wound dressing, maintaining the biodegradable character of the material, while acting as a matrix for the microwires. Defect-free nanofiber bilayer membrane was fully characterized and the results showed promising magnetically responsiveness and potential applicability as active wound dressing.

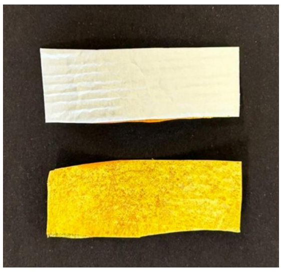


Figure 1. Membranes' pieces showing the outer PHBV/microwires layer (top) and the inner Cs/PEO/CUR one (down).

Acknowledgments

Basque Government grant to consolidated research groups (IT1690-22) and Basque Government PhD grant (Programa Ikertalent) 00035-PIT2021-22 to LV.

References

[1] Yang, J,; Xu, L;. Electrospun Nanofiber Membranes with Various Structures for Wound Dressing. *Materials (Basel)* **2023**, Sep 1;16(17):6021.
[2] Padhi, S.; Behera, A.; Hasnain, M.S.;3 , Nayak, A.K;. Uses of chitosan in drug delivery. *Chitosan in Biomedical Applications* **2022**, 139-162.
[3] O, Mitxelena-Iribarrena,b.; J, Campisia.; I, Martínez de Apellániz.; S, Lizarbe-Sanchaa.; S, Aranaa.; V, Zhukova.; M, Mujikaa.; A, Zhukov;. Glass-coated ferromagnetic microwire-induced magnetic hyperthermia for in vitro cancer cell treatment. *Materials Science & Engineering* **2020**, C 106 – 110261.

Self-assembled amphiphilic random copolymers as drug delivery system for highly hydrophobic anticancer Combretastatin A4

E. Martinelli, E. Guazzelli Author's
[1] *Università di Pisa - Department of Chemistry and Industrial Chemistry, Pisa, Italy*

Solvophobic interactions in amphiphilic random copolymers may lead to the formation of unimer micelles in selective solvents, typically water, through single-chain folding. These unimer micelles fall in the larger category of the so-called single-chain nanoparticles (SCNPs) and feature an extremely small size range (1–20 nm). A tailored synthesis and in-depth characterization of size, shape, and conformation of these materials might drive their future exploitation in environmental chemistry, industrial catalysis, biomedicine and drug delivery.[1,2]

In this work, PEGMAx-*co*-FAy copolymers were synthesized using ARGET-ATRP. Complementary techniques, including small angle X-ray scattering (SAXS) and dynamic light scattering were used to study the self-assembly behavior in water and different organic solvents. In particular, the SAXS studies confirmed the formation of compact-globular single-chain self-folded thermoresponsive unimer micelles in water, which generally presented small hydrodynamic diameters ($D_h < 10$ nm) as a result of the folding of the hydrophobic perfluorohexylethyl acrylate counits, and a cloud point temperature (T_{cp}) easily tunable by the copolymer structure in terms of composition and side-chain length of the hydrophilic component.[3] As a proof of concept, the formed hydrophobic nanocavities were used to encapsulate Combretastatin A-4 (CA-4), an active but poorly water-soluble anticancer drug.[4] The cellular internalization of the unimer micelles was studied with copolymers tagged with fluorescein O-methacrylate, in biodistribution assays. Cytotoxicity tests toward different cell lines demonstrated the effectiveness of the anticancer drug when encapsulated.

Acknowledgments

This work was supported by the Italian MUR (PRIN 2022 BIOCOMMON, CUP I53D23004120006, under the responsibility of E. Martinelli)

References

[1] Single-Chain Polymer Nanoparticles; Pomposo, J.A., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, **2017**; ISBN 9783527806386.
[2]Terashima, T. Controlled Self-Assembly of Amphiphilic Random Copolymers into Folded Micelles and Nanostructure Materials. J. Oleo Sci. 2020, 2020, 1–10.
[3] Guazzelli E., Masotti E., Kriechbaum M., Uhlig F., Galli G., Martinelli E., **2022**, *Macromol Chem Phys*, DOI: 10.1002/macp.202200360
[4] Calosi M., Guazzelli E., Braccini S., Lessi M., Bellina F., Galli G., Martinelli E., **2022**, *Polymers*, 14 (4), 774, DOI: 10.3390/polym14040774

Redox-responsive polymers for biomedicinal applications

D. Vašínová[1*], M. Hrubý[1], V. Lobaz[1]

[1]*Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského náměstí 1888/2, 162 00 Prague 6*
[*]*dominika.vasinova@gmail.com*

The synthetic glucocorticoid dexamethasone is used to treat inflammatory diseases, but the therapy is often accompanied by unwanted side effects. These negative impacts can be limited by the use of drug delivery systems. This study focuses on the synthesis and characterization of a redox responsive polymer carrier, which has ferrocene in its end group. The synthesized homopolymers of 2-ethyl-2-oxazoline and copolymers of 2-ethyl-2-oxazoline and 2-nonyl-2-oxazoline were analyzed in terms of their structure, self-assembly, drug encapsulation, response to the oxidative environment typical for inflammed and cancerous tissues and biocompatibility. The structure of the polymers was confirmed by NMR, GPC and MS. The approximate content of ferrocene and the critical micellar concentration were determined. Redox responsiveness was demonstrated using UV-VIS spectroscopy and isothermal titration calorimetry. Furthermore, low interaction with blood plasma proteins and the encapsulation of dexamethasone in polymer micelles were comfirmed. The non-toxicity of both the polymers themselves and the prepared formulations was determined by biological tests. The results show that the synthesized polymers could potentially be further biologically tested, possibly modified, and used for drug delivery.

Keywords: reactive oxygen species, polymer, ferrocene, drug delivery,
2-ethyl-2-oxazoline, 2-nonyl-2-oxazoline, dexamethasone

Acknowledgments
Financial support from MEYS CR (grants # LUAUS24272 and LUAUS24203) and the project to the project New Technologies for Trans-lational Research in Pharmaceutical Sciences /NETPHARM, project ID CZ.02.01.01/00/22_008/0004607, co-funded by the European Union, is gratefully acknowledged.

Preparation, Topography, Nanomechanical Properties and Crosllink Density of Soft Swollen Hydrated Micron-Sized Polypeptide Microgels

O. Kotko[1,2*], P. Šálek[1], J. Dvořáková[1], M. Dušková[1], J. Šomvarsky[3], M. Šlouf[1], J. Bonvent[4], S. Brochsztain[4], V. Proks[1]

[1]*Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, 162 06 Prague 6, Czech Republic*
[2]*Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, 12800 Prague 2, Czech Republic*
[3]*Faculty of Mathematics and Physics, Charles University in Prague, V Holešovičkách 2, 180 00 Prague 8, Czech Republic*
[4]*Universidade Federal do ABC, Av. dos Estados, 5001. Bairro Santa Terezinha, Santo Andre, SP, Brazil*
[*]*kotko@imc.cas.cz*

We report the innovative preparation of soft micron-sized polypeptide microgels by horseradish peroxidase (HRP)-mediated crosslinking in inverse suspension[1]. The prepared microgels were based on poly[N^5-(2-hydroxypropyl)-L-glutamine)-*ran*-(N^5-propargyl-L-glutamine)-*ran*-(N^5-(6-aminohexyl)-L-glutamine)]-*ran*-(N^5-[2-(4-hydroxyphenyl)ethyl)-L-glutamine)] polymer precursor (P2HPG-Tyr). We tested the effect of surfactants sorbitan monooleate (SPAN 80), polyoxyethylenesorbitan trioleate (TWEEN 85), and dioctyl sulfosuccinate sodium salt (AOT), on microgelation in inverse suspension without or with pre-emulsification step. The morphology, size, and particle size distribution of the P2HPG-Tyr microgels were evaluated by light microscopy technique. The crosslinking procedure employing surfactant SPAN 80 and 1-hour pre-emulsification yielded high-quality, spherical, and colloidally stable ~ 80 µm P2HPG-Tyr microgels, which were subsequently studied by cryo-SEM and atomic force microscopy (AFM). To evaluate the topography and nanomechanical properties of the developed P2HPG-Tyr microgels in the hydrated swollen state, the large swollen hydrated P2HPG-Tyr microgels were immobilized on Mica and glass substrates for investigation by atomic force microscopy (AFM) in PeakForce QNM mode in Q-H_2O and PBS buffer (pH 7.4). The AFM investigation revealed surface irregularities of the P2HPG-Tyr microgels and proved their viscoelasticity and softness, documented by Young´s moduli in the range of tens of kPa derived from force-separation curves. Finally, the crosslink density of the P2HPG-Tyr microgels was evaluated, revealing the concentrations of elastically active network chains (EANCs) in the range of 0.489×10^{-3} to 0.812×10^{-3} mol cm^{-3}. Following this work, the new series of P2HPG-Tyr microgels, which were prepared in the presence of the surfactant SPAN 80 and 1-hour pre-emulsification step, were prepared with various H_2O_2/Tyr ratio, and they are being tested for encapsulation of Lactobacillus, Streptococcus, and Saccharomyces.

Keywords: AFM, microgel, nanomechanical properties, polypeptide, topography.

Acknowledgments

Financial support from the Czech Science Foundation (no. 21-06524S), Horizon 2020 research and innovation program of the European Union Maria Sklodowska-Curie (grant agreement 823883-NanoPol-MSCA-RISE-2018) and The project National Institute for Cancer Research (Programme EXCELES, ID project no. LX22NPO5102) – Funded by the European Union – Next Generation EU are gratefully acknowledged. Miroslav Šlouf would like to thank Veronika Gajdosova and Pavel Nemecek for numerous sample preparations for Cryo-SEM and for the repeated Cryo-SEM measurements. The study was supported by the Charles University, project GA UK No. 425725.

References

[1] Kotko, O.; Šálek, P.; Dvořáková, J.; Dušková Smrčková, M.; Šomvarsky, J.; Bonvent, J.J.; Brochsztain, S.; Proks, V. Soft Micron-sized Polypeptide Microgels: Preparation, Crosslink Density, Topography and Nanomechanics in Swollen State. *Mater. Adv.* **2024**, *5*, 5984-5997.

Effect of side chain branching on the structural and dynamic properties of linear and cyclic polyacrylates

Z. Benková[1*], T. Hrivnák[1,2]

[1]Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia
[2]IT4Innovations, VSB – Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava Poruba, Czech Republic
*zuzana.benkova@savba.sk

Polyacrylates are extensively employed across various applications owing to their remarkable physico-chemical characteristics and the ease with which their properties can be taylored through modifications of the alkyl group in the alkoxycarbonyl substituent at relatively low cost.[1] Typically, this modification involves the linear extension of the alkyl group, which leads to monotonous trends in the structural and dynamic properties of polyacrylates in their melts.[2,3] Nevertheless, the impact of branching in the alkyl group on these properties remains inadequately explored and understood. This atomistic molecular dynamics study examines the structural and dynamic characteristics of poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), poly(isopropyl acrylate) (PiPA), poly(*tert*-butyl acrylate) (PtBA), and poly(methyl methacrylate) (PMMA) under different thermal conditions. The study considers both linear and cyclic polymer architectures. The distinction in architecture are detectable in the intermolecular radial distribution functions of Cα-Cα pairs. In the case of cyclic architecture, the radius of gyration and end-to-end distance of the polymer chains monotonously increase with the size of the alkyl group, whereas the polymer chain with linear architecture exhibit a non-monotonic trend in these quantities. This non-monotonous behavior for linear structures is explained by the competing effects of increased intrachain repulsion and diminished mutual penetration of the chain's pervaded volume as the alkyl group expands. The diffusion coefficient reflects an identical trend across the examined series for both architectures, with its non-monotonous behavior arising from the combined influence of the overall shape of the polymer chains and the symmetry of the alkyl group. Local dynamics are characterized by parameters related to α-relaxation and β-relaxation. Notable similarities in dynamic properties are observed between PEA and PiPA, as well as between PMA and PtBA, with the latter exhibiting slower dynamics. The slowest dynamics are recorded for PMMA.

Keywords: polyacrylates, molecular dynamics, diffusion, relaxation time, radius of gyration, radial distribution function, viscosity

Acknowledgments

This work was supported by grants APVV-21-0346, VEGA 2/0098/23, and SK-AT-20-0011.

References

[1] Cvek, M.; Kollar, J.; Mrlik, M.; Masar, M.; Suly, P.; Urbanek, M.; Mosnacek, J. Surface-Initiated Mechano-ATRP as a Convenient Tool for Tuning of Bidisperse Magnetorheological Suspensions toward Extreme Kinetic Stability. *Polym. Chem.* **2021**, *12*, 5093–5105.
[2] Kikuchi, H.; Tokumitsu, H.; Seki, K. Molecular Motions of Poly(ethyl acrylate) and Poly(*n*-butyl acrylate) Studied by Solid-State NMR and Molecular Dynamics Computer Experiments. *Macromolecules* **1993**, *26*, 7326–7332.
[3] He, X.; Wu, J.; Huang, G.; Wang, X. Effect of Alkyl Side Chain Length on Relaxation Behaviors in Poly(*n*- alkyl Acrylates) and Poly(*n*-alkyl Methacrylates), *J. Macromol. Sci. Phys. B* **2011**, *50*, 188–200.

Influence of cooling conditions on the structural morphology of high-density polyethylene

D. Pindrić[1*], G. Spiegel[1], C. Paulik[1,2]

[1]*Competence Center CHASE GmbH, Linz, Austria*
[2]*Johannes Kepler University, Linz, Austria*
[*]*dario.pindric@chasecenter.at*

High-density polyethylene (HDPE) is a semi-crystalline polymer, with its crystallinity significantly affecting mechanical and chemical resistance properties [1]. The crystal morphology consists of lamellae that form spherulites, while the amorphous chains are situated between the individual lamellaes [2]. By varying the crystallization temperature (T_c) the size of the resulting crystalline lamellae can be altered [3].

This study investigates various cooling conditions for the crystallization of HDPE, including different crystallization temperatures and cooling rates. A polymer solution with an organic solvent is utilized to enhance consistency. Figure 1 illustrates the experimental setup used for the process.

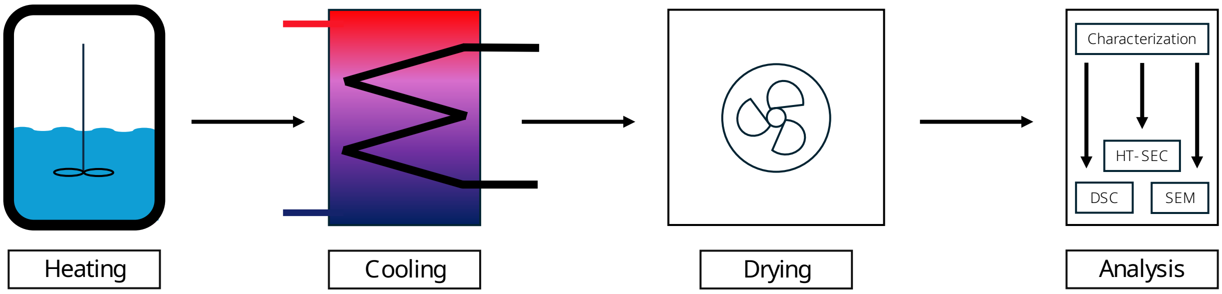


Figure 1: Experimental setup for the thermal treatment and characterization of the polymer solution.

The polymer solution is heated up to temperatures around the polymer´s melting point and then cooled at different conditions using a heat exchanger. The solvent is evaporated in a heating cabinet at low temperatures to maintain the structural integrity of the material. The dried polymer is characterized using Focused Ion Beam – Scanning Electron Microscopy (FIB-SEM). The resulting images are correlated with crystallinity data obtained from Differential Scanning Calorimetry (DSC) and the molecular weight distribution measurements using High Temperature – Size Exclusion Chromatography (HT-SEC).

Keywords: High-density polyethylene, SEM (scanning electron microscopy), crystallinity

Acknowledgments
The authors acknowledge financial support through the COMET Centre CHASE, funded within the COMET – Competence Centers for Excellent Technologies program by the BMIMI, the BMWET and the Federal Provinces of Upper Austria and Vienna. The COMET program is managed by the Austrian Research Promotion Agency (FFG).

References

[1] Tantry, S.; Anantharaman D.; Thimmappa B.; Kamalakaran R. Studying banded spherulites in HDPE by electron microscopy. *Polymer Testing* **2020**, *89*, 106631.
[2] Huang L.; Yang W.; Yang B.; Yang M.; Zheng G.; An H. Banded spherulites of HDPE molded by gas-assisted and conventional injection molding. *Polymer* **2008**, *49*,4051–4056.
[3] Sasaki S.; Sakaki Y.; Takahara A.; Kajiyama T. Microscopic lamellar organization in high-density polyethylene banded spherulites studied by scanning probe microscopy. *Polymer* **2002**, *43*, 3441–3446.

Molecular recognition of autoinducers by Molecularly Imprinted Polymers as anti-biofilm strategy

M. Lemarchand, O. Lezrak, A. Ortalo-Magné, C. Branger

Université de Toulon, Laboratoire Matériaux Polymères Interfaces Environnement Marin (MAPIEM), Toulon
mathieu-lemarchand@etud.univ-tln.fr

Molecularly Imprinted Polymers (MIP) are capable of selectively recognizing a targeted molecule, a property arising from their synthesis method **(Fig.1)**. MIP are crosslinked rigid networks designed to have specific cavities that are tailored to match the shape and chemical properties of a target molecule, which is used as a template during its preparation. The polymerization process involves one or more functional monomers that are carefully selected for their specific affinity with the target molecule. The use of a high amount of crosslinker locks the steric arrangement of functional monomers around this template. Upon removal of the template, complementary binding sites are created, enabling selective recognition of the target molecule through interactions such as hydrogen bonding [1].

Biofilm formation occurs and causes problems in various environments, leading to major economic and environmental impacts (navigation or water treatment sectors) as well as public health concerns (medical, food industry). Within a biofilm, bacteria can communicate and cooperate through a system known as *quorum sensing* (QS) using small signaling molecules called autoinducers (AI), which provide them with a collective adaptability to their environment [2]. The QS regulates processes like biofilm development. Inhibiting this chemical communication between bacteria by sequestring AI using MIP would contribute to the search for new biofilm control strategies [3].

The target molecules of the strategy here are the AI from the acylated homoserine lactone (AHL) family. Instead of using one AHL in particular as template molecule, an analog dummy template **(Fig.2)** was used with the aim of recognizing the entire AHL family with only one tailor-made MIP. The study of commercial and original functional monomers by proton and carbon NMR, highlighted the strength of H-bonding and led to the selection of acrylamide as a suitable monomer to specifically interact with AHL. Using EGDMA as the crosslinker, several MIPs and their non-imprinted polymer (NIP) counterparts were synthesized by precipitation polymerization under different conditions of time, temperature, and concentration. The characterization of these polymers, including their morphology (SEM), their porosity and specific area (BHJ, BET), along with the determination of their adsorption isotherm (LC-MS), demonstrated their ability to recognize and capture targeted AHL. Testing these polymers in complex microbiological environments (initially using *Vibrio harveyi* as AHL-producing baterium) has confirmed their ability to sequester AHL, their anti-biofilm properties, and their non-cytotoxicity, showcasing their potential for biofilm control.

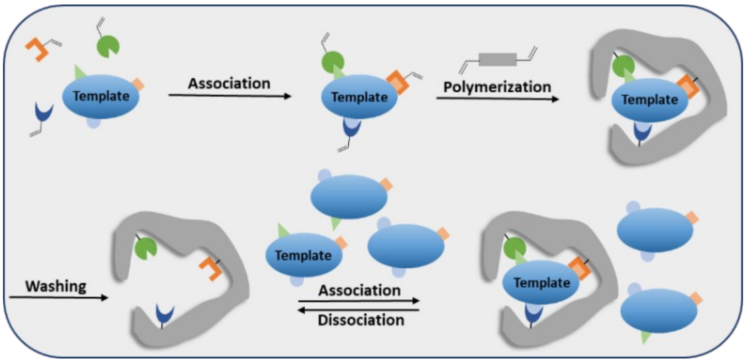


Figure 1 : Synthesis of Molecularly Imprinted Polymer

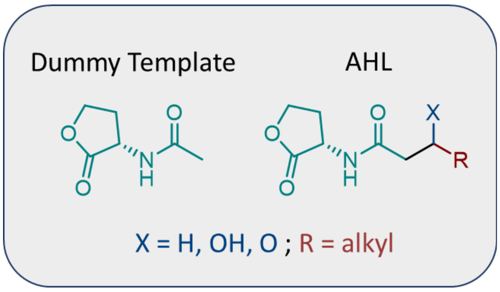


Figure 2 : Dummy Template and AHL family

References

[1] Tse Sum Bui, B.; Auroy, T.; Haupt, K., Fighting Antibiotic-Resistant Bacteria: Promising Strategies Orchestrated by Molecularly Imprinted Polymers. *Angew. Chem. Int.*, **2022**, 61, 1-18.

[2] Papenfort, K.; Bassler, B.L., Quorum sensing signal-response systems in Gram-negative bacteria. *Nat. Rev. Microbiol.*, **2016**, 14, 576-588

[3] Yangcui, Q.; Yi, Z; Guannan, W.; Yanxia, Z.; Qian Y., Disrupting of Communication: Recent Advances in Antibiofilm Materials with Anti-Quorum Sensing Properties. *Appl. Mater. Interfaces*, **2024**, 16, 13353-13383

PES-Membrane Meets polyHIPE: A Novel Approach to Separation Technology

J. Jüstel [1,2], A. Menner[1] & A. Bismarck [1,3*]

[1]Institute of Materials Chemistry and Research, Polymer and Composite Engineering (PaCE) Group, Faculty of Chemistry, University of Vienna, Währinger Straße 42, 1090, Vienna, Austria
[2] University of Vienna, Vienna Doctoral School in Chemistry (DoSChem), Währinger Str. 42, 1090 Vienna, Austria.
[3]Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, U.K.
[*]alexander.bismarck@univie.ac.at

Membrane technology plays a crucial role in various filtration and separation processes, with polyethersulfone (PES) being a widely used material. PES membranes are well-known for their excellent chemical stability and robustness, making them ideal for various filtration processes. However, their relatively low permeability and limited flexibility often restrict their application in more demanding environments.[1] To overcome these challenges, polymerized High Internal Phase Emulsions (polyHIPEs) were used as support material for PES membranes, offering a promising strategy for enhancing their properties. [2,3] PolyHIPEs, engineered using polyurethane diacrylate (PUDA), provide high porosity, structural stability, and tunable mechanical properties, making them suitable for membrane applications. [4] Additionally, the incorporation of silica nanoparticles enabled precise control over pore architecture, leading to optimized polyHIPEs with high permeability, improved mechanical strength, and enhanced resistance to deformation.[5] Rendering them potentially in an ideal membrane support. We will demonstrate that the polyHIPE-supported PES membrane not only enhances mechanical resilience but also opens new possibilities for developing a novel separation system. Therefore, we developed a flow cell which operates under dynamic flow conditions. This flow cell is suited to be integrated into our plant on a bench. For the first time, we will present this new flow cell in which the polyHIPE not only supports the membrane but also acts as a static mixer transporting the filtrate to the membrane. We will provide evidence that our polyHIPE-membrane-filtration-cell is effective for separation under dynamic filtration conditions.

Keywords: PES membrane, polyHIPE, flow separation

References

[1] Corvilain, M.; Klaysom, C.; Szymczyk, A.; Vankelecom, I. F. J. Formation Mechanism of sPEEK Hydrophilized PES Supports for Forward Osmosis. *Desalination* **2017**, *419*, 29–38. https://doi.org/10.1016/j.desal.2017.05.037.

[2] Foudazi, R. HIPEs to PolyHIPEs. *React. Funct. Polym.* **2021**, *164*, 104917. https://doi.org/10.1016/j.reactfunctpolym.2021.104917.

[3] Barkan-Öztürk, H.; Menner, A.; Bismarck, A. Emulsion-Templated Macroporous Polymer Micromixers. *Ind. Eng. Chem. Res.* **2021**, *60* (39), 14013–14025. https://doi.org/10.1021/acs.iecr.1c01949.

[4] Jiang, Q.; Menner, A.; Bismarck, A. Robust Macroporous Polymers: Using Polyurethane Diacrylate as Property Defining Crosslinker. *Polymer* **2016**, *97*, 598–603. https://doi.org/10.1016/j.polymer.2016.05.071.

[5] Ikem, V. O.; Menner, A.; Horozov, T. S.; Bismarck, A. Highly Permeable Macroporous Polymers Synthesized from 7Pickering Medium and High Internal Phase Emulsion Templates. *Adv. Mater. Deerfield Beach Fla* **2010**, *22* (32), 3588–3592. https://doi.org/10.1002/adma.201000729.

Mechanical Vibrations of Ultrathin Freestanding Polymer Films

N. M. Roberts[1*] and J. S. Sharp[1]

[1]*School of Physics and Astronomy, University of Nottingham, Nottingham, United Kingdom*
[*]*Corresponding Author: mbynmr@exmail.nottingham.ac.uk*

Piezolectric excitation and acoustic detection of the vibrations of ultrathin (30nm-300nm) freestanding polymer films was used to probe their physical properties. A simple method involving acoustic detection of the vibrational response of the films with an inexpensive microphone revealed that the resonant peaks of the films were in the kHz range. Polymer solutions were spin coated onto glass slides to create ultrathin films. These films were released from the slides by floating on to a water surface [1] before being picked up on inexpensive piezoelectric buzzers that had had been prepared with holes in the centre. This created a freestanding membrane whose vibrations could be driven by electrically exciting the piezo. The samples were annealed and quenched to room temperature before measurements were performed. A software-controlled waveform generator was used to drive the piezo and the response of the film was recorded with a microphone (figure 1). Two methods were employed to obtain a spectrum. The first method involved measuring the root mean square microphone signal as a function of the driving frequency. Alternatively, the sample was driven with a large impulse (10Vpp, 100µs in width) and the Fourier transform of the microphone signal was obtained. Both techniques gave identical results for the frequencies of the vibrational peaks which were used to extract information about the mechanical response of the ultrathin films. This approach was previously verified using thick Polydimethylsiloxane membranes [2]. In the current work, the temperature dependence of the frequency of the first mode of vibration of ultrathin poly(tert-butyl methacrylate) and polystyrene films were measured. These data were shown to have a strong dependence on film thickness, providing insights into how molecular confinement effects influence the thermal expansion properties and tension in ultrathin spincast polymer films.

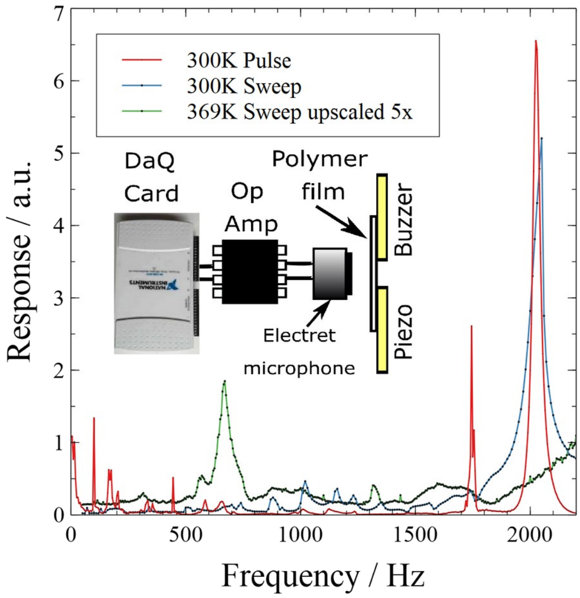


Figure 1. Three spectra generated from an 87nm polystyrene film freestanding over a circular area at two temperatures. At 300K the first mode appears at 2040Hz (blue and red) and at 369K the same mode appears at 670Hz (green) while the film is 10K away from bulk T_g. Inset is a schematic of the electronics that recorded sound generated by the film.

References

[1] Baxamusa, S.H., Stadermann, M., Aracne-Ruddle, C., Nelson, A.J., Chea, M., Li, S., Youngblood, K. and Suratwala, T.I. Enhanced delamination of ultrathin free-standing polymer films via self-limiting surface modification. *Langmuir* **2014**, *30*(18), 5126-5132.

[2] Roberts, N.M. and Sharp, J.S. Piezoelectric excitation and acoustic detection of thin film polymer membrane vibrations. *Physical Review E* **2024**, *109*(1), 014802.

The adsorption of soil-releasing polymers at model fabric interfaces and their effectiveness in the removal of complex soils

Josephine Binks, Richard Thompson

Department of Chemistry, Durham University, Durham, United Kingdom

Hydrophobic fabrics, such as polyester or poly(ethylene terephthalate) (PET), prove to be a challenging surface to remove complex soils, such as sweat and sebum from. Creating a more hydrophilic surface can inhibit the adsorption and redeposition of these soils, and this can be achieved by chemical surface modification. Soil-release polymers (SRPs) are designed to promote hydrophilicity at the fabric surface, and a novel family of biosourced pyridine dicarboxylate SRPs have been developed, which are specific to PET[1]. The SRPs are triblock copolymers of polyester and poly(ethylene glycol) (PEG), where polyester binds to the fabric surface and the PEG outer blocks extend into the PET/water interface, forming a hydrophilic layer (*Figure 1).* This improves soil removal by increasing the affinity for aqueous laundry liquor and reducing its redeposition. Furthermore, these polymers can have a positive environmental impact, improving cleaning effectiveness at lower temperatures and shorter wash cycles. The pyridine dicarboxylate monomers are a sustainable alternative to petroleum-derived terephthalate. Within the family, we find that small variations in their chemical structure significantly influences their performance. The detailed arrangement of SRP on PET must be established to understand the structure-property relationship. Recent experiments at ISIS Neutron and Muon Source, Didcot provided valuable insights to measure the SRP layer thickness before and after rinsing, the initial kinetics of the SRP-PET adsorption, and by using solutions with contrasting scattering length densities, their arrangement. Additionally, we accompanied these experiments with a rheometric analysis of soil adhesion, where we measured the shear rate $\dot{\gamma}$ at the point where complex soil droplets were removed from PET, then on SRP-treated PET *(Figure 2).* The adhesion of complex soils is dominated by ageing effects, due to changes in their physical and chemical conformation. Oily soils, i.e. human sebum, can produce a yellow discoloration on polyester/cotton during its aging when not completely removed during cleaning due to its oxidation[2]. Thus, by studying soil removal at day 1 vs day 7 of aging, and the effectiveness by SRPs, provides information on how the PET responds to stress.

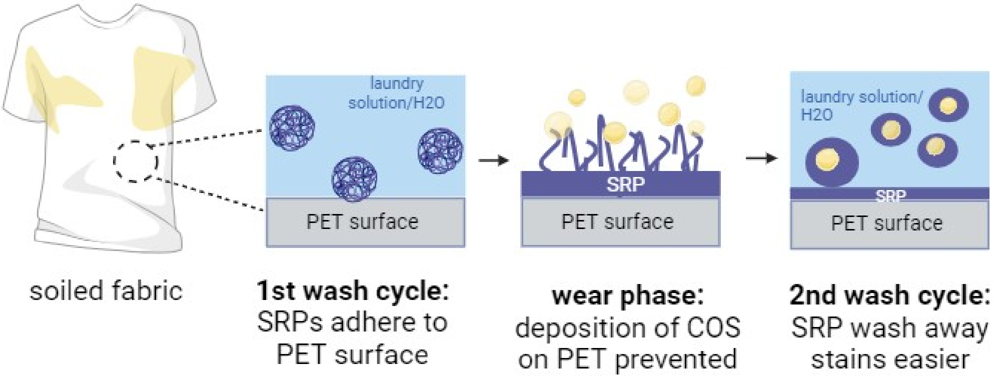


Figure 1: the adsorption of SRPs at the PET surface and their removal performance during washing.

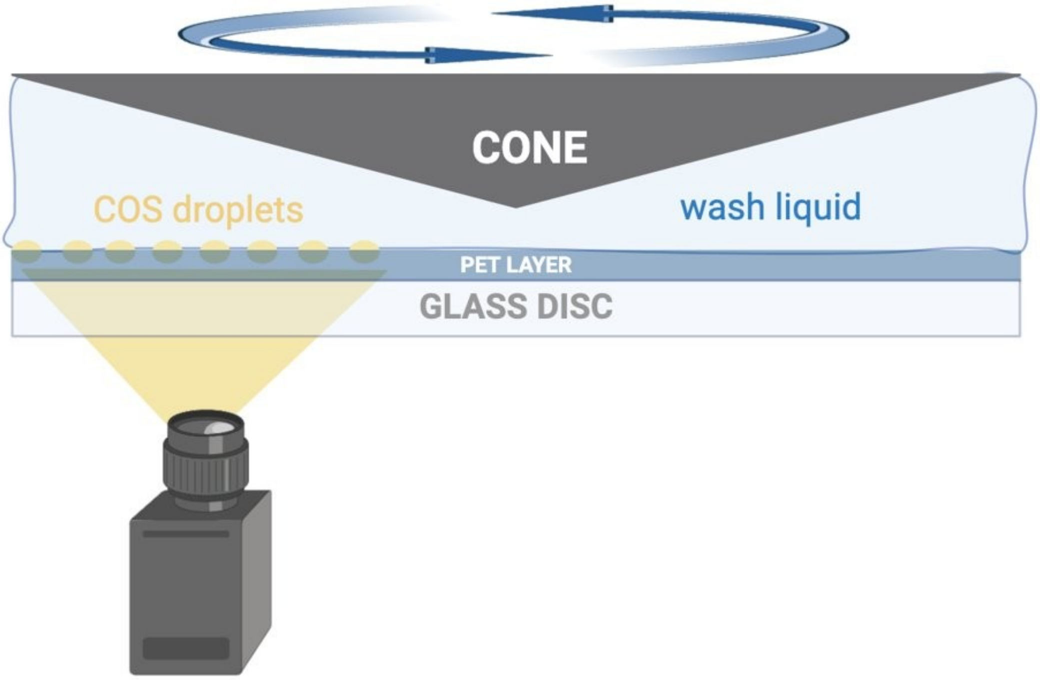


Figure 2: the rheology set up for complex soil stained PET.

Acknowledgements

Elle Fiandra and Dr Matthieu Starck within the Mahon Group at Durham University

The ANTENNA project with Durham University, Procter & Gamble and Imperial College London.

References

1. *Starck, M., Fiandra, E. F., Binks, J., Si, G., Chilton, R., Sivik, M., Thompson, R. L., Li, J., Wilson, M. R., & Mahon, C. S. (2025). Surface Modification of Polyesters UsingBiosourced Soil-Release Polymers. JACS Au, 5(2), 666-674*
2. *Chi, Y. and Obendorf, S.K. (1998) 'Aging of oily soils on textile materials: A literature review', Journal of Surfactants and Detergents, 1(3), pp. 407–418. doi:10.1007/s11743-998-0044-0.*

Lonely polymers split up faster

J. Beslac[1], L. Brandfellner[1,2], A. Bismarck[1,2], H. W. Müller[1]
[1]*IMCR, Faculty of Chemistry, University of Vienna, Vienna, Austria*
[2]*DCAFM, Faculty of Physics, University of Vienna, Vienna, Austria*
**a01363865@unet.univie.ac.at*

Concentration of dissolved polymers determines solution properties, like viscosity, polymer stability and interaction with turbulence. The polymer concentration is a key parameter in the application of polymeric drag reducing agents, high molecular weight polymers that can reduce drag in turbulent flow: Increasing concentration increases absolute drag reduction (DR) as well as polymer stability, counteracting polymer degradation in turbulent flow. Different theories attempt to reveal the mechanism of DR and to describe polymer degradation in turbulent flow [1]. Most numerical simulations of DR do not account for polymer degradation [2] and in many experimental works viscosity changes induced by the polymeric DR agent are omitted. We investigated the role of Polyethylene Oxide (PEO) concentration in dilute solutions using the pilot scale **Vienna Experiment for Drag Reducing Agents (ViEDRA)** [3], focusing on both the initial DR value of the undegraded polymer and on polymer degradation rate. Changes in solution viscosity by polymer addition and degradation were accounted for, in order to disentangle DR from viscosity effects alone. The experimental observations for polymer concentrations in the range of 25 to 200 wppm revealed a clear dependence of both the initial DR and the polymer degradation rate. The initial DR increased with polymer concentration as previously shown [4], levelling off at a concentration of 200 wppm, whereas degradation was more pronounced at low concentrations. The concentration dependence of degradation rate is not straightforward as all polymer solutions were still in the dilute regime where no polymer-polymer interaction is expected. Our observations challenge theories explaining DR by single polymer contributions.

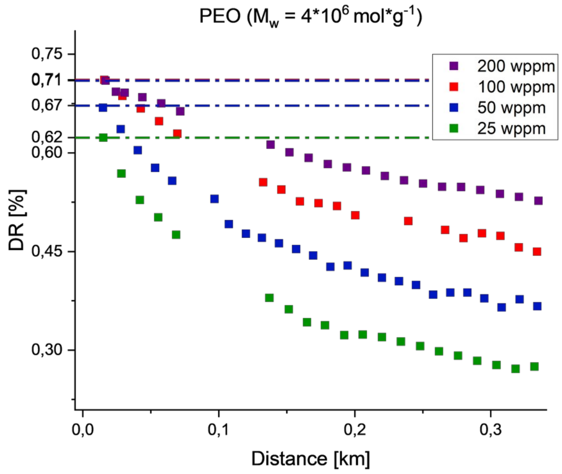


Figure 1: Initial drag reduction (DR) values and the decrease in DR, indicating polymer degradation over longer distances for various concentrations of PEO.

References:

[1] Grabowski, D. W., *Rochester Institute of Technology* (1990).
[2] Xi L., *Physics of Fluids* 31(12) (2019) 121302.
[3] Müller, H. W., Brandfellner, L., Bismarck, A., *Physics of Fluids* 35 (2023) 023102.
[4] Virk P.S., *AIChE J.* 21 (1975) 625–656.

Aggregating Alginate for Drag Reduction

L. Brandfellner[1,2*], A. Bismarck[1,2], H. W. Müller[1]
[1]IMCR, Faculty of Chemistry, University of Vienna, Vienna, Austria
[2]DCAFM, Faculty of Physics, University of Vienna, Vienna, Austria
*lukas.brandfellner@univie.ac.at

Polymeric drag reduction (DR) is the effect of reducing the flow resistance in turbulent flow of liquids achieved by polymers with high molecular weight dissolved in the flowing liquid [1]. Polymer degradation in turbulent flow limits the application, as interaction with turbulent vortices decreases the molecular weight and diminishes drag reduction [2]. Covalent bonds are broken irreversibly and DR is lost. We explored the potential of noncovalent bonds to provide structures of high molecular weight for DR which can reform after degradation and prevent covalent bond scission in turbulent flow DR [3]. Strong noncovalent bonds are needed in order not to be destroyed already at low shear rates [3]. The polysaccharide alginate forms strong aggregates in the precence of Ca^{2+} ions. In unaggregated state alginate is known as a DR agent albeit limited by its molecular weight and chain rigidity [4]. We varied alginate and Ca^{2+} concentration in flow experiments to achieve high molecular weight aggregates, resulting in increased DR. If the aggregates are exposed to turbulent flow, DR decreased rapidly, indicating the breakup of the supermolecular structures. When we applied some resting time at ambient conditions (1 to 7 days) after degradation and repeated the flow experiments high DR was recovered as visible in Figure 1, indicating a re-formation of the aggregates. Again turbulent flow lead to a decrease in DR. The cycle of degradation in flow and re-aggregation at ambient conditions was repeated multiple times, proofing the reversibility of the process in contrast to the irreversible loss of DR in polymer structures based solely on covalent bonds. Multi angle light scattering provided additional insight into polymer and aggregate size.

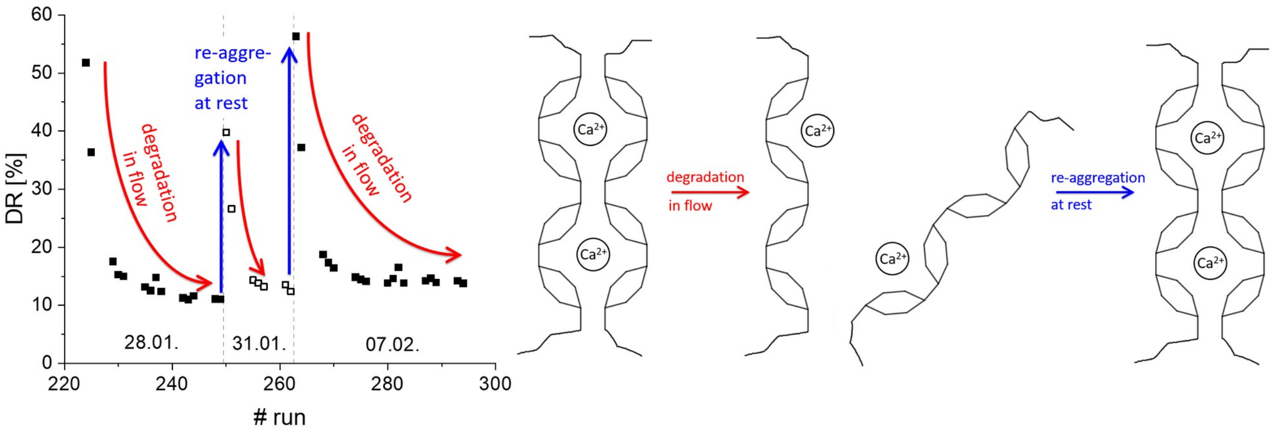


Figure 1: DR of an alginate solution in the presence of calcium ions. Turbulent flow led to a rapid decrease of DR within a few runs of the flow facility. DR was recovered if the solution rested for a few days. Repetability of decrease and recovery of DR for the alginate solutions indicated a reversible aggregation mechanism.

Acknowledgments

This work was supported by the Doctoral College Advanced Functional Materials (DCAFM) funded by the Austrian Science Fund (FWF, Grant No.: DOC 85 doc. funds).

References

[1] Toms, B.A. *Proceedings of the 1st International Congress on Rheology.* **1948**, 135.

[2] Soares, E. J. Review of mechanical degradation and de-aggregation of drag reducing polymers in turbulent flows. *J. Non-Newt. Fluid Mech.* **2020**, 276, 104225.

[3] Muratspahić, E.; Brandfellner L.; Schöffmann, J.; Bismarck, A.; Müller, H. W. Aqueous Solutions of Associating Poly(acrylamide-co-styrene): A Path to Improve Drag Reduction? *Macromolecules* **2022**, 55, 10479−10490.

[4] Han, W. J.; Choi, H. J. Role of bio-based polymers on improving turbulent flow characteristics: materials and applications. *Polymers* **2017**, 9, 209.

Understanding Fracture in Physically Crosslinked Hydrogels

A. Sanz de León[1], G. Song[1,2], I. Tunn[1], T. D. Singewald[2], K. G. Blank[1,2*]

[1]*Max Planck Institute of Colloids and Interfaces, Mechano(bio)chemistry, Potsdam, Germany*
[2]*Johannes Kepler University, Institute of Experimental Physics, Linz, Austria*
[*]*kerstin.blank@jku.at*

The development of hydrogels for cell culture applications has focused on controlling their linear elasticity and viscoelasticity. As cells exert tensile and compressive forces on their surroundings, it is crucial to also consider the non-linear responses of these materials. However, the complexities of non-linear deformation and hydrogel fracture remain inadequately understood. Our goal is to correlate linear and non-linear bulk hydrogel responses with the molecular properties of the hydrogel constituents. Employing a bottom-up approach, we synthesize hydrogels entirely composed of molecularly characterized building blocks. Using star-shaped polyethylene glycol with terminal crosslinking units, we create a material where the contour length of each crosslinked network chain is similar [1-3]. The crosslinks consist of self-assembling coiled coil forming peptides. Utilizing a library of coiled coils with tunable thermodynamic, kinetic, and mechanical stabilities [1,4], we investigate how these parameters correlate with the linear and non-linear properties of the resulting hydrogels.

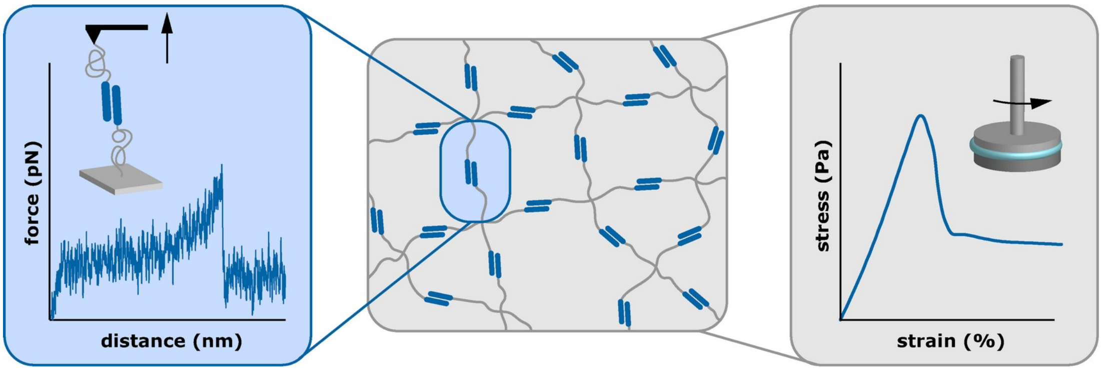


Figure 1. Structure and characterization of coiled coil-crosslinked star-PEG hydrogels. Single-molecule force spectroscopy yields information about the dynamic mechanical behaviour of individual crosslinked chains, whereas rheology provides complementary information about material failure and self-healing at different strains and strain rates.

Oscillatory shear rheology in the linear viscoelastic range reveals that the relaxation times are governed by the equilibrium properties of the crosslinks. More importantly, rotational stress-strain experiments reveal that fracture can be tuned when using crosslinks with different non-equilibrium bond rupture properties. A theoretical model for hydrogel fracture allows for extracting molecular bond rupture parameters of the crosslinks. These parameters are reproduced using atomic force microscope-based single-molecule force spectroscopy, underscoring our ability to link molecular and bulk mechanical properties. Our next step is to introduce a fluorescent reporter system to monitor the crosslink assembly state. This will ultimately enable the visualization of network topology and crosslink rupture in real-time.

Keywords: hydrogel, fracture, rheology, single-molecule force spectoscopy

References

[1] Tunn, I.; de Leon, A.S.; Blank, K.G.; Harrington, M.J. Tuning Coiled Coil Stability with Histidine-Metal Coordination. *Nanoscale* **2018**, *10*, 22725.
[2] Tunn, I.; Harrington, M.J.; Blank, K.G. Bio-inspired histidine-Zn^{2+} coordination for tuning the mechanical properties of self-healing coiled coil-crosslinked hydrogels. *Biomimetics* **2019**, *4*, 25.
[3] Grad, E.M.; Tunn, I.; Voerman, D.; de Léon, A.S.; Hammink, R.; Blank, K.G. Influence of network topology on the viscoelastic properties of dynamically crosslinked hydrogels. *Front. Chem.* **2020**, *8*, 536.

[4] Tsirigoni, A.M.; Goktas, M.; Atris, Z.; Valleriani, A.; Vila Verde, A.; Blank, K.G. Chain Sliding versus β-Sheet Formation upon Shearing α-Helical Coiled Coils. *Macromol. Biosci.*, **2023**, *23*, 2200563.

Accelerated environmental testing of painted galvanized steel sheets

T. Luger[1*], G. M. Wallner[1], M. Ninou Codina[1], G. Mayr[2], B. Strauß[2]

[1]Johannes Kepler Universität, Altenberger Straße 69, 4040 Linz, Austria
[2]voestalpine Stahl GmbH, voestalpine Straße 3, 4020 Linz, Austria
[*]Thomas.Luger@jku.at

Painted galvanized steel sheets are hybrid laminates which find applications in construction (such as facades and roof elements), the automotive, and the white goods industry. Especially in outdoor applications, such laminates are subjected to environmental factors like moisture, heat, and UV radiation and superimposed mechanical stresses due to temperature cycles. A common failure mode is blistering or local debonding of the coating in a brittle manner. The main objective of this study was to develop a lab test methodology which allows for accelerated, but service-relevant testing of coated galvanized steel. Therefore, an environmental fracture mechanics test facility was concepted and implemented. Due to service-relevant brittle failure mode, a linear elastic fracture mechanical fatigue method was employed. A model primer and top coated galvanized steel grade was examined. Double cantilever beam (DCB) specimens were fabricated by stacking and laminating pre-painted galvanized steel sheets with partially removed coating, a titanium reinforcement, and a non-polar polyolefin elastomer (POE) film adhesive. A PTFE release layer was inserted as a well-defined defect and crack starter. To assess the potential impact of pre-ageing on the environmental fracture mechanics crack growth kinetics, coated galvanized steel sheets were exposed to moist heat (condensation), UV-irradiation or hot QUVA weathering. Environmental stress corrosion fatigue tests in artificial acidic rain at an initial pH of 4.5 and a temperature of 60°C, allowed to induce a service-relevant brittle failure at the metal/primer interface, even for the non-pre-aged reference coating. Condensation pre-ageing of the coated steel above a hot water bath temperature controlled at 50°C, was more critical than hot QUVA or just UV-irradiated pre-ageing. Both, the debonding rate in the stable crack growth regime and the strain energy release rate in the threshold regime (Gth), were affected by pre-ageing. For example, the G_{th} values were reduced from 18 J/m^2 for the non-pre-aged coating to just 6 J/m^2 after 2000h of condensation pre-ageing. Using laser confocal microscopy, FTIR and Raman spectroscopy, the brittle failure at the metal/primer interface was confirmed. Moreover, it was shown that both, condensation or hot QUVA pre-ageing and environmental fracture mechanics testing in artificial acidic rain was associated with hydrolysis of urethane groups of the investigated primer. After successful implementation of a service-relevant lab test methodology, future research will deal with the establishment of structure-property-correlations varying the galvanization layer (e.g., Zn vs. ZnMg), the conversion coating or the polyester urethane primer formulation.

Keywords: painted galvanized steel sheets, environmental fracture mechanics, accelerated testing

Supramolecular Semiconductor Materials for Organic Electronics

Aurica Farcas and Ana-Maria Resmerita

''Petru Poni'' Institute of Macromolecular Chemistry-700487 Iasi, Romania
E-mail address: afarcas@icmpp.ro

Over the past decades, organic semiconducting materials (OSMs) have been actively investigated as an alternative to conventional inorganic materials in many optoelectronic applications. In order to replace inorganic semiconductors, OSMs need to render high photoluminescence and fluorescence quantum yield in the solid state, as well a better balance between the injection and transport of electrons and holes. Although tremendous effort has been devoted to tune OSMs's photophysical and charge-transport properties through molecular design, undesirable intermolecular interactions, considerably limit the application of these materials. The construction of mechanically interlocked assemblies such as pseudopolyrotaxane and polyrotaxane architectures has been employed as a powerful method to control the intermolecular interactions and to optimize OSMs optical and electronic properties [1-3]. These supramolecular architectures diminish the aggregation tendency and offer a way of constructing a better protective sheath around the conjugated chains.

Herein, we continue to provide extensive insights into the effect of macrocyclic encapsulations on the photophysical, surface morphology, wetting properties, as well as film forming ability of poly(3,4-ethylenedioxythiophene) (PEDOT), conjugated polyazomethines (PAMs), polythiophenes (PTs), and polyfluorenes (PFs) homo- or copolymers. The reported results have shown the beneficial effect of encapsulation resulting in the diminishing of interchain interactions and packing in insulated molecular wires. For the sake of comparison, the photophysical properties of these supramolecular OSMs were compared to those of their nonthreaded homologs. These findings provided a clear information about improvements of photophysical and transport properties of such encapsulated compounds relevant to applications where the prevention of luminescence quenching without hindering charge transport is essential. Meanwhile, recent achievements obtained by exploiting these supramolecular materials in optoelectronics will be highlighted.

With this study, we hope to provide further evidence and an opportunity to accurately quantify the effect of encapsulation on the solubility, photophysical and transport properties of OSMs, which exhibit a crucial importance for further development of organic electronics and represent a key bottom-up strategy to build and process relatively soft functional materials.

Keywords: Organic semiconductors, polyrotaxanes, quantum efficiency, surface morphology, monolayers, optoelectronics

Acknowledgments

This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS – UEFISCDI, project number PN-IV-P1-PCE-2023-0300.

References

[1] Farcas, A.; Liu, Y.-C.; Nilam, M.; Balan-Porcarasu, M.; Ursu, E.-L.; Nau, W. M.; Hennig, A. Synthesis and photophysical properties of inclusion complexes between conjugated polyazomethines with γ-cyclodextrin and its tris-O-methylated derivative. Eur. Polym. J. **2019**, 113, 236–243.

[2] Haitami, A. E.; Resmerita, A.-M.; Fichet, O.; Cantin, S.; Aubert, P.-H.; Farcas, A. Synthesis, Photophysics, and Langmuir Films of Polyfluorene/Permodified Cyclodextrin Polyrotaxanes. Langmuir : the ACS journal of surfaces and colloids **2021**, 37, 11406–11413.

[3] Ursu, C.; Resmerita, A.-M.; Tigoianu, R. I.; Farcas, A. Aromatic Co-Polyazomethine Polyrotaxane with Enhanced Solubility Applied as a Hole Carrier in a p–n Heterojunction Diode. ACS Appl. Polym. Mater. **2024**, 6, 14872–14884.

Eco-Friendly Dye–Porphyrin Copolymer for Organic Solar Cells: From Ternary Donor to Interfacial Layer

M. Marinelli,[1*] E. Salatelli,[1] M. Lanzi,[1] R. Medri,[1] L. Mazzocchetti[1]

[1]*Dpt. Of Industrial Chemistry “Toso Montanary”, University of Bologna, Italy*
[*]*E-mail address: martina.marinelli5@unibo.it*

Solar energy, particularly through organic solar cells (OSCs), presents an eco-friendly and promising solution to the challenges of global energy shortages and environmental pollution. OSCs offer notable advantages, including the use of non-critical raw materials, cost-effective production, flexibility, and the potential for large-area, semitransparent fabrication. As a result, significant progress has been made in both the design and synthesis of high-performance materials and the optimization of device architectures to enhance photovoltaic efficiency.

This work focuses on the synthesis and application of two novel conjugated thiophene-based polymers integrated with ionic phosphonium salts, providing enhanced solubility in water/alcohol mixtures. The first material - poly{3-(6-tributylphosphoniumhexyl)thiophene-co-3-[5-(4-phenoxy)-10,15,20-triphenylporphyrinyl]hexylthiophene bromide} (P1buP, ED1) - is a copolymer composed of ionic units and tetraphenylporphyrin dye-functionalized segments, while the second - poly[3,4-(6,6’-tributylphosphoniumhexyloxy)thiophene] bromide (P2buP, ED2) - is a disubstituted homopolymer incorporating ionic groups at the end of hexamethylenic side chains, linked to the main polythiophene backbone via ether bridges. The polymers were processed entirely using green solvents, such as ethanol, and evaluated as photoactive donor materials in ternary bulk-heterojunction (BHJ) OSCs, blended with an alcohol-soluble fullerene derivative (EA). The ternary devices exploit complementary absorption, improved energy level alignment, and a more homogeneous active layer morphology. Notably, the device with a ED1:ED2:EA weight ratio of 0.33:0.67:1 achieved a power conversion efficiency (PCE) of 5.22%, which further increased to 6.03% upon Zn metalation of the porphyrin units, without compromising solubility or film-forming properties. In addition to their role as active layer components, the ionic porphyrin-containing polymer was also successfully employed as an alcohol-soluble cathode interfacial layer, improving charge transport and device stability.

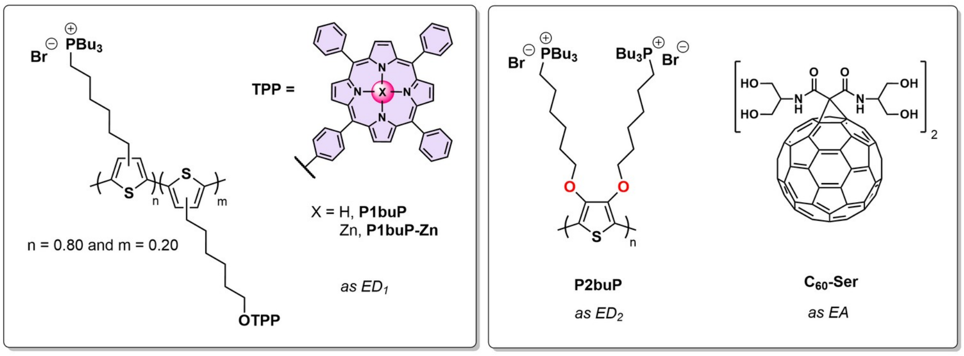


Figure 1. Overview of the synthesized materials.

Acknowledgments

This work was supported by the project “Ecosystem for Sustainable Transition in Emilia-Romagna” (Ecosister), funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.5 - Call for tender No. 3277 of 30/12/2021 of Italian Ministry of University and Research funded by the European Union – NextGenerationEU (project code ECS00000033, CUP D93C22000460001).

References

[1] Marinelli, M.; Lanzi, M.; Quadretti, D.; Ziai, Y.; Pierini, F.; Zanelli, A.; Medri, M.; Salatelli, E. A new alcohol-soluble dye-tetraphenyl porphyrin functionalized copolymer: Inside the role as a third component/cathode interlayer in halogen-free OSCs. *React. Funct. Polym.* **2024**, *200*, 105928.

Hypercrosslinked polymers as electrodes in enhanced structural composite supercapacitors

Anastasiia Naryshkina[1], Robert T. Woodward[1]

[1]*Institute of Materials Chemistry and Research, Faculty of Chemistry, University of Vienna, Währinger Straße 42, 1090 Vienna, Austria*

Composite structural energy storage systems are capable of both carrying mechanical loads and storing electrochemical energy simultaneously. Highly sulfonated hypercrosslinked polymers (SHCPs) offer promising potential as electrode materials for energy storage systems. In this research, I investigate the impact of varying SHCP chemistry on the capacitance of structural energy storage devices by the introduction of tertiary amine moieties.

Here, I successfully synthesise three sulfonated hypercrosslinked porous polymers via a simple one-pot route[1] containing various concentrations of tertiary amine via the inclusion of triphenylamine as a monomer in SHCP synthesis. The introduction of tertiary amine groups was hypothesized to induce pseudocapacitance in energy storage devices and to improve their overall capacitance. Resulting SHCPs were characterised using various methods, including N_2 gas sorption isotherms, thermogravimetric analysis, and FTIR spectroscopy. The polymers exhibited large surface areas of up to 600 $m^2 \cdot g^{-1}$ and demonstrated outstanding chemical and thermal stability, underscoring their potential as highly desirable materials for energy storage applications.

For the manufacturing of structural supercapacitors, SHCPs were deposited onto CF from solution by either electrophoretic deposition or casting via doctor blade. Coated fibres were then assembled into devices[2] with either liquid or structural electrolyte matrices. Using cyclic voltammetry, specific capacitances of up to 3.1 $F \cdot g^{-1}$ and 3.5 $F \cdot g^{-1}$ were measured for liquid and structural composite supercapacitors, respectively, and pseudocapacitive behaviour was induced upon the incorporation of tertiary amines.

Keywords: hypercrosslinked polymers, composite materials, energy storage.

References:

[1] Blocher A, Mayer F, Schweng P, Tikovits TM, Yousefi N, Woodward RT. One-pot route to fine-tuned hypercrosslinked polymer solid acid catalysts. Mater Adv. **2022**;3(15):6335-6342. doi:10.1039/D2MA00379A

[2] Hubert O, Todorovic N, Bismarck A. Towards separator-free structural composite supercapacitors. Compos Sci Technol. **2022**;217:109126. doi:10.1016/j.compscitech.2021.109126

Environmentally Friendly Sustainable Thermoset Vitrimer-Containing Polyrotaxane for Circular Economy

Shota Ando[1*], Masaki Hirano[1], Lisa Watakabe[1], Hideaki Yokoyama[1], Kohzo Ito[1]
[1]*Grad. Sch. of Front. Sci., The University of Tokyo, Kashiwa, Japan*
[*]*s-ando@g.ecc.u-tokyo.ac.jp*

Durable green plastics with extended lifespans have self-healing properties and shape memoryandare chemically recyclable and marine biodegradable. These plastics are attracting attention inapplicationssuch as adhesives and carbon fiber composite materials. Vitrimers satisfy many of theserequirements, interms of reprocessability and self-healing. Herein, we report significant improvements in theproperties ofvitrimers induced by the ester-exchange reaction between polyester-grafted polyrotaxane (PR)and the esterbonds of epoxy resin vitrimer to achieve the uniform molecular dispersion of PR. The optimalepoxy resinvitrimer incorporated with PR (VPR) exhibited enhanced toughness, with an elongation at break 5.3times greater than that of a vitrimer devoid of PR; it also showed self-healing properties, was chemicallyrecycled 10times faster, and was recovered twice as fast. These results can be ascribed to the sliding diffusionmotion ofthe PR, which lowers the energy required for transesterification. Furthermore, VPR showed 25 wt%biodegradation following exposure to seawater for 30 days. These findings may lead to the developmentofenvironmentally friendly plastics that exhibit most of the properties required for a circular economy.

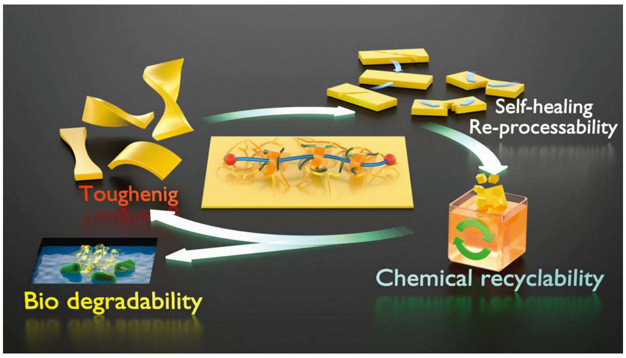


Figure. Vitrimer^containing poryrotaxane for circular economy.

Keywords: Polyrotaxane, Epoxy resin vitrimer, Dynamic covalent bond

Acknowledgments

This work was partially supported by NEDO (grant JPNP18016), the JST-Mirai Program (grant JPMJMI18A2), and the AIST-UTokyo Advanced Operando-Measurement Technology Open Innovation Laboratory (OPERANDO-OIL).

References

[1] D. Montarnal, et al., Silica-like malleable materials from permanent organic networks. *Science* **2011**, 334, 6058, 965– 968

[2] G. Li, et al., Efficient mechanical toughening of polylactic acid without substantial decreases in stiffness and transparency by the reactive grafting of polyrotaxanes. *Journal of Inclusion Phenomena and Macrocyclic Chemistry* **2019**, 93:107–116

[3] S. Pruksawan, et al., Homogeneously Dispersed Polyrotaxane in Epoxy Adhesive and Its Improvement in the Fracture Toughness. *Macromolecules* **2019**, 52, 6, 2464-2475.

[4] S. Ando, et al., Environmentally Friendly Sustainable Thermoset Vitrimer-Containing Polyrotaxane. ACS Mater. Lett., **2023**, 5, 12, 3156-3160.

Catalyst-free PLG based covalent adaptable networks

L. Schwarzer, S. Agarwal*

Macromolecular Chemistry II, Advanced Sustainable Polymers, University of Bayreuth, Bayreuth, Germany
**agarwal@uni-bayreuth.de*

Plastic waste recycling remains a significant challenge for modern societies. While thermoplastics can be recycled relatively easily, thermoset materials cannot. These crosslinked materials are insoluble and unmeltable, making their recycling possible only through methods such as mechanical crushing to obtain filler materials, incineration for energy recovery, pyrolysis to recover crude hydrocarbon mixtures, or disposal in landfills. However, these processes have major drawbacks, including significant environmental pollution such as high CO_2 emissions, as well as being highly energy- and cost-intensive.

To address this issue, a new class of polymers has emerged, aiming to combine the reprocessability of thermoplastics with the superior properties and stability of thermosets. These are referred to as covalent adaptable networks (CANs).[1] In general, bond exchange reactions during processing of thermosets require an appropriate catalysts, often metal-organic compounds, sometimes leading to the problem of leaching and their general toxicity.[2]

Here, we present catalyst-free poly(*DL*-lactide-*co*-glycolide) (PLG)-based covalent adaptable networks that can be easily processed using compression molding.[3] Once processed, the networks are insoluble and exhibit a high gel content. The resulting material demonstrates a high breaking force during tensile testing and can be reshaped easily when heated above the glass transition temperature. Reversibility is introduced via the linker pyromellitic dianhydride, which exists in two temperature-dependent states: open (diester) and closed (bisanhydride). Furthermore, the polymer network is rapidly hydrolyzable under basic conditions at room temperature, enabling accessible chemical recycling or degradation into lactic acid and glycolic acid.

Keywords: Covalent Adaptable Networks, Vitrimers, Crosslinked Polymers, Thermoset Recycling

References

[1] Kloxin, C.J.; Bowman, C.N.; Covalent adaptable networks: smart, reconfigurable and responsive network systems. *Chem. Soc. Rev.* **2013**, 42, 7161.
[2] Schwarzer, L.; Agarwal, S.; Adaptable Polyurethane Networks Containing Tertiary Amines as Intrinsic Bond Exchange Catalyst. *Macromol. Chem. Phys*. **2024**, 2400072.
[3] Eger, E.M.; Agarwal, S.; Poly(lactic-*co*-glycolic acid) Networks with Dynamic Covalent Bonds: Synthesis and Characterization. *ACS Apl. Polym. Mater.* **2023**, 5, 5141-5148.

CHEMIS-TREE ENGINEERED SANDWICH COMPOSITES

Debabèche, N.[a], Wagner, M[b]., Jiang, Q.[a] Feist, F[b], Bismarck A.[a,c*]

[a] *Institute of Material Chemistry and Research, Polymer and Composite Engineering (PaCE) Group, Faculty of Chemistry, University of Vienna, Währinger Straße 42, 1090 Vienna, Austria*

[b] *Vehicle Safety Institute, Graz University of Technology, Inffeldgasse 13/6, 8010 Graz, Austria*

[c] *Department of Chemical Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ, United Kingdom*

[a]*e-mail of presenting author:* nesrine.battoul.debabeche@univie.ac.at

Pulp foams are a potential alternative to porous polymers; however, their poor mechanical properties limit their application to packaging materials. We utilised the sandwich composite approach to produce panels (370 mm x 300 mm x 20 mm) comprising of pulp fibre foams and kraft liner papers to improve the mechanical properties of pulp fibre foams. Two types of sandwich structures are produced to improve the mechanical properties of pulp fibre foams: foam core sandwich panels and stiffened sandwich composites. The resulting sandwich structures materials have apparent densities ranging from 80 kg/m^3 to 161 kg/m^3. The mechanical properties are assessed in compression, three-point bending and double lap shear loading conditions. We show that pulp fibre foam sandwich structures possess significantly higher compression and flexural moduli and strengths when compared to pure pulp fibre foams. Stiffening the pulp fibre foam core further by incorporation of kraft liner paper stiffeners results in even higher mechanical, including lap shear, properties.

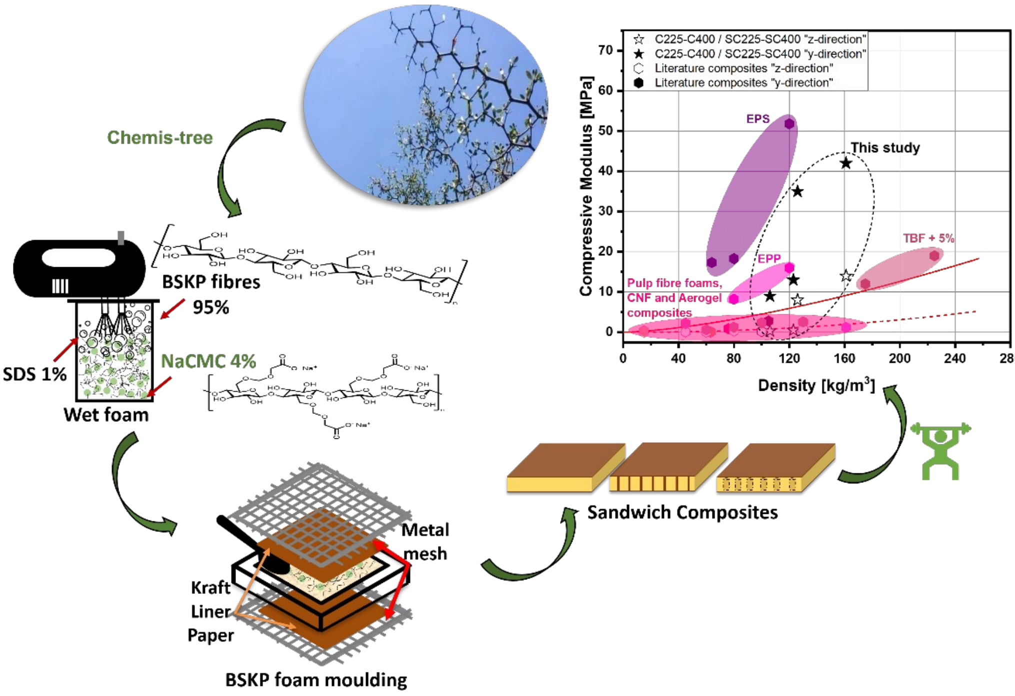


Figure 1. Graphical abstract of the Sandwich Composites.

Degradation behavior and lifetime assessment of novel PP liner materials for thermal energy storages

M. Posch[1*], L. Peham[1], G. M. Wallner[1]

[1] *Institute of Polymeric Materials and Testing, University of Linz, Linz, Austria*
**matthias.posch@jku.at*

Pit thermal energy storages (PTES) are of high relevance for reduction of the overall energy demand [1]. A polymeric liner is essential for sealing of the large hot water storage. While polyethylene (PE) has been established for temperatures up to 80°C [2], novel polypropylene (PP) based materials for maximum temperatures of 95°C are under development. The main objective of this study was to assess the ageing behavior of novel PP liner materials and to estimate their lifetime depending on the temperature profile of the PTES. Random PP-R copolymers differing in their formulation and stabilization were investigated. Ageing experiments were carried out at temperatures from 65 to 135°C on 100 µm thick micro-specimens [3]. Hence, diffusion-limited effects were negligible. Fourier transform infrared spectroscopy (FTIR) was employed to monitor the deterioration of stabilizers. Moreover, the time-to-embrittlement was determined by tensile testing. The best performance was obtained for a PP-R grade with a triple stabilizer package. In contrast to the PP-R base polymer with phenolic antioxidants, no transition in the ageing behavior was observed at around 100°C. By extrapolation of embrittlement times to service-relevant temperatures and by consideration of cumulative damages [3, 4], superior lifetime values exceeding 30 years were deduced for the optimized PP-R grade.

Keywords: Pit thermal energy storages, degradation behavior, polypropylene, ageing behavior, lifetime estimation

References

[1] Schmidt, T.; Pauschinger, T.; Sørensen, P. A.; Snijders, A.; Djebbar, R.; Boulter, R.; Thornton, J. Design Aspects for Large-scale Pit and Aquifer Thermal Energy Storage for District Heating and Cooling. Energy Procedia **2018**, 149, 585–594.

[2] Grabmann, M.; Wallner, G.; Buchberger, W.; Nitsche, D. Aging and Lifetime Assessment of Polyethylene Liners for Heat Storages: Effect of Liner Thickness. ISES Solar World Congress **2017**, 1–8.

[3] Grabmann, M.; Wallner, G.; Grabmayer, K.; Buchberger, W.; Nitsche, D. Effect of Thickness and Temperature on the Global Aging Behavior of Polypropylene Random Copolymers for Seasonal Thermal Energy Storages. Solar Energy **2018**, 172, 152–157.

[4] Wallner, G. M.; Povacz, M.; Hausner, R.; Lang, R. W. Lifetime Modeling of Polypropylene Absorber Materials for Overheating Protected Hot Water Collectors. Solar Energy **2016**, 125, 324–331.

Chemical and thermomechanical characterization of green, and ecofriendly PAFS-free battery separator films

Martin Tiefenthaler, Gernot M. Wallner
University of Linz (JKU), Institute of Polymeric Materials and Testing & Christian Doppler Laboratory for Superimposed Mechanical-Environmental Ageing of Polymeric Hybrid Laminates (CDL-AgePol), Linz, Austria

In 2024, global energy demand increased by 2.2%, driven by record-high temperatures and digitalization - exceeding the average annual growth rate observed over the past decade [1]. Li-ion batteries play a pivotal role in the transition towards renewable energy systems by allowing efficient short-term energy storage. Recently, polymethylmethacrylate (PMMA) coatings have been employed as an alternative to polyvinylidene fluoride (PVDF) based binders in porous polyolefin battery separators, enabling the development of eco-friendly, PFAS-free Li-ion batteries [2]. The chemical composition and the thermomechanical properties of a PMMA-PE-PMMA battery separator film were characterized using Fourier transform infrared microscopy (FTIR), dynamic mechanical analysis (DMA) and uniaxial tensile testing. FTIR microscopic images were recorded in attenuated total reflection (ATR) mode using a Spectrum 100 and a Spotlight 400 imaging system (Perkin Elmer, USA) equipped with a Ge-crystal. The thermomechanical properties were deduced by amplitude sweep tensile-mode DMA (-40 to 130°C, 3 K/min, 1 Hz, 4 N), using a TMA/SDTA 861 E (Mettler Toledo, USA). Additionally, tensile tests were performed on a Z005 (Zwick Roell, Germany) with the digital image correlation (DIC) system VIC-3D (Correlated Solutions, USA). FTIR microscopy revealed a thickness of about 10 µm for the PE core layer and 5 to 40 µm for the PMMA coating layer (see **Fig. 1a)**). Furthermore, absorption peaks related to PE and PMMA were confirmed by FTIR for the core and coating layers, respectively. Interestingly, absorption bands related to PMMA were also discernible within the porous PE core layer. The DMA thermogram, shown in **Fig.1b)**, revealed a decrease of the storage modulus (E') from 1800 at -25°C to 230 MPa at 100°C. Furthermore, the loss factor (tan(δ)) exhibited a small peak at -24°C associated with the glass transition temperature, and a broad peak ranging from 25 to 90°C presumably related to mobility in hinge segments (amorphous phase between two crystalline phases). The tensile modulus (E_t), maximum strength (σ_{max}) and strain at break (ε_b) values were ascertained at 1040 MPa, 70 MPa and 45%, respectively (see **Fig.1c)**). Overall, tensile (E_t) and storage (E') modulus values were well in agreement with a deviation of about 8%.

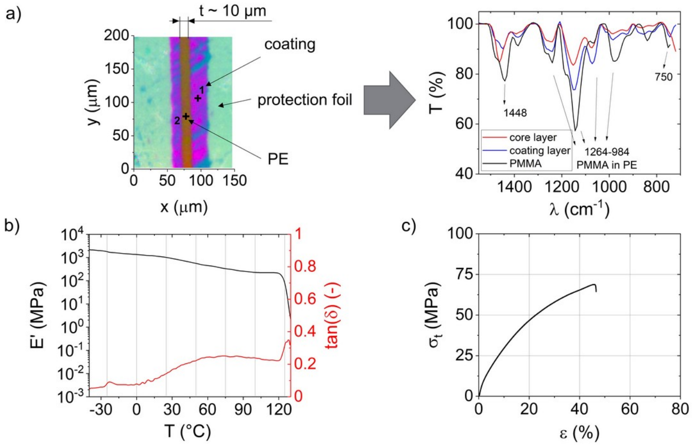


Fig. 1: Chemical and thermomechanical characterization of a PMMA-PE-PMMA based battery separator film: a) FTIR microscopy image and spectras, b) amplitude sweep tensile-mode DMA thermogram, and c) stress-strain curve obtained from tensile testing.

References

[1] Martinos, A., Spencer, T., Tapia, V. G., Roge, A. Global Energy Review 2025. IEA **2025**, Online available: https://www.iea.org/reports/global-energy-review-2025.

[2] Choi, J., Kim, P. J. A roadmap of battery separator development: Past and future, Current Opinion in Electrochemistry **2022**, 31, 100858.

Dipolar Glass Polymers Incorporating Sulfur-Containing Amino Acids: A First Step Toward More Sustainable High-Dielectric Polymer Materials

Sebastian Bonardd[1,2], David Díaz Díaz[3,4], José A. Pomposo[1,2,5], Jon Maiz[1,5], Angel Alegría[1,2]

[1]Centro de Física de Materiales (CFM-MPC), CSIC-UPV/EHU, Donostia-San Sebastián, Spain.
[2] Departamento de Polímeros y Materiales Avanzados: Física, Química y Tecnología, Universidad del País Vasco-Euskal Herriko Unibertsitatea (UPV/EHU), Donostia-San Sebastián, Spain.
[3] Departamento de Química Orgánica, Universidad de La Laguna, La Laguna, Spain.
[4] Instituto Universitario de Bio-Orgánica Antonio González, Universidad de La Laguna, La Laguna, Spain.
[5] IKERBASQUE – Basque Foundation for Science, Bilbao, Spain.

In the past decade, the field of polymer dielectrics has attracted significant attention due to their wide range of applications in electrical systems, particularly those related to energy storage and conversion, which are critical in today's energy landscape.[1] In this work, we report the synthesis and dielectric characterization of novel polymers incorporating sulfur-based amino acid residues as high-dipole moment functional groups. Specifically, we designed and synthesized polymers containing methionine and its oxidized derivatives—methionine sulfoxide and methionine sulfone—to investigate their influence on dielectric properties. The resulting materials were thoroughly characterized using spectroscopic (FTIR, NMR), thermal (TGA, DSC), and dielectric (BDS) techniques. The results confirmed the successful synthesis of these amino acid-based polymers, which exhibited high thermal stability—with onset degradation temperatures above 250 °C—and glass transition temperatures (T_g) well above room temperature (>100 °C), along with excellent dielectric performance. Notably, at room temperature, all systems displayed dielectric constants above 5.0—surpassing the benchmark for classification as high-dielectric polymers—and exhibited low dissipative behavior, making them promising candidates for capacitor applications.[2] This study highlights the potential of bio-derived amino acid residues as functional building blocks for high-dielectric polymer design, opening new avenues for the development of sustainable, high-performance dielectric materials tailored for next-generation electronic and energy storage applications.

Keywords: Polymer Dielectrics, Energy Storage, Dipolar Glass Polymers, Amino Acids

Acknowledgments
The authors thank the projects 2023-CIEN-000069-01 and IT-1566-22 funded by the Basque Government, the project PID2021-123438NB-I00 funded by Spanish Ministry of Science and Innovation and the project PID2022-142118OB-I00/MCIN/AEI/10.13039/501100011033/UE funded by Spanish Ministry of Science and Innovation and the Fundación Ramón Areces.

References

[1] Feng, Q. K., Zhong, S. L., Pei, J. Y., Zhao, Y., Zhang, D. L., Liu, D. F., Zhang Y. X. & Dang, Z. M. Recent progress and future prospects on all-organic polymer dielectrics for energy storage capacitors. *Chemical Reviews*, **2021**, *122*(3), 3820-3878.
[2] Baer, E. & Zhu, L. 50th anniversary perspective: dielectric phenomena in polymers and multilayered dielectric films. *Macromolecules,* **2017***,* 50.6, 2239-2256.

UV-Cured Coatings with Switchable Adhesion via Dynamic Covalent Bonds

Amir Akram[1,2], Roberta Maria Bongiovanni[1], Alessandra Vitale[1,*]

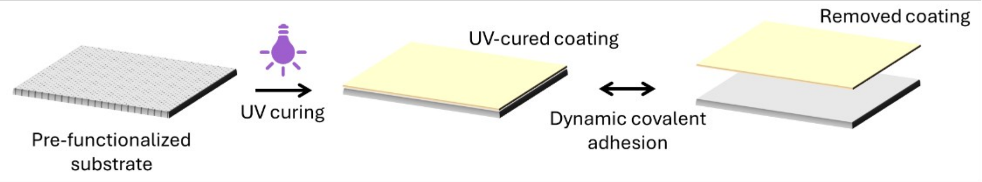
[1]*Politecnico di Torino, Torino, Italy*
[2]*Scuola Universitaria Superiore IUSS Pavia, Pavia, Italy*
[*]*alessandra.vitale@polito.it*

Abstract

Due to growing consumer awareness and stricter European Union regulations, there is an increasing demand for recyclable packaging materials. However, efficient recycling is often hindered oy coatings and multilayer structures composed of thermodynamically immiscible polymeric and non-polymeric materials. Innovative coating technologies that combine strong adhesion with controlled removability are essential to support recycling efforts.

This study explores a dynamic covalent bond (DCB) strategy [1,2] to develop UV-cured coatings with reversible adhesion on various substrates (i.e., glass, PET, and PE). Two types of DCBs were investigated, namely disulfide and imine bonds. In the first approach, the substrates were pretreated with bis(triethoxysilylpropyl)tetrasulfide (TESPT) silane, followed by UV curing of a novel disulfide-functionalized polyurethane diacrylate monomer to form thin and transparent coatings. During irradiation, sulfur–sulfur interactions enabled covalent bonding between the coating and the substrate. As a result, strong adhesion was obtained across all tested materials. The coatings could be efficiently removed by cleaving the disulfide bonds under specific conditions, such as in acidic media or in the presence of a reducing agent. In the second approach, the substrates were prefunctionalized with (3-aminopropyl)triethoxysilane (APTES), and vanillin-based coatings were subsequently UV-cured. Imine dynamic bonds formed between the aldehyde groups of vanillin and the amine groups of the APTES-modified substrates, yielding strong adhesion also in this case. These coatings were readily removed under mild acidic conditions.

Overall, the proposed dynamic covalent bonding strategies offer a promising way for developing recyclable UV-cured coatings that provide strong adhesion and are selectively removable under specific stimuli. This approach supports more efficient packaging waste recycling and aligns with the goals of a circular economy.



Keywords: UV-cured coatings, Dynamic covalent bonds (DCBs), Stimuli-responsive adhesion

References

[1] Zhipeng, L.; Ying, T.; Yuxuan, C.; Zhiyan, L.; Zebao, R. Dynamic covalent adhesives and their applications: Current progress and future perspectives. *Chemical Engineering Journal* **2024**, *497*, 154710.

[2] Li, L.; Peng, X.; Zhu, D.; Zhang, J.; Xiao, P. Recent Progress in Polymers with Dynamic Covalent Bonds. *Macromolecular Chemistry and Physics* **2023**, *224*, 2300224.

Mushroom Makeover: Revealing the Potential of Mushroom Residues in Skincare

A. Zhao[1*], K. Weiland[2] & A. Bismarck[1,3]

[1]*Institute of Materials Chemistry and Research, Polymer and Composite Engineering (PaCE) Group, Faculty of Chemistry, University of Vienna, Währinger Straße 42, 1090, Vienna, Austria*
[2]*Department of Life Science Engineering, Chemical Engineering & Ecotoxicology, FH Technikum Wien, Höchstädtplatz 6, 1200, Vienna, Austria*
[3]*Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, U.K.*
**alexander.bismarck@univie.ac.at*

Commercial mushroom production generates significant amounts of fruiting body waste, with up to 20-30% of harvested mushrooms being discarded due to mishappen caps or stalks [1]. Drawing inspiration from recent advancements in chitin-glucan nanofilm research [2], we propose repurposing waste mushrooms into value-added materials. By leveraging the chitin-glucan complex found in common mushrooms, we developed flexible chitin-glucan sheets with an innovative application as a fungi-based cosmetic sheet mask (see figure). The chitin-glucan complex was extracted from two different fungal types, namely white button mushroom (Agaricus bisporus) and lion's mane mushroom (Hericium erinaceus), both containing numerous valuable components beneficial for skin health [3]. Mild extraction processes were chosen to preserve cosmetical valuable compounds in the extracted chitin-glucan biomass. The resulting materials were characterized by porosity, mechanical properties, surface properties, water absorption and disintegration. Our findings demonstrate the potential of fungi-derived chitin-glucan sheets as viable alternatives to conventional cosmetic sheet masks. The developed materials exhibited tensile strength (up to 12.3 MPa) and strain to failure (up to 44.9%), comparable to commercial products. Moreover, our study highlights the eco-friendly and cost-effective nature of fungi-derived materials. By repurposing waste mushrooms, we not only address waste management challenges but also contribute to the development of a more sustainable and circular economy. The utilization of mild extraction processes together with the scalability of the sheet preparation enables cost-effective production, offering an economically viable solution for the cosmetic sector.

Figure 1: Final cosmetic sheet mask derived from white button mushrooms

Keywords: chitin-glucan, mushroom residue, mechanical properties, biobased products, biodegradability

References

[1] Guo, J., Zhang, M. & Fang, Z. Valorization of mushroom by-products: a review. *J. Sci. Food Agric*. **2022,** 102, 5593–5605.
[2] Nawawi, W. M., Lee, K.-Y., Kontturi, E., Murphy, R. J. & Bismarck, A. Chitin Nanopaper from Mushroom Extract: Natural Composite of Nanofibers and Glucan from a Single Biobased Source. *ACS Sustain. Chem. Eng.* **2019**, 7, 6492–6496.
[3] Hyde, K.D., Bahkali, A.H. & Moslem, M.A. Fungi—an unusual source for cosmetics. *Fungal Diversity* **2010**, 43, 1–9.

Revolutionizing polyesters: from microplastic-free composting to enzyme-driven recycling for sustainability and circularity

Ashank Upadhyay[1], Onur Turak[3], Emilia Fulajtar[1], Birte Höcker[3], Seema Agarwal[1,2*]

[1]*University of Bayreuth, Macromolecular Chemistry II, Advanced Sustainable Polymers, Bayreuth, Germany*
[2]*University of Bayreuth, Bavarian Polymer Institute, Bayreuth, Germany*
[3]*University of Bayreuth, Department of Biochemistry, Bayreuth, Germany*
[*]*Seema.agarwal@uni-bayreuth.de*

As the plastic production and consumption continue to rise, plastic pollution—and particularly microplastic contamination—has become pervasive. Developing polymers that are sustainable, non-toxic, recyclable, and compatible with a circular economy is therefore essential. [1] This study investigates the degradation behavior of tailor-made aliphatic–aromatic polyesters synthesized via melt polycondensation from 1,4-benzenedimethanol and aliphatic diacids of varying chain lengths. Degradation was assessed in alkaline solution, industrial compost, sludge water, and via enzymatic hydrolysis using five enzymes: Hi-Cutinase (HiC), Esterase EL-01, and three in-house-produced enzymes: *Ideonella sakaiensis* PETase (IsPETase), *Cryptosporangium aurantiacum* PETase variant M9 (CaPETase), and LCC^{ICCG} (a leaf-branch compost cutinase variant). Complete degradation was observed for selected polymers which was confirmed by compost extraction. Among enzymes, LCC^{ICCG} showed the highest activity at 60 °C, including partial PET degradation (X_c ~ 15%), while HiC was most effective at 30 °C. These results demonstrate the potential of these polyesters for sustainable use, combining efficient biodegradation with enzyme-driven recycling, and offer a promising strategy to combat microplastic pollution.

Keywords: Polycondensation, Enzymatic degradation, Composting, Compost Extraction, Microplastics, PET.

References

[1] Upadhyay, A., Turak, O., Fulajtar, E., Greve, C. R., Herzig, E. M., Höcker, B., & Agarwal, S. (2025). Degradation Behavior of Aliphatic–Aromatic Polyesters: From Microplastic-free Composting to Enzyme-Driven Recycling Possibility. ACS Applied Polymer Materials, 7(7), 4596–4608.
.

Cationic RAFT Polymerization of Styrenic Monomers

Andrei Leushukou,[1] Irina Vasilenko,[1] Maksim Hulnik,[1] Sergei Kostjuk[2]
[1] *Research Institute for Physical Chemical Problems of the Belarusian State University, 14 Leningradskaya st., 220006 Minsk, Belarus*
[2]*Sorbonne Universite, CNRS, Institut Parisien de Chimie Moleculaire, Equipe Chimie des Polymeres, 4 place Jussieu, 75252 Paris Cedex 05, France*
sergei.kostjuk@sorbonne-universite.fr

Reversible addition-fragmentation chain-transfer (RAFT) radical polymerization is a one of the most versatile and powerful polymerization techniques not only for the synthesis of (co)polymers with certain composition, controlled molecular weights and target functionality but also advanced macromolecular architectures (block-, graft-, star-shape, etc.) for diverse fields of applications.[1] Recently, the cationic RAFT polymerization was discovered that opens new possibilities to synthesize unique block copolymers via mechanistic transformation from radical to cationic polymerization.[2] Particularly, dithiocarbamates and xanthates as chain-transfer agents (CTA*s*) showed high efficiency in cationic RAFT polymerization of vinyl ethers affording well-defined polymers with low dispersity up to M_n=100,000 g mol^{-1}.[2] However, the efficiency of the above-mentioned CTAs in the cationic RAFT polymerization of p-methoxystyrene (pMOS) is much lower and zero efficiency was observed in polymerization of less reactive monomers.

In this work, the successful cationic RAFT polymerization of p-methoxystyrene (pMOS) with different dithiobenzoates as chain-transfer agents activated by very small amount of Lewis acid will be discussed. We will demonstrate that through rational design of the CTA structure the well-controlled cationic RAFT polymerization of pMOS could be achieved at room temperature to afford poly(p-methoxystyrene) with M_n up to 35,000 g mol^{-1} and low dispersity ($Đ \leq 1.25$). The further design of CTA*s* for performing cationic RAFT polymerization of less reactive monomers such as p-methylstyrene and styrene consisted in the introduction of electron-withdrawing groups into CTA structure. Cationic RAFT polymerization of less reactive p-methylstyrene and styrene was performed using CTAs bearing electron-withdrawing groups to give polymers with controlled molecular weight up to M_n< 10,000 g mol^{-1} (poly(p-methylstyrene)) and M_n< 5,000 g mol^{-1} (polystyrene) and moderate dispersity ($Đ$=1.8–2.2). The developed initiating systems showed high efficiency toward cationic RAFT (co)polymerization of bio-based monomer anethole.

Keywords: cationic polymerization, RAFT polymerization, controlled polymerization

Acknowledgments
This work was supported in part by State Program for Scientific Research of Belarus "Chemical processes, reagents and technologies, bioregulators and bioorganic chemistry" (project 2.1.01.03)

References

[1] Corrigan N.: Jung K.; Moad G.; Hawker C.J.; Matjyjaszewski K.; Boyer C. Reversible-deactivation radical polymerization (Controlled/living radical polymerization): From discovery to materials design and applications. *Prog. Polym. Sci.* **2020**, *111*, 101311
[2] Uchiyama, M.; Satoh, K.; Kamigaito, M. Cationic RAFT and DT polymerization. *Prog. Polym. Sci*. **2022**, *124*, 101485

Effects of a condensed mode approach on polymerization process, morphology and properties of high-impact ethylene-propylene copolymers

J. Molnar[1*], P. Shutov[1], R. Eckmayr[1], J. Wang[1], V. Touloupidis[1], M. Gahleitner[1]

[1] *Borealis Polyolefine GmbH,* Linz*, Austria*
[*] *janos.molnar@borealisgroup.com*

The amount of ethylene-propylene copolymer (EPC) is a decisive factor for the impact performance of multiphase impact copolymers (ICPs). It is well known that the stable production of ICPs with high EPC content is challenging, even in multi-reactor processes with highly porous catalysts, as the polymer powder can become sticky, resulting in production issues like fouling or sheeting. Slow diffusion of monomers into the core of the reactor powder particles during the EPC production stage has been identified as a root cause of powder stickiness, suggesting the use of induced condensing agents (ICAs) to enhance monomer diffusion inside the particles. Jiang *et al*. [1,2] have recently presented a condensed mode approach using n-hexane as an ICA in the EPC stage of an ICP polymerization process, reporting improved powder flowability and its effect on the comonomer content and molecular weight of the EPC phase.

In the present study, a set of bench-scale polymerizations was performed with Borealis' proprietary post-phthalate Ziegler-Natta catalyst (ZNC) [4] in the presence of either n-pentane (C5) or n-heptane (C7). To better understand the practical applicability of the approach in the Borstar PP hybrid process [3] and to check the generality of the concept, a more realistic bulk matrix polymerization in pure liquid ethylene was applied prior to the EPC production stage.

Our results showed that the ethylene response during polymerization and the comonomer distribution of the EPC phase remained the same, contrary to the claims in the literature. Both C5 and C7 were found to improve productivity. The mechanical performance, thermal properties, and molecular weight of the final polymers were unaffected. Samples containing high amounts of EPC and produced in the presence of C7 showed a pronounced improvement in powder flowability compared to samples containing lower amounts of EPC. In contrast, the powder stickiness of samples polymerized in the presence of C5 appeared comparable or even worse than the reference samples without ICA. AFM images revealed a distinct shift in the spatial distribution of dispersed EPC phases from the particle skin toward the core in case samples produced with the addition of C7. The condensed mode approach offers certain benefits, but only when high-boiling-point ICAs such as C6 or C7 are used in substantial amounts, which are costly to remove and thus may limit the practical applicability of the method.

Keywords: high-impact ethylene-propylene copolymer, condensed mode

References

[1] Jiang, C.; Yang, Y.; Jiang, B.; Huang, Z.; Liao, Z.; Sun, J.; Wang, J.; Yang, Y. Regulating the Monomers Composition Ratio inside the Particle Nanodomains with Induced Condensing Agent and Its Impact on Particle Growth. *Polymer* **2020**, *210*, 123022.

[2] Jiang, C.; Yang, Y.; Jiang, B.; Sun, J.; Huang, Z.; Liao, Z.; Wang, J.; Yang, Y. Reducing the Surface Stickiness of Multiphase Polypropylene Particles: An Environmentally Friendly and Scalable Method. *Industrial & Engineering Chemistry Research* **2022**, *61*, 11727–11734.

[3] Bergstra, M.F.; Denifl, P.; Gahleitner, M.; Jeremic, D.; Kanellopoulos, V.; Mileva, D.; Shutov, P.; Touloupidis, V.; Tranninger, C. Polymerization in the Borstar Polypropylene Hybrid Process: Combining Technology and Catalyst for Optimized Product Performance. *Polymers* **2022**, *14*, 4763.

[4] Pellecchia, R.; Shutov, P.; Wang, J.; Gahleitner, M. Copolymer Structure and Performance Consequences of High-Impact Ethylene-Propylene Copolymers Based on a Ziegler-Natta Catalyst with Novel Internal Donor. *Macromolecular Reaction Engineering* **2020**, *14*, 2000022.

Controlling Curing Kinetics in Thiol-ene Photopolymerization via Wavelength-Orthogonal Antagonistic Photochemistry

Thomas Griesser[1], Rita Hoeller[1]

[1]Institute of Chemistry of Polymeric Materials, Montanuniversitaeät Leoben, Otto Glöckel-Straße 2, A-8700 Leben, Austria
thomas.griesser@unileoben.ac.at

Orthogonal photoreactions have attracted growing interest in polymer chemistry over the past decade.[1] The wavelength-selective activation of chromophores enables precise spatial and temporal manipulation of material properties, particularly in lithography-based additive manufacturing.[2]

In this study, we present a strategy to control thiol-ene photopolymerization by combining two antagonistic photochemical processes activated at different wavelengths. As previously introduced by Bowman et al., basic amines retard the thiol-ene reaction under certain conditions – mostly dependent on the pKa of the thiol in comparison to the amines' conjugated acids pKa.[3] We transferred this concept to photochemically activated basic compounds to gain additional control over the thiol-ene curing reaction. Radical polymerization is initiated by a type II photoinitiator activated at 450 nm, while the inhibition mechanism is triggered by a photolatent base at 365 nm. The difference in absorption of these components allows fine-tuned modulation of the curing kinetics by the light dose used.

This approach enables precise local retardation or suppression of the curing reaction. Experiments such as laser writing and grayscale patterning confirm the resolution and versatility of this method. By integrating photochemically gated inhibition, such systems offer new capabilities in lithography-based additive manufacturing and advanced photolithography.

Keywords: antagonistic photoreactions, thiol-ene, photochemistry

Acknowledgments

We would like to thank the Austrian Federal Ministry for Climate Action, Environment, Energy, Mobility, Innovation and Technology and the Austrian Research Promotion Agency (FFG) for funding the "3DFit4Wear" project as part of the Production of the Future program line (project no. 891254).

References

[1] Lu, P.; Ahn, D.; Yunis, R.; Delafresnaye, L.; Corrigan, N.; Boyer, C.; Barner-Kowollik, C.; Page, Z.A. Wavelength-selective light-matter interactions in polymer science. *Matter* **2021**, *4*, 2172-2229.

[2] Müller, S.M.; Nelson, B.R.; Höller, R.; Waly, C.; Jelinek, A.; Kirkpatrick, B.E.; Keyser, S.P.; Naderer, C.; Sivun, D.; Jacak, J.; Anseth, K.S.; Bowman, C.N.; Schlögl, S.; Griesser, T. Chalcones as Wavelength-Selective Cross-Linkers: Multimaterial Additive Manufacturing of Macro- and Microscopic Soft Active Devices. *Chem. Mater.* **2025,** 37, 2699-2708.

[3] Love, D. M.; Kim, K.; Goodrich, J. T.; Fairbanks, B. D.; Worell, B. T.; Stoykovich, M. P.; Musgrave, C. B.; Bowman, C.N. Amine Induced Retardation of the Radical-Mediated Thiol–Ene Reaction via the Formation of Metastable Disulfide Radical Anions J. Org. Chem. **2018**, 83, 2912–2919.

2D Materials Based on Silicon as Polymer Fillers

J. Uřičář[1*], L. Reinšteinová[1], J. Brožek[1]

[1]*Department of Polymers, Faculty of Chemical Technology, University of Chemistry and Technology, Prague, Czech Republic*
**uricarj@vscht.cz*

Graphene and its derivates have been already widely studied as fillers for enhancement of polymer properties. However, recent progress in development of its silicon analogues enabled their preparation in higher quantities which enabled their usage as fillers as well.

In this work we describe the effect of addition of siloxene (analogue to graphene oxide), and silicene (analogue to graphene) into polymer matrixes based on polyamide 6, poly(ε-caprolactone), and polyvinyl fluoride. Effects on polymerization process, thermal properties, and mechanical properties were studied.

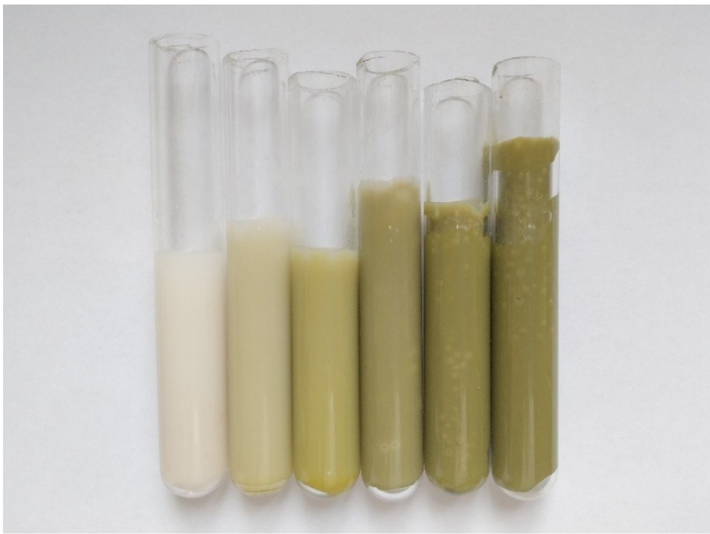


Fig. 1 Poly(ε-caprolactone) nanocomposites with increasing siloxene content

Keywords: nanocomposites, polyamide 6, polyvinyl fluoride, poly(ε-caprolactone)

Acknowledgments
This work was supported from the grant of Specific university research – grant No A1_FCHT_2025_001 and grant No A2_FCHT_2025_023.

High performance polyetherimide composites

Diana-Ioana Bratilescu[1], Alexander Bismarck[1,2]

[1]Polymer & Composite Engineering (PaCE) Group, Institute of Materials Chemistry & Research, Faculty of Chemistry, Vienna, Austria
[2]Department of Chemical Engineering, Imperial College of London, London, United Kingdom
*alexander.bismarck@univie.ac.at

For a multitude of applications, especially in the aerospace sector, it is very important that composite materials do not only poses superior mechanical properties but also perform at high service temperatures.[1,2] High-performance thermoplastics such as poly(ether ether ketone) (PEEK), poly(ether sulfone) (PES), and poly(phenylene sulfide) (PPS) have been extensively explored for this purpose.[2,3] Among these, polyetherimide (PEI) emerges as a promising matrix due to its high glass transition temperature (T_g) of ~ 220 °C at relatively lower cost compared to PEEK and PES.[3] PEI retains excellent mechanical properties up to 200 °C, making it a strong candidate for advanced composite applications. However, producing high T_g polymer composites remains challenging.[2]

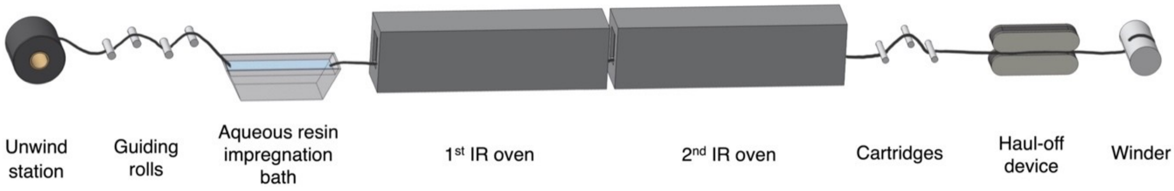


Figure *1*. Schematic of powder impregnation composite production line.

In this study, we present a simple and efficient method for fabricating carbon fibre-reinforced PEI tapes and laminates with a fibre volume fraction of 58 % using a purpose-built composite production line. HexTow® AS4D (12K) carbon fibres were impregnated with PEI through an aqueous resin bath. The wet impregnated tow was passed through two infrared (IR) ovens to remove the water and guided to a set of 3 heated shear pins operated at 350 °C with the purpose of melting the polymer. The thermoplastic prepreg was then consolidated in a hot press. Optical microscopy confirmed uniform fibre impregnation with minimal void content (1.4 – 2 %). Mechanical testing demonstrated strong interfacial adhesion and high compressive properties even at 90 °C.

Keywords: polyetherimide, high-performance polymers, carbon fibre-reinforced polymer composites

References

[1]. Åström, B. T. Manufacturing of Polymer Composites. 1st ed. Routledge, **1997**. https://doi.org/10.1201/9780203748169.

[2]. Gabrion, X., Placet, V., Trivaudey, F., Boubakar, L. About the thermomechanical behaviour of a carbon fibre reinforced high-temperature thermoplastic composite. *Composites Part B: Engineering*, **2016**, 95, 386-394. https://doi.org/10.1016/j.compositesb.2016.03.068.

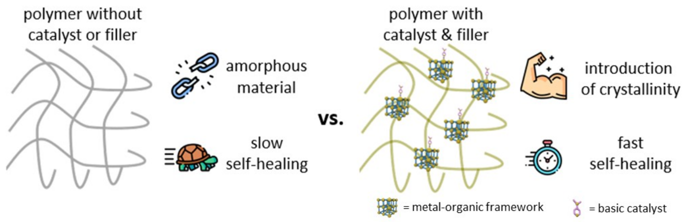
[3]. Iredale, R. J., Ward, C., Hamerton, I. Modern advances in bismaleimide resin technology: A 21st century perspective on the chemistry of addition polyimides. *Progress in Polymer Science*, **2017**, 69, 1-21. https://doi.org/10.1016/j.progpolymsci.2016.12.002.

A Two-in-One additive for vitrimers: catalysis and reinforcement in a single step

Simon Renner[1,2], Roman Korotkov[1,3], Christian Slugovc[2], Sandra Schlögl[1,3], Elisabeth Rossegger[1,2*]

[1]*Polymer Competence Center Leoben GmbH (PCCL), Sauraugasse 1, 8700 Leoben, Austria*
[2]*Institute of Chemistry and Technology of Materials, Graz University of Technology, Stremayrg. 9, 8010 Graz, Austria*
[3]*Department of Materials Science, Montanuniversität Leoben, Franz-Josef-Strasse 18, 8700 Leoben, Austria*
[*]*elisabeth.rossegger@pccl.at*

The polymer type dynamic covalent network is gaining increased interest as these materials bridge the properties of thermoplasts and thermosets[1] enabling the usage of these materials for shape shifting and self-healing.[2] To achieve this effect the covalent bonds in the polymer undergo thio-thioester exchange processes which can be catalyzed by various types of catalysts.[2,3] These catalysts can be e.g. initiated by heat or light.[4,5] Herein a new type of catalyst is suggested, namely a heterogenous and crystalline one. To achieve this goal, various base catalysts are immobilized on a Zr based metal-organic framework (MOF). This modified MOF was assessed using thermogravimetric analysis (TGA) and nuclear magnetic resonance spectroscopy (NMR) to quantify the efficiency of catalyst immobilisation. Equipped with this information, we successfully incorporated the modified MOF in a thiol-ene click photopolymer. Subsequent stress-relaxation experiments to evaluate the self-healing property of the polymer composite proved the catalytic effect of the MOF catalyst for thio-thioester exchange. In these measurements the here developed heterogeneous MOF catalyst shows a significant catalysis over the sample with no catalyst (see Fig 1a). Supplementary to the self-healing effect the integration of this crystalline catalyst (see Fig 1b) serves to modify the intrinsic properties of the thiol-ene click photopolymer which is generally known for having low toughness.[6] To characterise the beneficial impact of the MOF additive, measurements of the tensile strength, dynamic mechanical analysis (DMA), and X-Ray diffraction analysis (XRD) were conducted. In summary, we can report the first two-in-one additive for vitrimers to catalyse self-healing and reinforce the polymer composite simulatneously in a single step.



a) test of stress-relaxation

b) crystallinity measurement

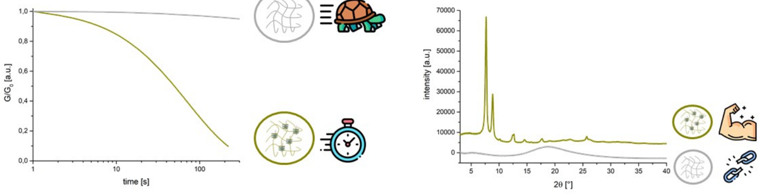


Figure 1: two-in-one additive changes speed of stress relaxation (a) and changes crystallinity of the polymer composite (b)

References

[1] M. O. Saed, X. Lin, E. M. Terentjew, *ACS Appl. Mater. Interfaces*, **2021**, 13, 35, 42044-42051.
[2] E. Rossegger, R. Höller, D. Reisinger, J. Strasser, M. Fleisch, T. Griesser, S. Schlögl, *Polym. Chem.,* **2021**, 12, 639
[3] W. Denissen, J. M. Winne, F. E. Du Prez, *Chem. Sci*., **2016**, 7, 30.
[4] D. Reisinger, M. Kriehuber, M. Bender, D. Bautista-Anguis, B. Rieger, S. Schlögl, *Adv. Mater*, **2023**, 35, 2300830.
[5] D. Reisinger, S. Kaiser, E. Rossegger, W. Alabiso, B. Rieger, S. Schlögl, *Angew. Chemie – Int. Ed.*, **2021**, 60, 14302-14306.
[6] C. Satheeshkumar, H. J. Yu, H. Park, M. Kim, J. S. Lee, M. Seo*, J. Mater. Chem. A*, **2018**, 6, 21961

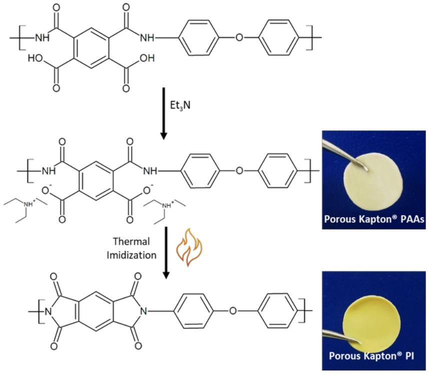
Fabrication of High-Flux Asymmetric Polyimide Membrane from Water-Soluble Poly(amic acid) Precursors via an Aqueous Route

Lauran MAMA[a], Irshad KAMMAKAKAM[a], Damien QUEMENER[a*]

[a] *Institut Européen des Membranes, IEM-UMR 5635, Univ Montpellier, ENSCM, CNRS,34090 Montpellier, France*

**Corresponding Author's E-mail address: damien.quemener@umontpellier.fr*

The current membrane manufacturing process relies on traditional solvents such as chloroform, dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP) and dimethylacetamide (DMAc), which pose significant risks to the environment and human health due to their toxicity and environmental persistence[1],[2]. To address these concerns, the adoption of green solvents as alternatives to conventional ones has emerged as an inevitable trend in membrane fabrication, particularly in non-solvent-induced phase separation (NIPS) and thermally induced phase separation (TIPS) processes[3]. Among these, water stands out as the most sustainable and accessible solvent option. Poly(amic acid) (PAA), a water-soluble precursor to polyimide (PI), offers a viable route for fabricating high-performance membranes in aqueous media[4]. The salt form of PAA, poly(amic acid) salt (PAAS), presents enhanced water processability while retaining the ability to be thermally converted into robust PI structures[5]. In this study, we report a monovalent salt-induced phase separation method to fabricate asymmetric porous Kapton® PI membranes using triethylamine-neutralized PAA. The influence of sodium chloride (NaCl) concentration on phase behavior was examined, and the membranes were prepared via aqueous phase inversion followed by thermal curing. The resulting asymmetric Kapton® membranes demonstrated outstanding thermal and mechanical stability, coupled with remarkably high water flux. Detailed morphological and permeability analyses were conducted to assess performance under varying operational parameters, including applied pressure and temperature ramping, confirming the viability of this sustainable fabrication strategy for advanced separation applications.



Keywords: polyimide membranes, green solvents, aqueous phase inversion, Kapton®.

Acknowledgments: This work was supported by the French National Research Agency (POMENVI, ANR-22-CE43-0008).

References

[1] M. A. Rasool et I. F. J. Vankelecom, « Use of γ-valerolactone and glycerol derivatives as bio-based renewable solvents for membrane preparation », *Green Chem.*, vol. 21, n° 5, p. 1054-1064, mars 2019, doi: 10.1039/C8GC03652G.

[2] T. B. Hofstetter, C. Capello, et K. Hungerbühler, « Environmentally Preferable Treatment Options for Industrial Waste Solvent Management: A Case Study of a Toluene Containing Waste Solvent », *Process Safety and Environmental Protection*, vol. 81, n° 3, p. 189-202, mai 2003, doi: 10.1205/095758203765639898.

[3] W. Xie *et al.*, « Toward the Next Generation of Sustainable Membranes from Green Chemistry Principles », *ACS Sustainable Chem. Eng.*, vol. 9, n° 1, p. 50-75, janv. 2021, doi: 10.1021/acssuschemeng.0c07119.

[4] Y. Ding, B. Bikson, et J. K. Nelson, « Polyimide Membranes Derived from Poly(amic acid) Salt Precursor Polymers. 1. Synthesis and Characterization », *Macromolecules*, vol. 35, n° 3, p. 905-911, janv. 2002, doi: 10.1021/ma0116102.

[5] « PHASE SEPARATION OF POLY(AMIC ACID-CO-IMIDE) SOLUTION », *ResearchGate*, oct. 2024, doi: 10.1080/00986440903088710.

Sulfur-Enhanced Degradability: Tuning Polymer Properties to Accelerate Polyester Breakdown in Environmental Conditions

Emilia Fulajtar[1], Seema Agarwal[1,2*]

[1]*Advanced Sustainable Polymers, Macromolecular Chemistry II, University of Bayreuth,*
Bayreuth 95440, Germany
[2] *Bavarian Polymer Institute, University of Bayreuth, Bayreuth 95440, Germany*
[*]*Email: agarwal@unibayreuth.de*

Plastic waste mismanagement and increasing masses of microplastics in the environment, underline the neccessity of new solutions, like recycling possibilities or biodegradable materials. The latter brings up the question, how commonly used, non-degrading, polymers can be tranformed into degradable materials or how and in which field they can be replaced by degradable options. For enhanced degradation in the evironment or composting/ sewage plants, innovative strategies need to be pursued. In this study we investigated the influence of hydrophilicity and electronic effects of incorporated sulfur groups in two different oxidation states (thioether and sulfone) on the degradation of poly(benzenedimethylene succinate) (PBDMS).[1] The co-polyesters, PBDMS-*co*-poly(benzenedimethylene thioglycolate) with different amounts of sulfur were synthesized via melt polycondensation and oxidized post polymerization.[1] Oxidation to the sulfone resulted in faster degradation in compost due to decreased crystallinity and increased hydrophilicity.[1] However, the influence of the electron-withdrawing nature of the sulfone also contributed to faster degradation time, especially in basic conditions. These polymers bring promising properties as degradable polymers for several applications. [1]

Keywords: *polycondensation, degradation, poly(benzenedimethylene succinate), poly(benzenedimethylene thioglycolate),sulfur-containing*

References

[1] E. Fulajtar, S. Agarwal, *ACS Appl. Polym. Mater*. **2024**, 6, 17, 10768–10778.

Synthesis of High Molecular Weight Poly(Itaconic Acid Esters)

E. Mierzwa[1*], K. Mielczarek[1], S. Bednarz[1], H. Beneš[2]

[1] *Cracow University of Technology, Faculty of Chemical Engineering and Technology, Cracow, Poland*
[2] *Institute of Macromolecular Chemistry of the Czech Academy of Sciences, Prague, Czech Republic*
[*] *ewa.mierzwa@doktorant.pk.edu.pl*

Itaconic acid (IA) is a vinyl monomer obtained biotechnologically on an industrial scale. It is a non-toxic, renewable biomaterial. Due to structural similarity, IA and its esters can be used in polymerization processes as an alternative to petrochemical-derived monomers such as acrylic or methacrylic acid. IA contains an α,β-unsaturated double bond that allows it to polymerize via free-radical mechanism, while the two carboxyl groups can be modified before or after polymerization [1, 2]. Standard polymerization methods for itaconic esters produce low molecular weight polymers. The aim of the research is to develop a method for synthesis of high molecular weight poly(itaconic esters) and comparison of their properties with the polymers of typical molecular weights. In the presented alternative approach, the first step is to obtain a high molecular weight poli(itaconic acid) (PIA), followed by esterification of the carboxyl groups.

IA can be esterified directly in the presence of alcohols, e.g. using lipase enzymes such as CALB or without a catalyst by opening the ring of IA anhydride [3]. Copolymerization of IA mono- and diesters in different molar ratios in bulk was carried out in the presence of AIBN as an initiator. As a result of the reaction, polymers with molecular weights in the range of 40 000–200 000 g/mol were obtained, with the content of carboxyl groups being close to the values resulting from the type and molar ratio of monomers.

Here, we proposed a new approach to the synthesis and modification of poly(itaconic acid) esters. In this method, IA polymerization was carried out in an equimolar DMSO/H_2O solution with an azo initiator (VA-044). The molecular weight of PIA can be adjusted in the range of 30 000–700 000 g/mol by changing the initial concentration of IA in the reaction mixture [2]. PIA samples of various molecular weights were esterified using 1,1,3,3-Tetramethylguanidine (TMG) and halogenated compounds, such as methyl iodide, in DMSO solution [4]. Different temperatures and reaction times were tested (up to 50°C and 72 h). Esterification reactions were carried out on purified PIA and directly on the reaction mixture after PIA synthesis, without prior isolation and purification of the polymer.

Polymers from both synthesis paths were subjected to NMR and GPC analysis to confirm the structure and determine the degree of esterification of COOH groups. TGA and DSC analyses were also performed to compare the thermal properties of the polymers. As a result of the esterification reaction of PIA in the presence of TMG, it is possible to obtain polymers with a much higher molecular weight than in the case of polymerization of IA esters and still achieve a significant degree of esterification of COOH groups (up to 90%).

Keywords: itaconic acid, poly(itaconic acid), radical polymerization, esterification, renewable monomers

Acknowledgments

This work was financially supported by the Lead Agency bilateral a Czech-Polish project provided by the Czech Science Foundation (25-15669K) and National Science Center Poland (WEAVE-UNISONO project grant no. 2024/06/Y/ST5/00062).

References

[1] Robert, T.; Friebel, S. Itaconic acid – a versatile building block for renewable polyesters with enhanced functionality. *Green Chemistry* **2016**, *18*, 2922–2934.

[2] Mielczarek, K.; Beneš, H.; Bednarz, S. Radical polymerization of itaconic acid in dipolar aprotic solvents − The effect of high monomer concentration. *European Polymer Journal* **2025**, *223*, 113632.

[3] Pérocheau Arnaud, S.; Andreou, E.; Pereira Köster, L. V. G. ; Robert, T. Selective Synthesis of Monoesters of Itaconic Acid with Broad Substrate Scope: Biobased Alternatives to Acrylic Acid? *ACS Sustain Chem Eng* **2020**, *8*, 1583–1590.

[4] Li, Q.; Bao, Y.; Wang, H.; Du, F.; Li, Q.; Jin, B.; Bai, R. A facile and highly efficient strategy for esterification of poly(meth)acrylic acid with halogenated compounds at room temperature promoted by 1,1,3,3-tetramethylguanidine. *Polymer Chemistry* **2013**, *4*, 2891–2897.

Investigation of eggshell membrane effect on curing kinetics of epoxy resin system with 100 % bio-based carbon content

K. Novotný[1,a)], M. Feuchter[1,b)], K. Resch-Fauster[1,c)]

[1]*Chair of Materials Science and Testing of Polymers, Montanuniversität Leoben, Leoben, Austria*

a) Kamil.Novotny@unileoben.ac.at
b) Michael.Feuchter@unileoben.ac.at
c) Katharina.Resch-Fauster@unileoben.ac.at

Bio-based epoxy systems have gained significant attention in recent year, primarily due to efforts to replace commercial fossil-based products with greener alternatives derived from renewable resources. Reinhardt et al. have demonstrated a fully bio-based epoxy thermoset based on epoxidized linseed oil (ELSO) and tannic acid, exhibiting a glass transition temperature of 147 °C and a flexular modulus of 2986 MPa, demonstrating competitive mechanical performance relative to traditional petroleum-based products. [1] Using ELSO and citric acid (CA), Anusic et al. prepared a high-performance thermoset with a storage modulus of 1380 MPa. [2] However, the primary limitation of such systems usually resides in long curing times at high temperatures, thus impeding their broader adoption in commercial applications.
Over the past several decades, eggshell (ES) waste has become a significant food industry pollution hazard with an estimated 8 milion metric tons produced anually. [3] Efforts of reducing the environmental impact and improving the sustainability of ES waste via recycling and valorization include production of composite materials, where ES replace traditional non-renewable mineral resources of $CaCO_3$. Recently, chicken eggshell powders were also explored as promising curing catalysts of bisphenol A diglycidyl ether epoxy resins [4] .
The presented work studies the effects of increasing eggshell powder additions in an ELSO resin with CA hardener resulting in a composite with 100 % bio-based carbon content. Curing kinetics of the respective compositions are investigated using differential scanning calorimetry and kinetic parameters are assessed using several isoconversional models. Additionally, the effects of eggshell powder fillers on thermal, thermomechanical and mechanical properties are evaluated.

Keywords: epoxy, bio-based, eggshell membrane, curing kinetics

Acknowledgments

This study was performed within the COMET-project bio-ART which is funded within COMET – Competence Centers for Excellent Technologies – by BMK, BMAW as well as the co-financing federal province Styria. The COMET programme is managed by FFG. www.ffg.at/comet

References

ADDIN CitaviBibliography[1] N. Reinhardt, J. M. Breitsameter, K. Drechsler, B. Rieger, Macro Materials & Eng 2022, 307.
[2] A. Anusic, Y. Blößl, G. Oreski, K. Resch-Fauster, *Polymer Degradation and Stability* **2020**, *181*, 109284.
[3] B. M. Babalola, L. D. Wilson, *J. Compos. Sci.* **2024**, *8*, 414.
[4] J. J. P. Barros, N. G. Jaques, I. D. d. S. Silva, A. K. C. de Albuquerque, A. M. Araújo, R. M. R. Wellen, *Polímeros* **2022**, *32*.

Impact of chain extension on the melt strength properties of 3d printed high-performance polyphtalamides using fused granulate fabrication (FGF) process

N. Pierson[1*], M. Yousfi[1*], K. Delage[1], M. Colella[1], T. Barrière[2], T. Joffre[3], J. Duchet-Rumeau[1]

[1]*Université de Lyon, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, Université Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, 69621 Villeurbanne Cedex, France*
[2]*Université de Franche-Comté, CNRS, Institut FEMTO-ST, Besançon, France*
[3]*Centre Technique Industriel de la Plasturgie et des Composites (CT-IPC), Bellignat, France*
[*]*Corresponding Author: mohamed.yousfi@insa-lyon.fr*

The Fused Filament Fabrication (FFF) 3D printing is the most common and widespread additive manufacturing (AM) technique, but it requires the manufacturing of filaments. Fused Granular Fabrication (FGF), in which pellets are directly 3D printed, has become a promising technique for AM technology [1]. The prsent study is particularly focused on injection molding grade high performance polyphtalamides (PPAs) used in the automotive industry because of their excellent mechanical and thermal resistance properties. Two strategies were deployed to enhance the melt strength of PPAs in order to be suitable for the FGF process. The first was a partially reactive way where PA6T/6I copolymers continue to post-polymerize when they melt and the holding time in the extruder of the 3D printer was in-depth controled [2]. The collected PPA samples were further examined and demonstrated an increase in the molar mass and in the melt viscosity with time as measured by GPC and rheological tests, respectively. The second route was a reactive way where the reaction of the PPAs in the presence of 1, 3-Phenylene-Bis-2-Oxazoline (PBO) and 1,1′-Carbonyl-Bis-Caprolactam (CBC) as chain extender were performed using a twin-screw extruder [3]. The effect of concentration of PBO reacting with the carboxylic end groups and the CBC with the amine end groups on the melt processability behavior were investigated. A design of experiments was then employed to optimize the most important printing parameters based on Charpy impact, three-point bending and short-beam shear tests. The effectiveness of developped approaches to easily improve the melt strength of high performances semiaromatic copolyamides (PPAs) for direct pellet printing is thus demonstrated, allowing the possibility of transposing these finding to highly-filled glass fiber PPAs composites dedicated to aerospace industry.

Keywords: Polyphalamide, Chain extender**,** Fused Granular Fabrication, Reactive extrusion.

Acknowledgments
This work has been funded through financial support from the French Carnot Institute "Ingénierie@Lyon" assigned to the project RETPAM.

References

[1] Yousfi, M., Belhadj, A., Lamnawar, K., & Maazouz, A. 3D printing of PLA and PMMA multilayered model polymers: An innovative approach for a better-controlled pellet multi-extrusion process. In ESAFORM 2021, 14 – 16 April, Liège, Belgium.
[2] Yousfi, M.; Dkier, M.; Colella, M.; Lamnawar, K.; Maazouz, A. Composites based on polyphtalamides matrices and continuous glass fibers: structure-processing and properties relationships. International Journal of Material Forming 2021, 14, 175-190.
[3] Buccella, M.; Dorigato, A.; Caldara, M.; Pasqualini, E.; Fambri, L. (2013). Thermo-mechanical behaviour of polyamide 6 chain extended with 1, 1′-carbonyl-bis-caprolactam and 1, 3-phenylene-bis-2-oxazoline. Journal of Polymer Research 2013, 20, 1-9.

Impact of Impurities in the Mechanical Recycling of Mixed Fiber Textiles

E. Sykacek[1], R. Rihl[1], J. Hintenberger[1], F. Quartinello[1,2], B. Herbinger[2], C.B. Schimper[2], A. Mautner[1,3*]

[1]*Institute of Environmental Biotechnology, Department of Agricultural Sciences, University of Natural Resources and Life Sciences Vienna (BOKU), Konrad-Lorenz-Straße 20, A-3430 Tulln, Austria*
[2]*Josef Ressel Centre Recovery Strategies for Textiles, Fachhochschule Wiener Neustadt, Biotech Campus Tulln, Konrad-Lorenz-Straße 10, A-3430 Tulln a.d. Donau, Austria*
[3]*Polymer & Composite Engineering (PaCE) Group, Institute of Materials Chemistry and Research, University of Vienna, Währinger Straße 42, A-1090 Vienna, Austria*
[*]*andreas.mautner@boku.ac.at*

Globally, the share of post-consumer textile waste that is subjected to recycling amounts to only 0.5%, while most textile waste ends up in landfills or incineration [1]. Direct mechanical recycling of mixed textile waste, e.g. cotton and polyester fibers, is hampered because of fundamental differences in the structure and chemical constitution of the constituents, which require completely different approaches for their reprocessing. To separate different fiber types, chemical recycling, biotechnological approaches, or mechanical separation processes can be utilized, all of which are connected to their very own drawbacks [2]. The approach of mechanically separating fibers yields reasonably pure material streams of the main fibrous ingredients, however, impurities and contaminants as well as residues from the other fiber type(s), have to be accepted. In particular, minor elements of textiles, e.g. rubber bands or labels, are frequently not completely rejected because of chemical similarities between the main textile fibers and those elements. This would require manual sorting processes, which are economically not feasible. Thus, in a compounding process of recovered polymers, those elements are inevitably present and are hypothesized to play a major role in the mechanical properties of recovered polymers. The aim of this study is to identify potential impurities present in mixed fiber textile apparel and to evaluate their impact onto the mechanical performance of recovered polymers from mechanical recycling. Upon identification and characterization of disruptive elements, model formulations of polyester with known contents of the impurity were processed on a conical, co-rotating twin screw extruder and evaluated for their mechanical performance.

Keywords: polyester fiber, cotton, mixed fiber textil, textile recycling

Acknowledgments

This study has received funding from the Christian Doppler Research Society on behalf of the Austrian Federal Ministry of Labor and Economic Affairs and the National Foundation for Research & Technology via the Josef Ressel Centre for Recovery Strategies of Textiles.

References

[1] Andini, E.; Bhalode, P.; E. Gantert, E.; Sadula, S.; Vlachos, D.G. Chemical recycling of mixed textile waste. *Science Advances* **2024**, 10, eado6827.
[2] Mihalyi, S.; Sykacek, E.; Campano, C.; Hernández-Herreros, N.; Rodríguez, A.; Mautner, A.; Prieto, M.A.; Quartinello, F.; Guebitz, G.M.; Bio-upcycling of viscose/polyamide textile blends waste to biopolymers and fibers. *Resources, Conservation & Recycling* **2024**, 208, 107712.

Surface Modification Strategies for Nanofiltration Membranes

Richard Thompson, Ian Cahuzac and Purneema Kaur

Department of Chemistry, Durham University, Durham, United Kingdom

Nanofiltration membranes play a vital role in water remediation strategies and with a quarter of the world's population without safely managed drinking water, the need for reliable, effective and robust technologies is ever increasing. Improving accessibility to clean water and sanitation is a key priority of the United Nations Sustainable Development Goals (UNSDG6).

Graphene oxide (GO) is a promising material for nanofiltration membranes, having an appropriate interlayer spacing and hydrophilicity to provide selectivity and anti-fouling properties that are required for nanofiltration applications. However, the resilience of these membranes is limited because exposure to water causes some exfoliation and therefore a change in filtration properties. Our recent results for the reinforcement of GO membranes highlight the influence of flexibility in the cross-linking agent and filtration performance, figure 1.[1] Through this detailed rheological assessment of membrane materials we find, surprisingly, that the flexibility of the crosslinker has little bearing on the flexibility of the GO composite, but the overall reinforcement is much improved with the use of flexible PEI crosslinkers. Our results also suggest a maximum level of reinforcement beyond which additional crosslinker appears to reduce performance, figure 2. We attribute this to the saturation of the GO surface preventing cross-linkers from forming effective bridges. Results for nanofiltration performance indicate that significant improvements to resilience can be achieved even at cross-linker concentrations as low as 0.2%(w/w) with respect to mass of GO.

Finally, we explore an entirely new approach to control surface modification of PES nanofiltration membranes, exploiting viscous reactive solutions to restrict the depth within a membrane to which modification occurs. Surface analysis with AFM (figure 3) shows that the rate of polydopamine deposition onto a surface is relatively independent of solution viscosity. Results for nanofiltration using a dead-end cell indicate that this strategy can provide an effective means to control selectivity for size whilst minimising the impact on flux because the surface modification from a viscous solution does not block the channels within the membrane as severely as when a more fluid solution is used.

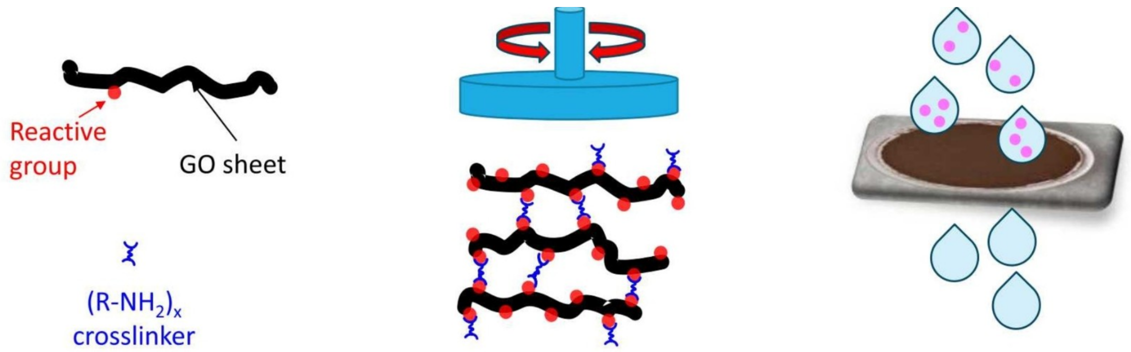


Figure 1. Sketch of cross-linking strategy for GO sheets, reinforcement analysis with oscillatory rheology and nanofiltration process.

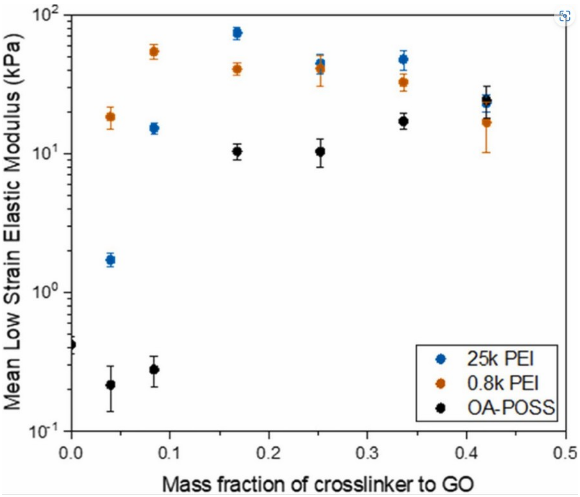


Figure 2. Dependence of GO composite reinforcement on cross-linker concentration

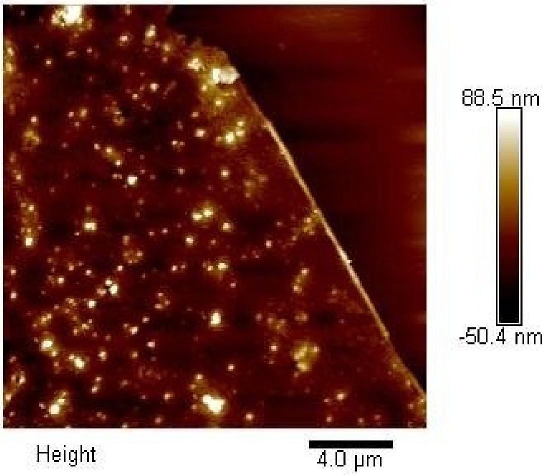


Figure 3. AFM image of polydopamine layer deposited onto flat silicon surface

Acknowledgements

We thank EU-RDF for financial support of this work through the ERDF – Intensive Industrial Innovation Programme – 25R17P01847.

References

(1) Kaur, P.; Bowen, L.; Hutchings, L. R.; Chaudhry, M. U.; Pugh, T.; Thompson, R. L. Reinforcement of GO composites using rigid and flexible crosslinkers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2025**, *709*, 136156. DOI: https://doi.org/10.1016/j.colsurfa.2025.136156.

Effect of Functional Nanofillers on the Thermo-Rheological Properties of PLA-Based Nanocomposites

M. Kostenko1*[1,2], Y. Stetsyshyn[2], M. Kracalik*[1]

[1] Johannes Kepler University Linz, Institute of Polymer Science, Altenberger Str. 69, 4040 Linz, Austria
[2] Lviv Polytechnic National University, 3/4 St. Yura Square, 79013 Lviv, Ukraine
* Corresponding Author's E-mail address:
mariia.kostenko@jku.at, milan.kracalik@jku.at

Keywords: biodegradable nanocomposites, Ecovio, PLA/PBAT blend, montmorillonite, thermal properties, rheology

Developing biodegradable polymer composites with enhanced performance is a key challenge in advancing sustainable materials. In this study, nanocomposites based on Ecovio®, a commercial blend of polylactide and poly(butylene adipate-co-terephthalate), were prepared using a range of functional nanofillers. These nanofillers encompassed modified montmorillonite clays and polymeric brushes derived from poly(butyl acrylate) and poly(butyl methacrylate).

Thermal analysis showed typical two-step degradation (PLA, then PBAT), with (3-aminopropyl)triethoxysilane-functionalized clays reducing thermal stability and poly(butyl acrylate) functionalised clays improving it. Thermomechanical and FTIR analyses confirmed that (3-aminopropyl)triethoxysilane functionalised clay promoted degradation during processing, while poly(butyl acrylate) functionalised clays mitigated these effects. At the same time, differential scanning calorimetry analysis revealed no significant effects of the fillers on the glass transition, melting, or crystallisation temperatures [1, 2]. These observations are consistent with the established behaviour of polylactide-based systems, which are known to be sensitive to nucleating agents and blend morphology [3].

The composites' rheological behaviour was evaluated through dynamic shear experiments. Advanced data interpretation techniques, including Cole–Cole and van Gurp–Palmen plots, have led to the discernment of alterations in viscoelastic properties and interfacial interactions. This, in turn, has furnished insights into the structure–property relationships of the modified systems [4, 5].

While the thermal characteristics remained largely unaffected by nanofiller incorporation, subtle shifts in crystallisation behaviour and notable changes in viscoelastic properties point to underlying modifications at the filler–matrix interface. These findings provide a foundation for optimising the performance of biodegradable composites in environmentally conscious applications.

Acknowledgement

We would like to express our gratitude for the financial support provided by the LIT Institute of Technology at Johannes Kepler University Linz, project number: LIT-2022-11-SEE-123. Furthermore, we would like to acknowledge the financial support from OeAD-GmbH, Ernst Mach Grant, EM UKR/Batch II, Nr. MPC-2022-04295 and Mobility Program Nr. MPC-2021-01858.

References

[1] Chatiras, N.; Georgiopoulos, P.; Christopoulos, A.; Kontou, E. *Effect of poly(lactic acid) matrix on the mechanical and thermal behavior of biodegradable composites*. *Polymer Composites* **2019**, 40, 4340–4350.

[2] Hamad, K.; Kaseem, M.; Ayyoob, M.; Joo, J.; Deri, F. Sustainable approach of the synthesis and applications of biodegradable polymers. *Progress in Polymer Science* **2018**, 85, 83–113.

[3] Farah, S.; Anderson, D.G.; Langer, R Physical and mechanical properties of PLA, and their functions in widespread applications—A comprehensive review. *Advanced Drug Delivery Reviews* **2016**, 107, 367–392.

[4] Kostenko, M.; Stetsyshyn, Y.; Harhay, K.; Melnyk, Y.; Donchak, V.; Gubriy, Z.; Kracalik, M. Impact of the functionalized clay nanofillers on the properties of the recycled polyethylene terephthalate nanocomposites. *Journal of Applied Polymer Science* 2024, 141, e55543.

[5] Kracalik, M.; Laske, S.; Witschnigg, A.; Holzer, C. *Evaluation of the molecular structure of polymer blends by means of van Gurp–Palmen and Cole–Cole plots*. *Rheologica Acta* **2011**, 50, 937–946.

Tuning the Heat: Thermally Latent Catalysts for Next-Generation Covalent Adaptable Networks

M. U. Mayer-Kriehuber[1], D. Reisinger[1], D. Bautista-Anguis[1], S. Gaca[1], S. Schlögl[1]*

[1]*Polymer Competence Center Leoben GmbH, Sauraugasse 1, 8700 Leoben, Austria*
**sandra.schlögl@pccl.at*

The advancement of thermally activated self-healing materials has attracted considerable interest in recent years, largely due to their potential to minimize waste and extend the durability of polymer-based products. Among these materials, vitrimers stand out as covalent adaptable networks capable of intrinsic healing through thermo-driven associative exchange reactions. Above their topology freezing transition temperature (Tv), these dynamic exchanges accelerate rapidly, allowing vitrimers to exhibit viscoelastic flow while maintaining their crosslinked solid-state structure. [1] Vitrimers utilizing dynamic hydroxyl-ester linkages typically require a transesterification catalyst to promote efficient bond exchange above Tv. In response, a diverse collection of thermally latent base catalysts for transesterification in vitrimers have been evaluated. [2] A series of thermo-base generators (TBGs) were synthesized and comprehensively characterized using thermogravimetric analysis (TGA), evolved gas analysis (EGA), nuclear magnetic resonance,- (NMR), and infrared (IR) spectroscopy to assess their decomposition behavior and thermally triggered base release (T_{TBG}). These catalysts enable precise thermal control over activation and deactivation, facilitating the development of multiple thermally switchable dynamic polymer networks. The effectiveness of this strategy was validated through stress relaxation tests, reshaping studies, self-healing evaluations, and tensile experiments. By tuning the molecular structure of the latent bases, decomposition temperatures and activation timelines could be finely adjusted across a broad thermal window. This tunability allows for seamless integration into vitrimers with various Tv values, ultimately supporting a wide range of potential applications in the polymer field and opening new paths for the design of dynamic, sustainable polymeric systems.

Keywords: Thermally Latent Catalysts; Covalent Adaptable Networks; Sustainable Polymer Networks; Green Chemistry in Polymer Design.

References

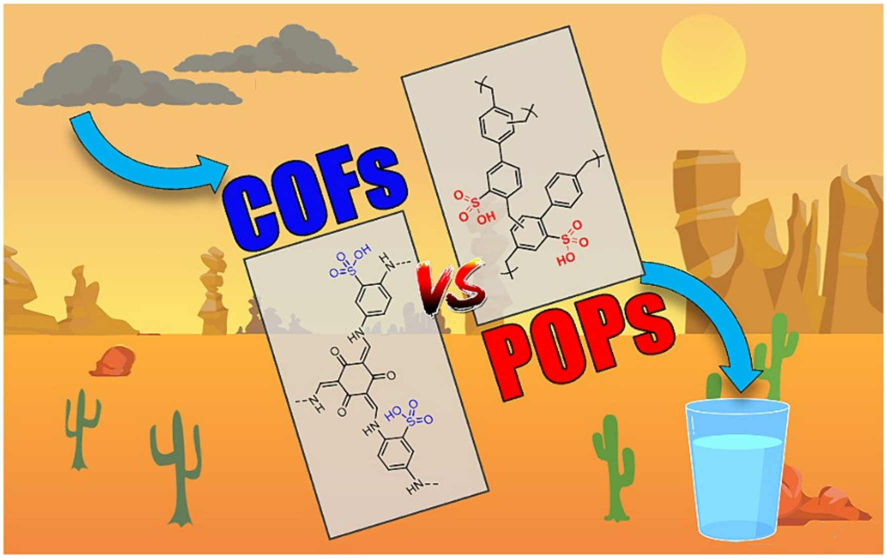
[1] Reisinger, D.; Kaiser, S.; Rossegger, E.; Alabiso, W.; Rieger, B.; Schlögl, S. Introduction of Photolatent Bases for Locally Controlling Dynamic Exchange Reactions in Thermo-Activated Vitrimers. Angew. Chem., Int. Ed. **2021**, 60, 14302-14306.

[2] Reisinger, D; Kriehuber, M; Bender, M; Bautista-Anguis, D; Rieger, B; Schlögl, S; Thermally Latent Bases as Advanced Catalysts for Highly Dy-namic Covalent Polymer Networks without Creep and their Emerging Applications. Advanced Materials, **2023**, Volume 35, Issue 24.

Atmospheric water harvesting using sulfonated porous organic polymers: is crystallinity key?

Paul Schweng,[a,c] Florian Mayer,[a] Changxia Li,[b] Patrick Guggenberger,[b,c]
Freddy Kleitz,[b] Robert T. Woodward[a*]

a Institute of Materials Chemistry and Research, Faculty of Chemistry, University of Vienna,
Währinger Straße 42, 1090, Vienna, Austria
b Department of Functional Materials and Catalysis, Faculty of Chemistry, University of Vienna,
Währinger Straße 42, 1090 Vienna, Austria
c Vienna Doctoral School in Chemistry, University of Vienna, Währinger Straße 42, 1090, Vienna, Austria



Despite access to clean drinking water being recognised as a human right by the United Nations, multiple parts of the globe are already facing significant freshwater scarcity and the number of affected areas is set to rise even further.[1] To tackle this issue, atmospheric humidity represents a supplementary source of fresh water, since it is generally not geographically restricted. In this talk, I will demonstrate the ability of a sulfonated hypercrosslinked polymer, SHCP-10,[2] and a sulfonated covalent organic framework, COF-SO_3H,[3] to repeatedly harvest significant amounts of water via direct air capture. High water uptake is retained in relative humidities as low as 10%, mimicking some of the harshest environments on Earth. To demonstrate the viability of water harvesting in real-world applications, we constructed an atmospheric water harvesting device. After conditioning in various RHs and temperatures, captured water was readily desorbed using simulated sunlight, presenting a low-energy route to water harvesting and adsorbent regeneration. Post-cycling, both materials retained excellent water uptake capacity over a broad range of relative humidities. We believe that this technique has the potential to greatly enhance our ability to address water scarcity concerns due to the use of low-cost and readily available reagents during synthesis and an almost limitless supply of water vapour from air. By contrasting a reticular material and an amorphous network, we will attempt to elucidate the role of crystallinity in sorbents for atmospheric water harvesting.

United Nations, The Sustainable Development Goals Report **2022**. https://unstats.un.org/sdgs/report/2022/ (accessed 2025-03-08).

[2] P. Schweng, F. Mayer, D. Galehdari, K. Weiland, R. T. Woodward, *Small* **2023**, 2304562. DOI: 10.1002/smll.202304562

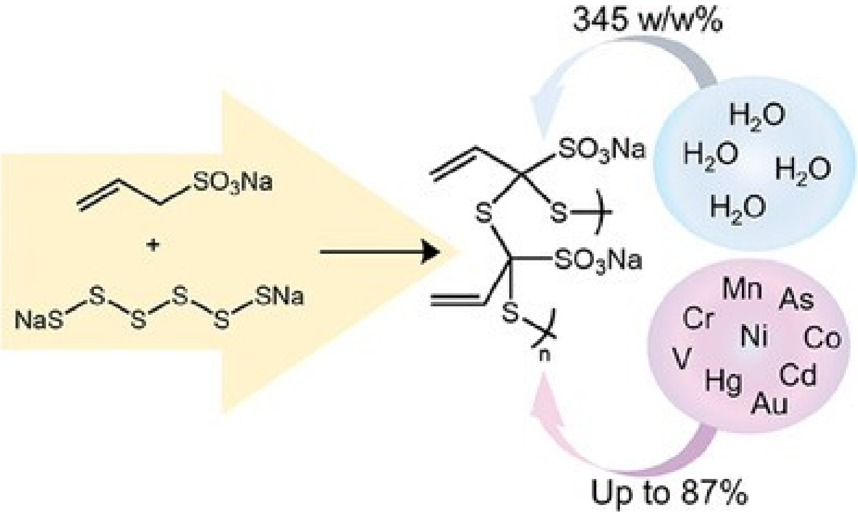
[3] P. Schweng, C. Li, P. Guggenberger, F. Kleitz, R. T. Woodward, *ChemSusChem* **2024**, e202301906. DOI: 10.1002/cssc.202301906

Hygroscopic, ionically generated sulfur polymers

Joseph. J. Dale[1], Martin W. Smith[2], and Tom Hasell[3]

[1] *Waehringer Straße 42, 1090 Vienna, Austria*
[2] *Defence Science and Technology Laboratory, Porton Down, Salisbury, Wiltshire SP4 0JQ, UK*
[3] *Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD.*
* *Corresponding Author's E-mail address (Calibri, 11 pt., Italic)*

Sulfur is a waste product generated on the scale of 60 million tonnes per annum. Efforts to use this sulfur as a feedstock for functional polymer materials have resulted in the process of inverse vulcanisation and the products of this process. These polymers have been used in applications such as Li-S batteries, 2 mercury sequestration from wastewater, and as antibacterial surfaces. Problems arise in this process however, including polymer solubility in only organic solvents, the high temperatures (>120 °C) required for the synthesis, and the production of hydrogen sulfide as a by-product of the reaction. A new synthesis involving the nucleophilic decomposition of sodium polysulfides by a carbanion generated from the common surfactant sodium allyl sulfide yielded a linear polymer with exceptional water solubility. This polymer demonstrated a high capacity for atmospheric water harvesting with a capacity of 345 W/w%, and the ability to act as a flocculant to remove up to 87% of mercury ions from a 1 ppm solution.



Keywords: Sulfur polymer, water harvesting, water remediation, polysulfide

References

[1] Boyd, D. A, Sulfur and Its Role in Modern Materials Science, Angew. Chem., Int. Ed., 2016, 55, 15486 —15502, doi.org/10.1002/anie.201604615

[2] W. J. Chung , J. J. Griebel , E. T. Kim , H. Yoon , A. G. Simmonds , H. J. Ji , P. T. Dirlam , R. S. Glass , J. J. Wie , N. A. Nguyen , B. W. Guralnick , J. Park , A. Somogyi , P. Theato , M. E. Mackay , Y. E. Sung , K. Char and J. Pyun, The use of elemental sulfur as an alternative feedstock for polymeric materials, Nat. Chem., 2013, 5 , 518 —524, doi: 10.1038/nchem.1624

[3] D. J. Parker , H. A. Jones , S. Petcher , L. Cervini , J. M. Griffin , R. Akhtar and T. Hasell, Low cost and renewable sulfur-polymers by inverse vulcanisation, and their potential for mercury capture, J. Mater. Chem. A, 2017, 5 , 11682 —11692, doi: 10.1038/nchem.1624

[4] R. A. Dop , D. R. Neill and T. Hasell, Antibacterial Activity of Inverse Vulcanized Polymers, Biomacromolecules, 2021, 22 , 5223 —5233, doi: 10.1021/acs.biomac.1c01138

[5] J. J. Dale, M. W. Smith and T. Hasell, Water soluble, ionically generated sulfur polymers, Adv. Funct. Mater. 2024, 34, 2314567, doi.org/10.1002/adfm.202314567

Self-standing Macroscopic Objects Based on Functionalized Covalent Organic Frameworks for Ion Transport

Y. Eich[1], C. Ding[1], S. Agarwal[1,2*]

[1]Advanced Sustainable Polymers, Macromolecular Chemistry II, University of Bayreuth,
95440 Bayreuth, Germany
[2]Bavarian Polymer Institute, University of Bayreuth, 95440 Bayreuth, Germany
*agarwal@uni-bayreuth.de

Covalent Organic Frameworks (COFs) are crystalline porous organic polymers known for their high surface area, chemical stability, and tunable morphology. These properties make COFs promising candidates for diverse applications, including gas storage, filtration, catalysis, and energy storage. However, their usage is often limited by traditional synthesis methods, which predominantly yield insoluble powders.[1]

To overcome this limitation in processability, we explored new synthetic strategies to fabricate macroscopic COF objects. Electrospinning in particular has proven to be a versatile technique to produce fibrous 2D and 3D COF architectures. In this approach, thermoplastic polymers are processed from a solution into fibrous templates, which serve as scaffolds. COFs can replicate these fibers in the next step and form flexible, macroscopic objects.[1-3]

In the context of energy applications, functionalities such as sulfonic acid groups play an important role in providing a high proton and lithium-ion conductivity. These functionalities can be incorporated either by a *de novo* synthesis or by post-synthetic modifications techniques. We are working with sulfonation in the gas-phase, which provides the functionalization of COFs across a wide range of aromatic building blocks.

By utilizing electrospinning and post-synthetic modifications, we present promising ways to develop COF-based materials for fuel cells and lithium-ion batteries.

Keywords: Covalent organic frameworks (COFs), electrospinning, energy storage

Acknowledgments:
Deutsche Forschungsgemeinschaft (DFG) (SFB 1585, 492723217; Project A01)
Bayerisches Polymerinstitut (KeyLab Synthesis and Molecular Characterization and KeyLab Electron and Optical Microscopy)

References

[1] Ding, C.; Breunig, M; Timm, J.; Marschall, R.; Senker, J.; Agarwal, S. Flexible, Mechanically Stable, Porous Self-Standing Microfiber Network Membranes of Covalent Organic Frameworks: Preparation Method and Characterization. *Adv. Funct. Mater.* **2021**, 31, 2106507.
[2] Ding, C.; Du, Y; Agarwal, S. Open-Cell Robust COF-Nanowire Network Sponges as Sustainable Adsorbent and Filter. *Adv. Funct. Mater*. **2024**, 34, 2309938.
[3] Ding, C.; Du, Y; Fischer, T; Senker, J.; Agarwal, S. *Angew. Chem. Int. Ed.* **2025**, e202502513.

PEDOT/hydroxypropyl β-cyclodextrin polyrotaxane: Synthesis and photophysical characteristics

Ana-Maria Resmerita*and Aurica Farcas

“Petru Poni” Institute of Macromolecular Chemistry, Iasi, Romania
**E-mail address:resmerita.ana@icmpp.ro*

In the past decades, much attention has been dedicated to the development of new polyrotaxane (PRs) architectures, which offer the opportunity to generate smart polymeric functional materials. In this regard, poly(3,4-ethylenedioxythiophene) (PEDOT) has received tremendous attention due to its practical optoelectronic applications. Herein, we present a continuation of our work regarding the beneficial effect of the encapsulation of poly(3,4-ethylenedioxythiophene) (PEDOT) chains into the cavity of the hydroxypropyl β-cyclodextrins (HPβCD) [1,2].

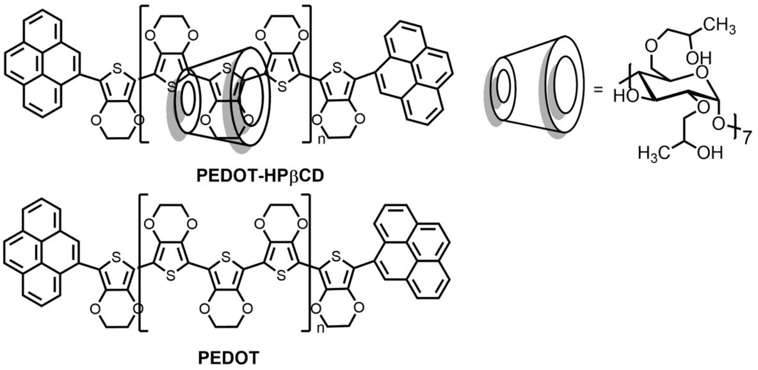


Figure 1. Schematic representation of the PEDOT-HPβCD polyrotaxane and the reference polymer structures.

The morphological, photophysical, and thermal properties of this material have been evaluated and compared to the pristine PEDOT. The achieved results indicated improvements in the photophysical and thermal properties of the polyrotaxane structures.

Keywords: PEDOT, hydroxypropyl β-cyclodextrin, polyrotaxane, optical properties

Acknowledgments

This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS-UEFISCDI, project number PN-IV-P1-PCE-2023-0300, within PNCDI IV.

References

[1] Resmerita, A.-M.; Asandulesa, M.; Bulai, G.; Farcas, A. Novel Supramolecular Networks Based on PEG and PEDOT Cross-linked Polyrotaxanes as Electrical Conductive Materials. *Eur. Polym. J.* **2019**, *114*, 39-46.

[2] Haitami, A. E.; Resmerita, A.-M.; Ursu, L.E.; .; Asandulesa, M.; Cantin, S.;Farcas, A. Novel Insight into the Photophysical Properties and 2D Supramolecular Organization of Poly(3,4-ethylenedioxythiophene)/Permodified Cyclodextrins Polyrotaxanes at the Air-Water Interface. *Materials* **2023**, *16*, 4754.

Polymer Cubosomes: Synthesis, Self-Assembly and Conversion to Functional Materials

Marvin Foith[1], André H. Gröschel[1,2,*]

[1]*Polymer Materials for Electrochemical Storage (PES), Bavarian Center for Battery Technology (BayBatt) , Weiherstr. 26, 95448 Bayreuth*
[2]*Bavarian Polymer Institute (BPI), University of Bayreuth, Universitätsstr. 30, 95447 Bayreuth, Germany*
[*]*andre.groeschel@uni-bayreuth.de*

The self-assembly of block copolymers is nowadays well understood. The resulting block copolymer morphology is mainly influenced by the packing parameter $p = v/a_0 l_c$; where v and l_c are the volume and the length of the hydrophobic block, and a_0 is the surface area of the hydrophilic block. If $p < 1/3$ spheres are formed,for $1/3 < p < 1/2$ cylinders are found, and a $1/2 < p < 1$ will result in vesicles.[1,2] Exceeding a $p > 1$ results in the formation of cubosomes and hexosomes.[2] The polymer cubosomes have a bicontinuous pore network and a high surface area, therefore they can be used as templating platform for different materials like metal oxides and MOFs to introduce high surface area and ordered porous structure.[3,4] Herein, we show the synthesis of poly(ethylene oxide)-based amphiphilic block copolymers via RAFT polymerization, discuss the influence of chain lengths and cosolvent on the self-assembly process. We also present an alternative formation route (redispersion) to the commonly used nanoprecipitation method. The resulting poylmer cubosomes are be used as a templating platform for TiO_2, Co_3O_4 and porous carbon.

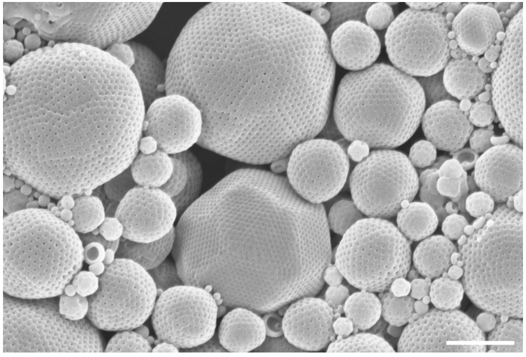


Figure 1. SEM image of block copolymer cubosomes. (scale bar 1 µm).

Keywords: block copolymers, mesoporous materials, metal oxides, self-assembly, templating

Acknowledgments
Studies presented in this presentation were conducted at the Bavarian Center for Battery Technology. The authors acknowledge the financial support of the DFG project (526222003). Furthermore, we would like to thank the Keylab Electron and Optical Microscopy giving us access to their laboratories and devices.

References

[1] Mai, Y.; Eisenberg, A. Self-assembly of block copolymers. *Chem. Soc. Rev.* **2012**, *41* (18), 5969–5985.
[2] Chen, H.; Li, M.-H. Recent Progress in Polymer Cubosomes and Hexosomes. *Macromol. rapid Commun.* **2021**, *42* (15), e2100194.
[3] Xie,W.; Huang, X.; Zhu, C.; Jiang, F.; Deng, Y.; Yu, B.; Wu, L.; Yue, Q.; Deng, Y. A Versatile Synthesis Platform Based on Polymer Cubosomes for a Library of Highly Ordered Nanoporous Metal Oxides Particles. *Adv. Mater.* **2024**, 36, 2313920.
[4] Li, C.; Pan, Y.; Xiao, T.; Xiang, L.; Li, Q.; Tian, F.; Manners, I.; Mai, Y. *Angew. Chem. Int. Ed.* **2023**, 62, e202215985; *Angew. Chem.* **2023**, *135*, e202215985.

The road to tyre-to-tyre recycling: Tensile testing as a tool for determining the incorporation of rubber particles in a vulcanized matrix

P. Manhart[1*], C. Burgstaller[1, 3], C. Paulik[2]

[1]*Transfercenter für Kunststofftechnik GmbH, Wels, Austria*
[2]*Institute for Chemical Technology of Organic Materials at Johannes Kepler University, Linz, Austria*
[3]*University of Applied Sciences Upper Austria, Wels, Austria*
[*]*pauline.manhart@tckt.at*

The amount of end-of-life tyres generated in the EU exceeded 3 million tons in 2021. 58 % of these are recycled, the remainder is thermally recovered. [1] However, recycling in this context mostly refers to open-loop recycling: Grinding of the tyre and usage of the resulting ground tyre rubber without further treatment, often as a substitute fuel for the cement industry. Devulcanization of rubber, the selective scission of S– S and C– S-bonds without breaking the main chain, is a necessary step for closing the loop, as it allows for reprocessing and revulcanization. Ideally, this can be realized without a decrease in the resulting material's mechanical properties. [2] With this in mind, the influence of untreated ground tyre rubber on the mechanical properties of vulcanized rubber mixtures commonly used in tyre formulations is investigated. Additionally, mixtures containing glass beads, an inert filling material, are investigated to gain conclusions about whether rubber particles are chemically integrated into the matrix. The aim of this work is to better understand the chemical incorporation of untreated rubber particles and devulcanizates in rubber virgin material.

Ground tire rubber with different particle sizes and glass beads of different diameters were mixed into two rubber mixtures, that are industrially used for retreading of tires. After vulcanization, tensile testing was performed according to ISO 37 and cyclic tests were conducted to calculate the crosslink density of the materials according to YEOH [3,4].

Tensile strength and elongation at break decrease to a greater extent when larger particles are contained in the material. Glass beads lead to similar effects as rubber particles, if the diameters are comparable. The decrease in crosslink density is also similar for materials with rubber particles and glass beads, which suggests that untreated rubber particles are not chemically bound into the rubber matrix through the vulcanization process.

Keywords: Rubber Recycling, Tensile Testing, Crosslink Density

References

[1] European Tyre & Rubber Manufacturers' Association ETRma. 2021 End-of-Life Tyre Recover. https://www.etrma.org/wp-content/uploads/2024/03/2021-End-of-Life-Tyre-Recover.pdf (accessed March 19, 2025).
[2] Wiśniewska, P.; Wang, S.; Formela, K. Waste tire rubber devulcanization technologies: State-of-the-art, limitations and future perspectives. *Waste management* **2022**, *150*, 174–184.
[3] Yeoh, O. H. Characterization of elastic properties of carbon-black-filled rubber vulcanizates. *Rubber Chemistry and Technology* **1990**, *63*, 792–805.
[4] Anssari-Benam, A.; Bucchi, A.; Destrade, M.; Saccomandi, G. The Generalised Mooney Space for Modelling the Response of Rubber-Like Materials. *Journal of Elasticity* **2022**, *151*, 127–141.

(Bio)degradable polyurethanes with amino-acid phosphorodiamidates as breakage points

N. Vennemann[1*], O. Brüggemann[1]

[1]*Institute of Polymer Chemistry, Johannes Kepler University Linz, Austria*
[*]nico.vennemann@jku.at

Degradable polymers are of ever-growing interest to combat the global plastic waste crisis. Often the degradation of polymers should be fast and without toxic by-products while still maintaining mechanical properties. For this, cleavable linkers are necessary.

Amino-acid based phosphorodiamidates (APDA) present a promising option as cleavable linker[1]. They degrade at neutral or acidic pH, but remain stable under alkaline conditions. Upon hydrolytic cleavage, the phospohorodiamidate group yields ammonium cations and phosphates, which are biocompatible.

APDAs offer a high degree of chemical functionalisation. It is possible to synthesize small APDAs, which can be incoperated into the hard segment of thermoplastic polyurethanes, as well as high molecular APDAs for soft segments. Furthermore phosphorotriamidates (APTAs) can be used as crosslinkers, for example in degradable polyurethane foams. Of course, APDAs and APTAs are not limited to PUR applications, they can also be used in polysiloxane networks or acrylates [2].

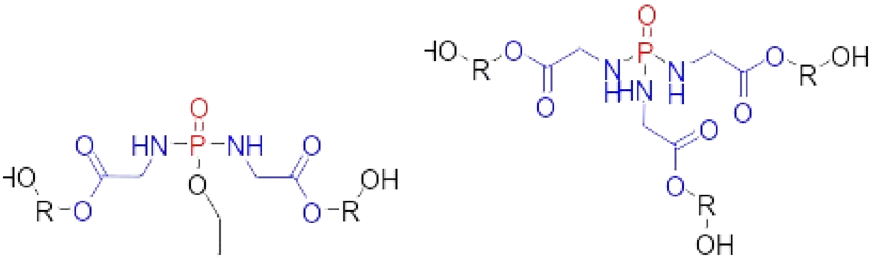


Figure 1: Structure of APDA (left) and APTA (right) as monomer; R = Alkyl, PEG, pTHF.

The degradation of APDAs and APTAs depends on the monomer structure, most of the monomers degrade completely within a few weeks up to a few months. Higher temperatures and lower pHs accelerate the degradation process.

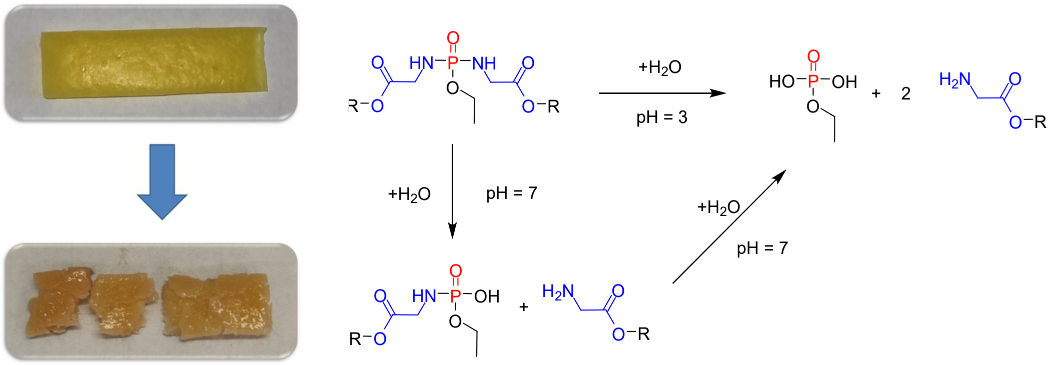


Figure 2: Degradation of TPU containing APDA (left) and degradation mechanism depending on pH (right).

Keywords: Polyurethanes, degradable polymers, phosphorous compounds

References

[1] Haudum S.; Teasdale I., Amino Acid-Based Polyphosphorodiamidates with Hydrolytically Labile Bonds for Degradation-Tuned Photopolymers, ASC Macro Letters, 2023, 12, 6, 673-378
[2] Haudum S.; Teasdale I.; Brüggemann O.; Vennemann N., Patent AT 526 968 B1, 2023

Mechanical recycling of biopolyesters: Influence of multiple extrusion cycles on degradation and properties

B. Liedl[1*], C. Burgstaller[1,2]

[1]*Transfercenter für Kunststofftechnik GmbH, Wels, Austria*
[2]*FH Oberösterreich F&E-GmbH, Wels, Austria*
[*]*barbara.liedl@tckt.at*

The use of bioplastics is increasing, and biodegradable polyesters such as polylactic acid (PLA) and polyhydroxy alcanoates (PHAs) in particular are considered to have a large growth potential. Even though these materials are compostable, and biodegradation is a feature for some applications such as mulch films in the agricultural sector or to reduce waste pollution in case of accidental spreading to the environment, the majority of these biopolyesters are used for packaging [1]. After only a short period of use, packaging ends up in waste again very quickly. In terms of energy consumption and general value retention, recycling could be the better approach for EoL of biopolyesters than incineration or composting (**Figure 1**).

Biopolyesters characteristically have ester bonds that are relatively easy to split, and several mechanisms contribute to their degradation. What is a feature in composting, is more of an obstacle in mechanical recycling: thermal, oxidative, and hydrolytic chain scissions are detrimental to the retention of high material properties, especially after multiple recycling.

We exposed biopolyesters to exactly this scenario: a multiple recycling process, represented by five successive extrusions of PLA and PHA. After each cycle, the extent of degradation and its influence on the optical appearance, rheological and mechanical properties was evaluated. Depending on the process conditions, a degradation in chain length was observed, progressing after each extrusion cycle. Nevertheless, good mechanical properties could be preserved, which in turn suggests that these bioplastics should also be mechanically recycled in the interests of sustainability, and ultimate EoL solutions can only be an option for special application cases.

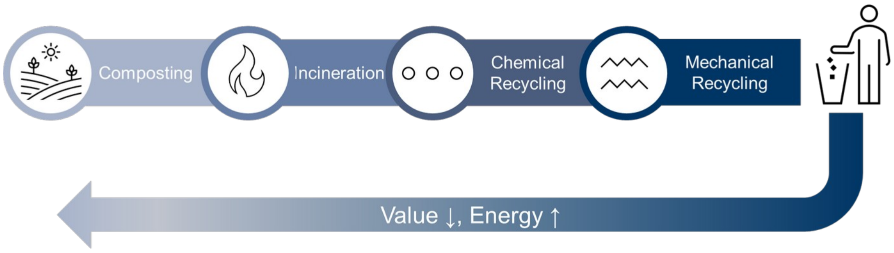


Figure 1: EoL scenarios for plastics according to "value" and energy loss.

Keywords: biopolyesters, PLA, PHA, mechanical recycling, multiple extrusion, characterisation

Acknowledgments

The research is carried out within the project BIOCYCLE-UA II (Kreislaufwirtschaft am Beispiel von ausgewählten Biopolymeren (Herstellung - Verarbeitung - Recycling)), subsidised by the province of Upper Austria and the European Regional Development Fund (ERDF).

References

[1] European Bioplastics e.V. (2025, April 1), https://www.european-bioplastics.org/

Design of Smart Flocculants for the Harvesting of Microalgae via a Grafting – to Strategy of thermosensitive polymers onto Cellulose Nanocrystals

S. ALAMEDDINE[1*], D. Vuluga[1], W. Thielemans[2], K. Muylaert[2], G. Morandi[1]
[1] *INSA Rouen Normandie – Université de Rouen Normandie – UMR6270 PBS*
(Polymères, Biopolymères, Surfaces) – Rouen – France
[2] *KU Leuven- Campus Kulak Kortrijk (Sustainable Materials Lab) (Aquatic Biology Lab)-Kortrijk-Belgium*
[*] *souraya.alameddine@insa-rouen.fr*

Microalgae are a promising feedstock for biosourced materials (biofuels, pigments, vitamins, etc.). However, the production of microalgae on a large scale remains limited by the enormous cost of the harvesting phase which constitutes 20 to 30% of the total cost, due to the small size of the microalgae (3 – 30 µm), and the low concentration in the culture medium (0.5 – 5 g/L) which makes all conventional harvesting techniques long and energy-intensive [1].

In order to solve this problem, the use of a flocculating agent in the harvest process seems an interesting approach [2]. Microalgae have negatively charged proteins on their membrane walls which give them significant colloidal stability in their culture medium. Flocculants are chemical compounds, positively charged, which interact with microalgae to form aggregates which can then be separated by sedimentation or flotation. However, the flocculants used generally remain trapped in the biomass and contaminate it with toxic residues, which limits their final applications [3].

This thesis subject therefore aims to develop a new family of flocculants based on cellulose nanocrystals modified by cationic centers (to induce flocculation) and by thermosensitive polymer chains (to selectively mask and unmask the cationic charges to harvest and/or recycle the flocculant). This approach will constitute the first example of the use of cellulose nanocrystals modified with thermosensitive polymers in the field of microalgae harvest.

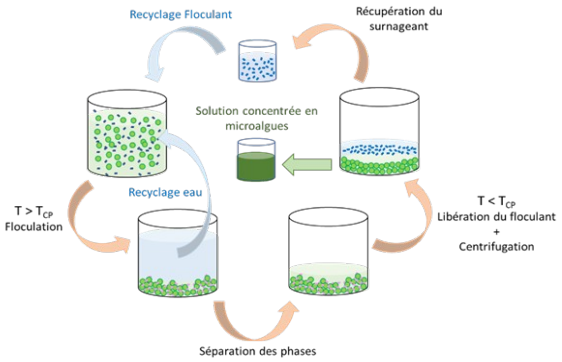


Figure 1 Representation of the complete targeted microalgae culture cycle, flocculation, concentration of the solution in microalgae and release/recycling of flocculant.

Keywords: Microalgae, Flocculant, Thermosensitive polymers, Cellulose nanocrystals (CNCs)

Acknowledgments

The authors gratefully acknowledge the "Région Normandie" for the funding of this PhD, and the ERASMUS+ program for the financial support provided during the research mobility to Belgium.

References

[1] U, Suparmaniam; M.K, Lam.; Y. Uemura, ;J.W, Lim; K.T, Lee;S.H, Shuit, . Insights into the microalgae cultivation technology and harvesting process for biofuel production: A review Sustain. Energy Rev. 2019, 115, 109361.

[2]D, Vandamme; I, Foubert; K, Muylaert, . Flocculation as a low-cost method for harvesting microalgae for bulk biomass production. Trends Biotechnol. 2013, 31, 233–239.

[3]N, Uduman; Y, Qi; M, Danquah; G, Forde; A, Hoadley. Dewatering of microalgal cultures: A major bottleneck to algae-based fuels J. Renew. Sustain. Energy. 2010, 2.

Ready, steady, flow: Pd-loaded hypercrosslinked microreactors for the flow synthesis of paracetamol

Sebastian Hummer[1,2], Hande Barkan-Öztürk[1], Alexander Bismarck[1,3,*], Robert T. Woodward[1,*]

[1]*Institute of Material Chemistry and Research, Faculty of Chemistry, University of Vienna, Vienna, Austria*
[2]*Vienna Doctoral School in Chemistry (DoSChem), University of Vienna, Vienna, Austria*
[3]*Department of Chemical Engineering, Imperial College London, London, United Kingdom*
[*]*alexander.bismarck@univie.ac.at (A. Bismarck), robert.woodward@univie.ac.at (R.T. Woodward)*

Porous organic materials have garnered increasing interest in various scientific and industrial fields due to their versatile properties.[1] A promising application for porous polymers is their use as noble metal catalyst supports, due to their excellent stability, reusability, and high density of active sites.[2] We describe the implementation of monolithic polymerised high internal phase emulsions (polyHIPEs) as catalyst supports for the continuous flow synthesis of paracetamol. PolyHIPEs are formed by polymerisation of particle and surfactant-stabilised water-in-oil HIPEs comprising of a divinylbenzene and divinylbenzene/4-vinylbenzyl chloride monomer continuous phase. The polyHIPEs were post-functionalised by hypercrosslinking using the Scholl coupling reaction to yield polymers decorated with organophosphorus moieties and surface areas of up to 500 m²/g. The phosphorus moieties act as catalyst anchor sites for the subsequent loading of Pd via a Pd−O=P ligand bridge. The Pd-loaded polyHIPEs are used as catalysts for the reduction of 4-nitrophenol to 4-aminophenol, achieving turnover numbers of ~2,000. The Pd-loaded polyHIPEs and a non-functionalised divinylbenzene-based polyHIPEs are fabricated into flow-cells and used en route to Plant-on-a-Bench as microreactor/mixer for the continuous flow synthesis of paracetamol with a yield of 66%.[3]

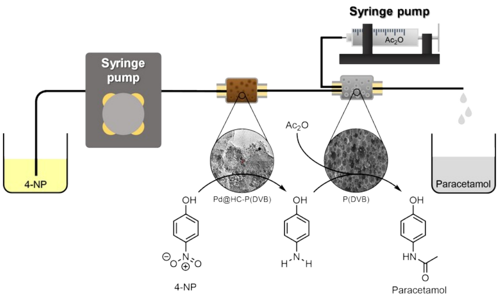


Figure 1: Flow cell assembly for the continuous synthesis of paracetamol

Keywords: Flow synthesis, Micromixer, Microreactor, polyHIPE, Catalysis

Acknowledgments

We acknowledge the financial support of the Faculty of Chemistry, University of Vienna. We thank Christoph Baumgartinger for ICP-MS analysis, Johannes Theiner for XRF measurements and elemental analysis, Soheil Mahmoudi for TEM imaging, Hanspeter Kählig for NMR and ssNMR measurements, and Paul Schweng for XPS measurements.

References

[1] Das, S.; Heasman, P.; Ben, T.; Qiu, S. Porous Organic Materials: Strategic Design and Structure–Function Correlation. *Chem. Rev.* **2017**, 117 (3), 1515–1563.

[2] Liu, T.-P.; Cheng, Q.; Song, W.-J.; Cai, L.-Z.; Tao, X.-C. Triphenylphosphine as a Ligand for the Pd-Catalyzed Amination of Unactivated Aryl Chlorides with Anilines Promoted by Salicylaldimine. *Synlett* **2012**, 23, 2333–2336.

[3] Hummer, S.; Barkan- Öztürk, H.; Bismarck, A.; Woodward, R. T. Ready, steady, flow: Pd-loaded hypercrosslinked microreactors for the flow synthesis of paracetamol. *Appl. Mater. Today* **2025**, 43, 102632.

Well-defined poly(HPMAm) brushes via surface-initiated RAFT polymerization; a mixed-chain transfer agent approach

Manisha Singh*, Zdeňka Sedláková, Jan Svoboda, Eliezer Jäger* and Rafal Poreba*

Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovsky sq. 2, Prague, 162 00, Czech Republic

Developing well-defined antifouling coatings remains a challenge in biomaterials research. This study presents an optimized protocol for the surface-initiated reversible addition-fragmentation chain transfer (SI-RAFT) polymerization of poly(N-(2-hydroxypropyl) methacrylamide) (poly(HPMAm)) brushes, employing a mixed-chain transfer agent (CTA) approach, Figure 1. By systematically evaluating different combinations of surface-tethered and free CTAs, we demonstrate that utilizing structurally distinct CTA classes simultaneously; dithiobenzoate (DTB) and trithiocarbonate (TTC), enhances polymerization control and brush growth rates. Our optimized conditions enable the fabrication of poly(HPMAm) brushes exceeding 70 nm in thickness within only 4 hours at 50 °C, and in aqueous media. Spectroscopic ellipsometry confirmed that the mixed-CTA approach significantly outperforms single-CTA systems, yielding higher polymerization efficiency and greater brush thickness. X-ray photoelectron spectroscopy (XPS) analysis revealed that the enhanced surface coverage achieved with DTB-based CTAs plays a crucial role in facilitating rapid brush growth. Additionally, size exclusion chromatography (SEC) confirmed that the solution-born polymers exhibited narrow dispersity (Đ = 1.05–1.15), ensuring well-defined polymer structures. Our findings highlight the advantages of combining different CTAs in a single polymerization system, leading to a more efficient and scalable method for fabricating antifouling poly(HPMAm) coatings. This approach offers a significant potential for biomedical applications, including biosensors, blood-contacting devices, and implantable materials.

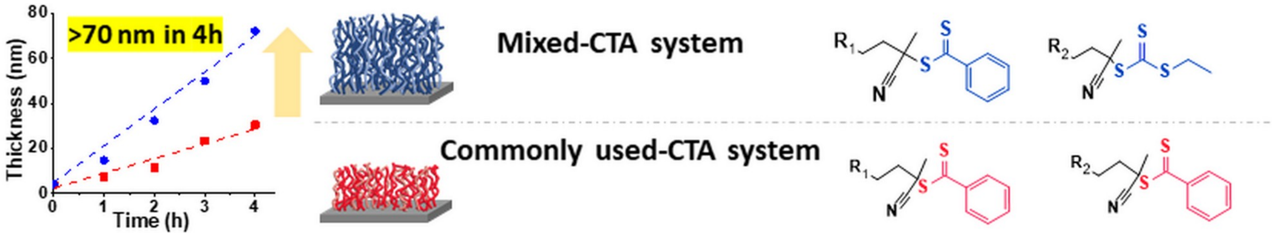


Figure 1. surface-initiated RAFT polymerization using a mixed chain transfer agent (mixed-CTA) approach to grow well-defined poly(HPMAm) brushes with precise control, achieving >70 nm thickness in 4 hours at moderate temperature, 50 °C.

Keywords: surface-Initiated RAFT, poly(HPMAm) brushes, poly(HPMA) brushes

Acknowledgments

The authors thank to the project New Technologies for Translational Research in Pharmaceutical Sciences/NETPHARM, project ID CZ.02.01.01/00/22_008/0004607, co-funded by the European Union, and to the Ministry of Education, Youth and Sports of the Czech Republic (grant # LUAUS24137).

Recyclability of Virgin and Recycled Compounds for Mobility Applications

I. Traxler[1*], D. Mileva[1], G. Grestenberger[1], M. Gall[1],

[1]*Borealis Polyolefine GmbH, St. Peter-Straße 25, 4021 Linz, Austria*
[*]*ines.traxler@borealisgroup.com*

The mechanical recycling of polypropylene is usually done by milling post-consumer goods followed by extrusion and pelletisation. Multiple cycles, longer exposure to high temperatures and intensive shearing may give rise to thermal, thermo-oxidative or mechanical degradation. Thus, it is essential to enlarge the knowledge about recyclability of PP and PP-based compounds.

In this study, a systematic assessment of the recyclability of a polypropylene (PP) based compound, containing 30 wt.-% mechanically recycled polypropylene from rigid packaging was carried out. For the sake of comparison, a virgin PP-based composition was analyzed as well. To simulate the effect of multiple processing in the recycling process, the materials were sent five times over a twin screw extruder. After selected runs the material properties were characterized.

The main properties influenced after multiple extrusion of the virgin compound and the recycled compound (30 wt.-% post-consumer recyclate, PCR) were flexural modulus, deformation behaviour during instrumented puncture test at -30°C, and emissions. OCS (optical control systems) analysis demonstrated reduction of inhomogeneities after each extrusion step for the virgin and the PCR-compound. Thermoanalytical and rheological measurement did not show any traces of degradation. Apparently, each compounding step only improved the talc dispersion and reduced the emissions which impacted the relevant properties positively. The fact that especially puncture resistance improved significantly for the virgin compound pointed at improvement potential for the respective production.

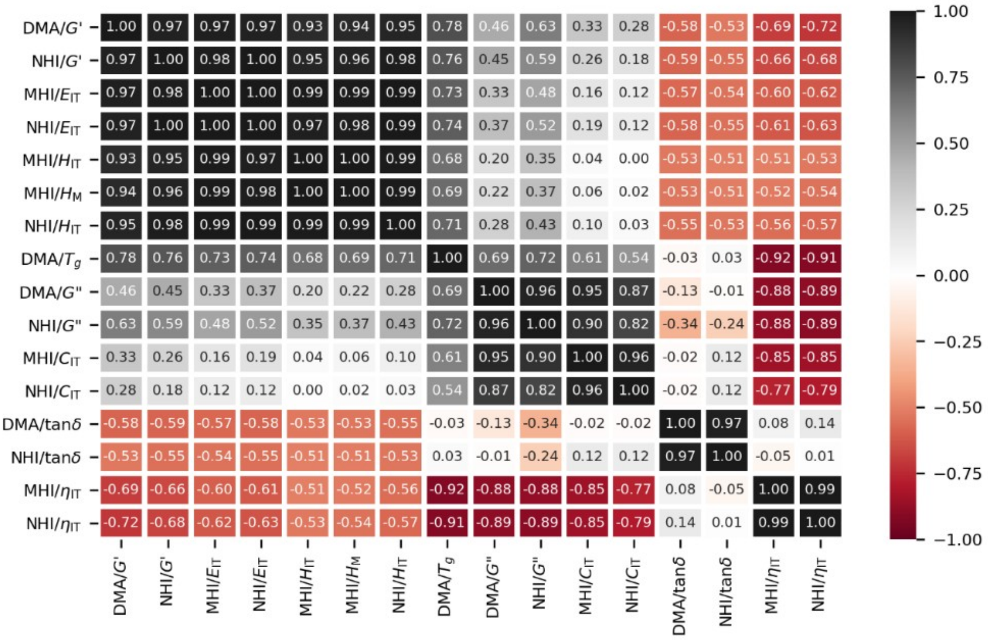
Keywords: mechanical recycling, polypropylene, automotive compound

Macro-, micro- and nanomechanical characterization of crosslinked polymers with very broad range of mechanical properties

M. Slouf[1*], V. Gajdosova[1], B. Strachota[1], A. Strachota[1], J. Nohava[2]

[1]*Institute of Macromolecular Chemistry CAS, Prague, Czech Republic*
[2] *Anton Paar TriTec SA, Vernets 6, 2035 Corcelles, Switzerland*
[*]*Corresponding author e-mail: slouf@imc.cas.cz*

We compared of macro-, micro- and nanomechanical properties of a series of eleven highly homogeneous and chemically very similar crosslined polymers [1]. By means of synthesis parameters, the mechanical properties of the samples were deliberately changed from very hard and stiff (elastic moduli of 4 GPa), through semi-hard and ductile, to very soft and elastic (elastic moduli of 0.006 GPa).



	DMA/G'	NHI/G'	MHI/E_{IT}	NHI/E_{IT}	MHI/H_{IT}	MHI/H_M	NHI/H_{IT}	DMA/T_g	DMA/G''	NHI/G''	MHI/C_{IT}	NHI/C_{IT}	DMA/tanδ	NHI/tanδ	MHI/η_{IT}	NHI/η_{IT}
DMA/G'	1.00	0.97	0.97	0.97	0.93	0.94	0.95	0.78	0.46	0.63	0.33	0.28	-0.58	-0.53	-0.69	-0.72
NHI/G'	0.97	1.00	0.98	1.00	0.95	0.96	0.98	0.76	0.45	0.59	0.26	0.18	-0.59	-0.55	-0.66	-0.68
MHI/E_{IT}	0.97	0.98	1.00	1.00	0.99	0.99	0.99	0.73	0.33	0.48	0.16	0.12	-0.57	-0.54	-0.60	-0.62
NHI/E_{IT}	0.97	1.00	1.00	1.00	0.97	0.98	0.99	0.74	0.37	0.52	0.19	0.12	-0.58	-0.55	-0.61	-0.63
MHI/H_{IT}	0.93	0.95	0.99	0.97	1.00	1.00	0.99	0.68	0.20	0.35	0.04	0.00	-0.53	-0.51	-0.51	-0.53
MHI/H_M	0.94	0.96	0.99	0.98	1.00	1.00	0.99	0.69	0.22	0.37	0.06	0.02	-0.53	-0.51	-0.52	-0.54
NHI/H_{IT}	0.95	0.98	0.99	0.99	0.99	0.99	1.00	0.71	0.28	0.43	0.10	0.03	-0.55	-0.53	-0.56	-0.57
DMA/T_g	0.78	0.76	0.73	0.74	0.68	0.69	0.71	1.00	0.69	0.72	0.61	0.54	-0.03	0.03	-0.92	-0.91
DMA/G''	0.46	0.45	0.33	0.37	0.20	0.22	0.28	0.69	1.00	0.96	0.95	0.87	-0.13	-0.01	-0.88	-0.89
NHI/G''	0.63	0.59	0.48	0.52	0.35	0.37	0.43	0.72	0.96	1.00	0.90	0.82	-0.34	-0.24	-0.88	-0.89
MHI/C_{IT}	0.33	0.26	0.16	0.19	0.04	0.06	0.10	0.61	0.95	0.90	1.00	0.96	-0.02	0.12	-0.85	-0.85
NHI/C_{IT}	0.28	0.18	0.12	0.12	0.00	0.02	0.03	0.54	0.87	0.82	0.96	1.00	-0.02	0.12	-0.77	-0.79
DMA/tanδ	-0.58	-0.59	-0.57	-0.58	-0.53	-0.53	-0.55	-0.03	-0.13	-0.34	-0.02	-0.02	1.00	0.97	0.08	0.14
NHI/tanδ	-0.53	-0.55	-0.54	-0.55	-0.51	-0.51	-0.53	0.03	-0.01	-0.24	0.12	0.12	0.97	1.00	-0.05	0.01
MHI/η_{IT}	-0.69	-0.66	-0.60	-0.61	-0.51	-0.52	-0.56	-0.92	-0.88	-0.88	-0.85	-0.77	0.08	-0.05	1.00	0.99
NHI/η_{IT}	-0.72	-0.68	-0.62	-0.63	-0.53	-0.54	-0.57	-0.91	-0.89	-0.89	-0.85	-0.79	0.14	0.01	0.99	1.00

Figure 1: Correlation matrix table showing Pearson's coefficients r for all pairs of experimentally determined macro-, micro- and nanomechanical properties: storage and loss modulus, damping factor and glass transition temperature from dynamic mechanical analysis (DMA/G', DMA/G'', DMA/tan(δ) and DMA/T_g), analogous properties from dynamic nanoindentation experiments (NHI/G', NHI/G'', NHI/tan(δ)), indentation hardness, modulus, creep and elasticity from quasi-static microindentation experiments (MHI/H_{IT}, MHI/E_{IT}, MHI/η_{IT} and MHI/C_{IT}), and analogous properties from quasi-static nanoindentation (NHI/H_{IT}, NHI/E_{IT}, NHI/η_{IT} and NHI/C_{IT}).

Mechanical properties at all length scales showed similar trends (as documented in Fig. 1), which confirmed the reliability of the state-of-the art micro- and nanoindentaion methods. The observed correlations between stiffness-related and viscosity-related properties were closely connected with brittle-ductile-rubbery transitions. In the conculding remarks, we will generalize how the observed macro-micro-nano correlations work for other polymer systems, such as semicrystalline polymers, blends, and composites [2].

Keywords: microindentation, nanoindentation, local mechanical properties of polymer systems

Acknowledgments: *Technology Agency of the Czech Republic, project TN02000020.*

References

[1] Slouf, M. et al. *Polymers* **2020**, *12*, 2951/1–2951/26.

[2] Slouf, M. and Henning, S. Micromechanical Properties, In: Wiley Encyclopedia of Polymer Science and Technology. John Wiley & Sons, Inc., **2022**, pp. 1-50. DOI: 10.1002/0471440264.pst199.pub2

From waste PU foams to secondary raw materials

E. Koša[1], D. Pahovnik[1], E. Žagar[1*]

[1]*National Institute of Chemistry, Ljubljana, Slovenia*
[*]*ema.zagar@ki.si*

Polyurethane foams (PUFs) are versatile materials that are widely used as comfort and insulation materials. With the increasing production of PUFs, the amount of PUF waste is also increasing. Currently, these materials are usually disposed of in landfills at the end of their life. With the drive towards a circular economy, recycling is becoming increasingly important. For PUFs, mechanical recycling is not the most suitable method due to the loss of material properties and the associated downcycling. Recently, attention has turned to more suitable chemical recycling technologies based on the cleavage of urethane groups in the PUF structure.

Over the years, various chemical recycling processes based on the cleavage of the urethane bonds have been developed to produce recycled polyols as secondary raw materials. The recycled polyols are generally used for less demanding applications such as the synthesis of rigid PUFs or as a partial substitute for virgin polyols in the synthesis of flexible PUFs. Unfortunately, the degradation of the urethane bonds in the PU foam structure is not selective and, depending on the reaction conditions, the hard segments are also degraded, leading to the formation of unwanted amines. Only acidolysis of PU foams allows the formation of a small amount of amines during the process, as the carboxyl groups act as amine scavengers, but at the expense of functionalizing the polyol with carboxyl groups by esterification as a side reaction, which has a negative impact on the synthesis of new PUFs.[1]

Here we present a chemical recycling process for PUFs using a cheap and readily available reagent that produces recycled polyols that are good equivalents to the corresponding virgin polyols, while the formation of amines during the process is low.[2] Recycled polyols have been successfully used for the synthesis of new flexible PUFs with properties comparable to those of PUFs synthesized from virgin polyols.

Keywords: flexible polyurethane foams, recycling, secondary raw materials

Acknowledgments

The authors acknowledge the financial support from the Slovenian Research and Inovation Agency, ARIS (Research project No. J2-50054 and Research Core Funding No. P2-0145).

References

[1] Grdadolnik, M.; Drinčić, A.; Oreški, A.; Onder, O. C.; Utroša, P.; Pahovnik, D.; Žagar, E. Insight into Chemical Recycling of Flexible Polyurethane Foams by Acidolysis. *ACS Sustainable Chem. Eng.* **2022**, 10 (3), 1323–1332.
[2] Žagar, E.; Pahovnik, D.; Koša, E.; Grdadolnik, M.; Pavlica, D. J. Process for recovering raw materials from polyurethane waste. 2024, LU506968

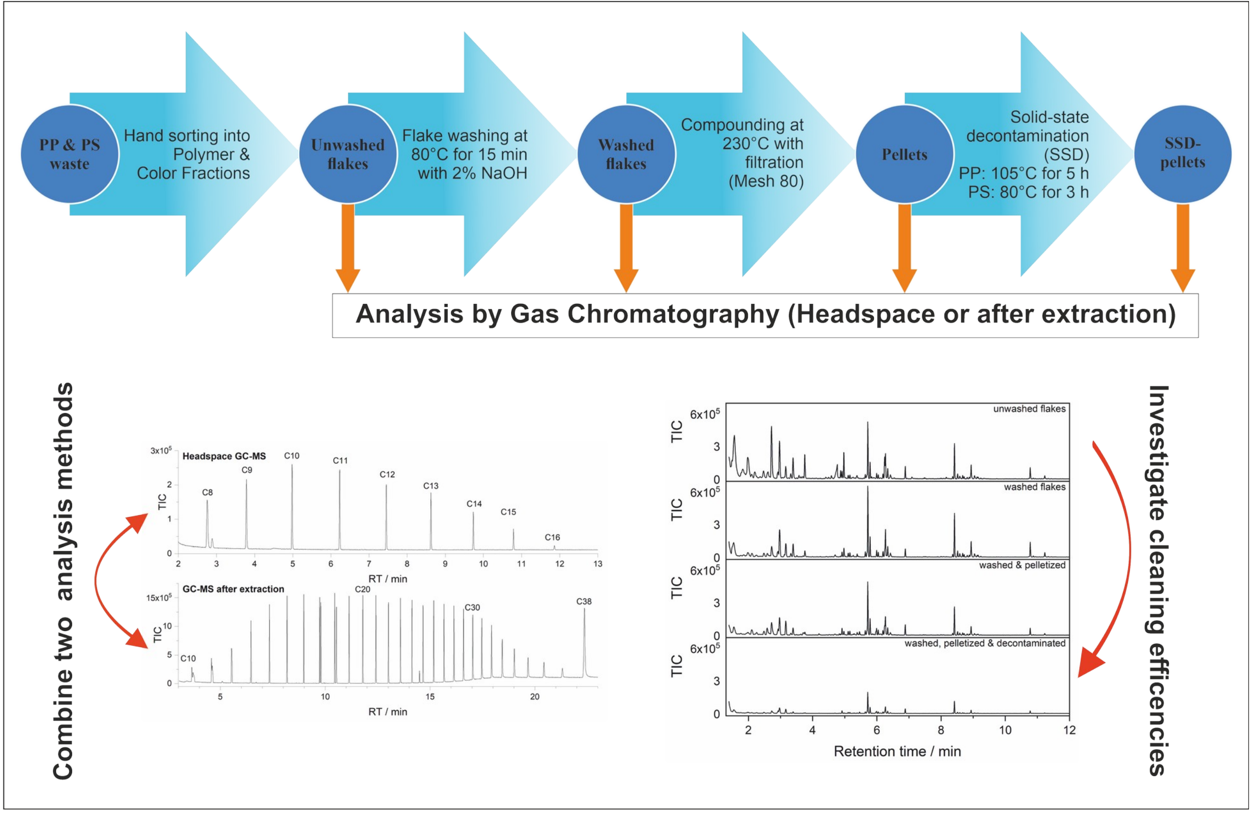
Gaschromatographic Analysis of Process-Induced Changes during Mechanical Recycling of PP and PS Waste Streams

A. Felgel-Farnholz[1,2,*], C.W. Kampfl[1], P.J. Freud[4], F. Rittmannsberger[5], J. Fischer[2,3]

[1]Johannes Kepler University, Institute of Analytical and General Chemistry, Linz, Austria
[2]Johannes Kepler University, Institute of Polymeric Materials and Testing, Linz, Austria
[3]Johannes Kepler University, LIT Factory, Linz, Austria
[4]Borealis Polyolefine GmbH, Innovation Headquaters, Linz, Austria
[5]PreZero Polymers Austria GmbH, Haimburg, Austria
[*]alexander.felgel-farnholz@jku.at

The uncertain origin of post-consumer plastics waste often contributes to the difficulty of effective recycling, particularly in the case of food-contact materials (FCM). Given the extensive range of potential applications, the number and concentration of possible contaminations is similarly vast. For this study, FCM waste was hand sorted, initially according to polymer type (PP and PS) and subsequently according to color fraction. The sorted waste was reprocessed along the mechanical recycling path: washing, compounding, and solid-state decontamination. Changes in the analyte profile were monitored during each step by two separate methods for gas chromatography coupled to mass spectrometric detection. Three important conclusions were drawn from the results. First, the morphological differences between PP and PS resulted in very different cleaning efficiencies for each of the individual processing steps. Second, the previous fields of application had a massive influence on the observed levels of contamination for each of the color fractions and thus also affecting the cleaning process. Third, the presence of fillers, such as colorants, also visibly affected both contamination levels and cleaning efficiencies of the individual steps.

Figure 1: Investigated process chain (top graph), Comparision of analytical methods (bottom left) and observed cleaning trends along process chain (bottom right graph).



Keywords: Plastics recyling, Food-contact material, Polypropylene, Polystyrene, Washing efficencies, Gas chromatography

Star-like Molecular Brushes with Poly(2-oxazoline)-based Amphiphilic Diblock Copolymer Side Arms

W. Xu[1*], L. Fietzke[2], R. Gumerov[3], P. Zhang[1], F. Zheng[1], C. Jeffreis[4],
I. Potemkin[3], R. Jordan[2], C. Papadakis[1]

[1] *Soft Matter Physics Group,Technical University of Munich, Garching, Germany*
[2] *Faculty of Chemistry and Food Chemistry, Technical University of Dresden, Dresden, Germany*
[3] *DWI Leibniz-Institute for Interactive Materials, RWTH Aachen University, Aachen, Germany*
[4] *European Molecular Biology Laboratory (EMBL), Hamburg, German*
[*]*wenqi.xu@tum.de*

Poly(2-oxazoline)s (POx) are a class of biocompatible polymers which have attracted great interest in biomedicine [1]. In this study, we focus on the structure of several star-like molecular brushes, which feature stars of poly(methyl methacrylate) having different functionalities as the backbones. They are grafted by amphiphilic diblock copolymers of poly(2-methyl-2-oxazoline) (PMeOx) and poly(*n*-butyl-2-oxazoline) (PBuOx). A molecular brush having fully hydrophilic side arms is studied as well. The sizes and inner structures of the star-like molecular brushes are investigated in dilute aqueous solution using dynamic light scattering, synchrotron small-angle X-ray scattering and computer simulations. Our results show that, at room temperature, the molecular brushes with amphiphilic side arms form small ellipsoidal clusters, while the fully hydrophilic brushes remain molecularly dissolved. Upon heating, an unexpected size growth is observed for the clusters. This is tentatively attributed to a change in the compatibility between the PMeOx and the PBuOx blocks [2], which is reflected by structural rearrangements of the individual brushes inside the cluster. The findings may offer a new approach to the development of stimuli-responsive polymers.

Keywords: Poly(2-oxazoline)s, polymer brush, polymer solution, light scattering

References

[1] Glassner M.; Vergaelen, M.; Hoogenboom, R.; Poly(2-oxazoline)s: A comprehensive overview of polymer structures and their physical properties. *Polymer International* **2017**, *67*, 32-45.
[2] Daoud L.; Arsenie, L. V.; Benkhaled, B. T.; Caillaud, K.; Semsarilar, M.; Picton, L.; Le Cerf, D.; Lapinte, V.; Shorter might be better: oligo(oxazoline)s for thermoresponsive polymersomes. *Polymer Chemistry* **2024**, *36*, 3641-3656.

The Low-Fouling Effectively Charged Polybetaine Brushes

Alina Pilipenco[a]*, Michala Forinová*[a]*, Zulfiya Černochová*[b*]*, Zdeňka Kolská*[c]*, Hana Vaisocherová-Lísalová*[a]*, Milan Houska*[a]

[a] FZU - Institute of Physics of the Czech Academy of Sciences, Na Slovance 1999/2, 180 00 Prague, Czech Republic

[b] Institute of Macromolecular Chemistry CAS, Institute of Macromolecular Chemistry CAS, Heyrovského nám. 2, Prague, 16206 Czech Republic

[c] Faculty of Science, J. E. Purkyně University in Ústí nad Labem, České Mládeže 8, Ústí nad Labem, 400 96 Czech Republic

Polybetaine nanobrushes are widely used as inert platforms for label-free biosensing due to their resistance to non-specific interactions. Despite being considered cationic or electrically neutral, these nanobrushes can exhibit negative zeta potential (ZP) at pHs above their isoelectric point (pI). To investigate whether negative ZP contributes to surface interactions, we studied three types of nanobrush deposited on a gold substrate: poly(carboxybetaine methacrylamide) (pCBMAA), poly(sulfobetaine methacrylamide) (pSBMAA), and poly[N-(2-hydroxypropyl)methacrylamide] (pHPMAA), which has no ionic groups. All three nanobrushes have well-defined pI and a negative surface ZP [1] above their pIs. The pH-dependent interactions of these nanobrushes with anionic dextran sulfate (DS) and cationic poly[(N-trimethylammonium)ethyl methacrylate] (PTMAEMA) were monitored by infrared reflection spectroscopy (IRRAS and GAATR).. DS adsorbs strongly to pCBMAA and only weakly to pSBMAA at pH values below their isoelectric points (pI), but can also adsorb slightly to both polybetaine polymers even at pH values above their pIs. This is because the sulfate groups on DS displace the carboxylate or sulfonate groups from interacting with the quaternary ammonium cations. However, DS does not adsorb to pHPMAA at any pH, and PTMAEMA does not interact with any of the polymers, regardless of the pH. These results [2] suggest that zeta potential measurements alone may not be enough to predict electrostatic interactions, as an apparent negative charge does not always translate into a functional surface charge that influences macromolecular interactions.

Keywords: surface zeta potential, polymer brushes.

Acknowledgments

This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic (grants # LM2023053 and LUAUS24272.

References

(Calibri, 10 pt.)Please ensure that every reference cited in the text is also present in the reference list. Follow the format below for this purpose:

[1] Tomsik E., Cernochova Z., Scheibe M. and Tadyszak K. Lithium phthalocyanine (γ-structure) as a molecular oxygen sensor. *RSC Adv*. **2025**,*15*, 3738-3748.

[2] Alina Pilipencoa, Michala Forinováa, Zulfiya Černochovváb, Zdeňka Kolskác, Hana Vaisocherová-Lísalováa, Milan Houska. The Effective Charge of Polybetaine Brushes. *Langmuir*, 2025 in press.

Towards Degradable Poly(acrylic acid): Efficient Strategies for Hydrolyzable Breaking Points

Sophia B. Däbritz[1], Seema Agarwal*[1,2]

[1]*Advanced Sustainable Polymers, Macromolecular Chemistry II, University of Bayreuth,*
Bayreuth 95440, Germany
[2]*Bavarian Polymer Institute, University of Bayreuth, Bayreuth 95440, Germany*
*Email: *agarwal@uni-bayreuth.de*

The persistence of hydrophilic polymers in wastewater streams is a growing problem, due to their abundant use in e.g. household products. They can enter the environment by being discarded on landfills through sewage sludge or incineration. Introducing easily fragmentable functional groups (breaking points) into their stable C-C backbone facilitates fragmentation into bio-assimilable, water soluble pieces in the disposal phase, while maintaining material stability during use. Poly(acrylic acid) (PAA) is the ideal candidate for this approach, as low molecular weight samples have been shown to exhibit significantly higher biodegradation rates compared to their high molecular weight counterparts. In our study, we incorporated cleavable ester groups into the C-C backbone of PAA *via* radical ring-opening polymerization of a cyclic ketene acetal.[1] These monomers enable polyester formation through a radical pathway. The copolymer was produced by copolymerizing *tert*-butyl acrylate and 2-methylene-1,3-dioxepane (MDO) and deprotected post polymerization. Direct copolymerization of MDO and acrylic acid is impossible due to a side reaction between the two monomers. We thoroughly investigated different polymerization methods. Deprotection was optimized to minimize chemical waste.[1] The poly(acrylic acid-co-ester)s degraded in KOH solution, leaving oligomeric fragments of PAA. These are easily assimilable for microbes. By preparing PAA-copolymer with hydrophobic MDO, maintaining water solubility is crucial for future applications. Hydrophilicity of the PAA-copolyesters was successfully maintained at higher pH levels for materials with a PAA content greater than 50%.[1]

Keywords: radical ring-opening polymerization, 2-methylene-1,3-dioxepane, acrylic acid, hydrolysis

References

[1] S. B. Däbritz, S. Agarwal, Evaluating Polymerization Methods and Deprotection Strategies for Making Water Soluble Poly(acrylic acid) with Hydrolyzable Breaking Points, *Macromol. Chem. Phys.* **2025**, 2500080.

Stretch and scission: estimations on polymer cleavage in small scale turbulent vortices during drag reduction

H.W. Müller[1*], L. Brandfellner[1,2], J. Beslac[1], A. Bismarck[1,2]
[1]*IMCR, Faculty of Chemistry, University of Vienna, Vienna, Austria*
[2]*DCAFM, Faculty of Physics, University of Vienna, Vienna, Austria*
[*]*hans.werner.mueller@univie.ac.at*

Polymer additives have been found to efficiently reduce drag in turbulent pipe flows [1] and diminish the energy required for mass transfer through pipes. This is intrinsically accompanied by scission of the long, flexible polymer chains required for drag reduction (DR). Not only the mechanism of polymer DR is not fully understood, also the physics of polymer cleavage is still under discussion. Some studies claim polymers will be fully stretched in the shear of the boundary layer [2]. Others expect a partial stretching of the polymers in the local shear of turbulent flow vortices [3,4]. Both mechanisms require stretching of the polymer to be faster than its relaxation. We focus on the potential interaction of the polymers with turbulent vortice structures in the bulk since our experiments indicate DR to be dominated by volume processes rather than boundary layer effects [5]. Estimations of the involved length and time scales of polymer and turbulence and of the forces acting on the polymer chain are compared to our recent observations of polymer degradation in tubulent pipe flow [6,7]. Polymer stretching in turbulent vortices has to be expected, but scission is predicted for molecules of very high molecular mass only; much larger than observed in experiment where the fragments had molecular weights of 10^6 g/mol and less.

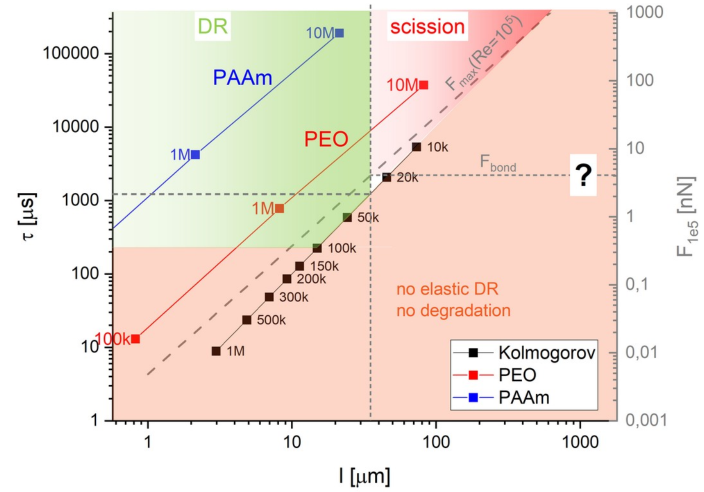


Figure: Time – size relation of turbulent structures in the Kolmogorov cascade (black solid line). Labels provide the minimum vortex size in dependence of the Reynolds number. Zimm time and maximum extensibility for two polymers (red and blue solid line, labels indicate the molecular weight). The broken line represents the maximum force acting on the polymer chain in dependence of the chain length for Re=10^5. Background colours in the graph display the parameter range where polymer scission (red) and drag reduction is expected (green and red).

Acknowledgments

This work was supported by the Doctoral College Advanced Functional Materials (DCAFM) funded by the Austrian Science Fund (FWF, Grant No.: DOC 85 doc. funds).

References

[1] Toms B.A. *Proceedings of the 1st International Congress on Rheology* **1948**, 135.
[2] Lumley J.L. *Annu. Rev. Fluid Mech.* **1969** 1 (1), 367
[3] Tabor M.; de Gennes P.G. *Europhysics Letters* **1986** 2(7):519
[4] Vanapalli S.A., et al. *PNAS* **2006** 103(45):16660
[5] Brandfellner L.; Bismarck A.; Müller H.W. *Physics of Fluids* **2025**, 37, 035175
[6] Müller H.W.; Brandfellner L.; Bismarck A. *Physics of Fluids*, **2023**, 35(2):023102.
[7] Brandfellner L.; Muratspahić, E.; Bismarck A.; Müller H.W. *JNNFM* **2024**, 325:105185

Synthesis of high-molecular-weight poly (itaconic-co-methacrylic acid) copolymers for fabrication of nanocomposite hydrogels for cationic dyes removal

Gloria Huerta-Angeles[1], Lívia Kanizsová,[1] Kacper Mielczarek,[2] Jiří Hodan,[1] Szczepan Bednarz[2], Hynek Beneš[1.]

[1] *Institute of Macromolecular Chemistry of the Czech Academy of Sciences, Heyrovského nám. 2, 162 00, Prague, 6, Czech Republic*

[2]*Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland*

**huerta@imc.cas.cz*

This study reports the synthesis and characterization of copolymers of itaconic acid (IA) and methacrylic acid (MAA) as precursors for fabricating physically and ionically crosslinked nanocomposite hydrogels (NCHs) for cationic dye removal. Copolymers were synthesized via free-radical polymerization in a deep eutectic solvent using VA-044 as initiator, yielding high-molecular-weight polymers characterized by NMR, IR, and TGA. Thermal analysis revealed four degradation stages, with increased MAA content enhancing thermal stability at early decomposition stages, while poly(itaconic acid) showed the highest thermal resistance and char yield.

Hydrogels were formed with Laponite RD, resulting in stable, elastic 3D networks (G′ > G″). Higher IA content correlated with increased stiffness, while high MAA content reduced mechanical integrity. WAXS/SAXS and TEM confirmed complete clay exfoliation and polymer intercalation, with further basal spacing expansion upon dye adsorption, indicating dye intercalation between platelets.

Swelling behavior varied with ionic conditions: hydrogels expanded significantly in deionized water but shrank in saline solutions, particularly in $CaCl_2$, where swelling was reduced by 60%. Batch adsorption tests using basic fuchsin (BF) showed 99.5% removal under optimized conditions with only 0.2 $g\,L^{-1}$ of adsorbent. Kinetic modeling indicated that adsorption followed a pseudo-first-order model (physisorption). Thermodynamic analysis confirmed the process was spontaneous and exothermic ($\Delta H° = -39.19$ kJ mol^{-1}), with decreased entropy—hallmarks of physical adsorption. IR and NMR analyses supported the physisorption mechanism.

Calcium ion co-crosslinking significantly enhanced hydrogel mechanical strength and reduced swelling, enabling efficient reuse. Reusability tests demonstrated BF removal (99.2 ± 0.2%) over five adsorption–desorption cycles. Overall, IA/MAA-based NCHs offer a green, robust, and reusable platform for efficient removal of cationic dyes from wastewater, highlighting their potential for sustainable water treatment applications.

Keywords: Itaconic acid, deep eutectic solvents, adsorption, cationic dyes, organic-inorganic composite, Freundlich isotherm.

Acknowledgments

This work was supported by the Lead Agency bilateral Czech–Polish project, funded by the Czech Science Foundation (grant no. 25-15669K) and the National Science Centre Poland (CEUS-UNISONO project grant no. 2024/06/Y/ST5/00062).

Why do polyolefin microplastics sink?

Vaibhav Budhiraja [1,2], Tomaž Kotnik [3], Sebastijan Kovačič [3], Branka Mušič [4], Andrej Kržan [1,2*]

[1] Department of Polymer Chemistry and Technology, National Institute of Chemistry (Kemijski inštitut), Ljubljana, Slovenia.
[2] University of Nova Gorica, Nova Gorica, Slovenia.
[3] Department of Inorganic Chemistry and Technology, National Institute of Chemistry (Kemijski inštitut), Ljubljana, Slovenia.
[4] Slovenian National Building and Civil Engineering Institute, Dimičeva ulica 12, 1000 Ljubljana, Slovenia.

[*]*Corresponding author:* andrej.krzan@ki.si

ABSTRACT

Microplastics (MPs) in the ocean is a serious concern and a potential threat to marine ecology. The abundance of MP leaked and observed in the oceans reveals a massive imbalance. Buoyant polyolefin MPs such as polyethylene (PE) and polypropylene (PP) are expected to be floating on the ocean surface, but a large amount is found in the deep ocean and sediments. In the present study, we examined the accelerated weathering of low-density PE, PP films, as well as high-density PE (HDPE), PP fragment MPs that mimic environmental conditions. We found that weathering increases the density of polyolefin MP, which is one of the main reasons for its sinking. We assessed the effect of accelerated weathering on their physical, chemical, thermal and surface properties and correlated it with the change in density. The density of pristine HDPE and PP fragments are 0.94 g/cm^3 and 0.89 g/cm^3, which increase to 1.00 g/cm^3 and 1.02 g/cm^3 after 1000 h of weathering, respectively. The weathering time was found to be proportional to the increase in density of polyolefin MPs. Thus, it is critical to consider MP degradation to accurately predict its fate and transport in the marine environment.

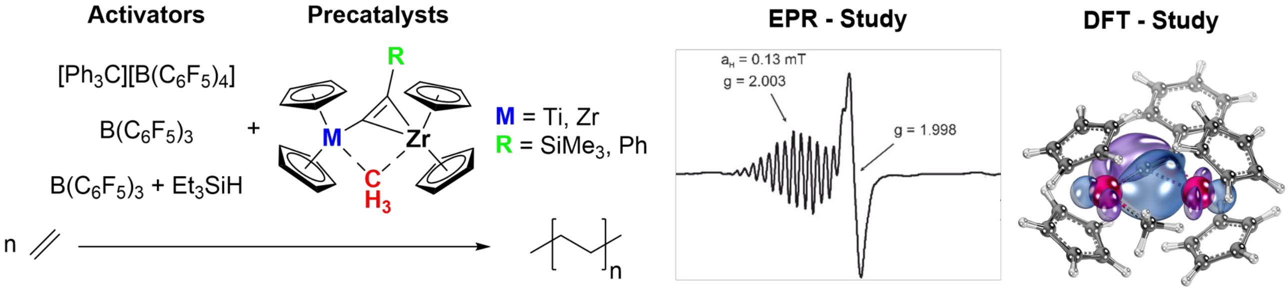
KEYWORDS: Accelerated weathering, degradation, density, polyethylene (PE), polypropylene (PP).

Posters

Dinuclear Group 4 Metallocene Catalysts of the Type $[(Cp_2M)_2(\mu\text{-}Me)(\mu\text{-}C_2R)]$: Structure-Activity Relationships in Ethylene Polymerisation

F. Reiß[1*], H. Al Hamwi[1], Torsten Beweries[1]
Martin Lamač[2*], Michal Horáček[2], Jiří Pinkas[2], Vojtěch Varga[2]
[1]*Leibniz Institute for Catalysis, Albert-Einstein-Strasse 29a, 18059 Rostock, Germany*
[2]*J. Heyrovsky Institute of Physical Chemistry of the Czech Academy of Sciences, Dolejškova 2155/3, 182 23 Prague 8, Czech*
[*]*fabian.reiss@catalysis.de; martin.lamac@jh-inst.cas.cz*

The modular synthesis of the alkynyl methyl bridged dinuclear group 4 complexes was first reported by Erker in 1998.[1] Recently, some of us found that these species serve as precatalysts in the dehydrocoupling of amine boranes[2] and can be used for the activation of small molecules.[3]
In this contribution, we systematically investigate four representatives of this class of complexes $[(Cp_2M)_2(\mu\text{-}Me)(\mu\text{-}C_2R)]$ (M = Ti, Zr; R = $SiMe_3$, Ph) with regard to their catalytic activity in the polymerisation of ethylene (Figure, left). The modular structure of the bridged complexes facilitates the preparation of homodinuclear (Zr, Zr) and heterodinuclear (Ti, Zr) complexes, as well as the variation of the substituents at the alkynyl unit. The study evaluates the influence of three different activation sequences on the catalytic activity of the precatalysts (Figure, left). In particular, the phenylalkynyl-bridged precatalysts show high activity similar to that of the reference complex Cp_2ZrMe_2,[4] while the $SiMe_3$-substituted derivatives are significantly less active. With the help of EPR, NMR and DFT studies, a structure-activity relationship is revealed that can contribute to the further development of analogous precatalysts.



Figures: Investigated dinuclear group 4 precatalyst's and activators (left), representative EPR signals after activation with $[Ph_3C]^+$ (middle), and alkynyl assisted intermetallic intrinsic binding orbital (right).

Keywords: Dinuclear Catalysts, Polyethylene, Structure-Activity-Relationship

Acknowledgments

We thank the German Research Foundation (419924354), MEYS Czech Republic and the European Union for support (CZ.02.01.01/00/22_008/0004558).

References

[1] J. Schottek, G. Erker, R. Frohlich, *Eur. J. Inorg. Chem.* **1998**, 551-558.
[2] K. Lindenau, N. Jannsen, M. Rippke, H. Al Hamwi, C. Selle, H. J. Drexler, A. Spannenberg, M. Sawall, K. Neymeyr, D. Heller, F. Reiss, T. Beweries, *Catalysis Science & Technology* **2021**, *11*, 4034-4050.
[3] H. Al Hamwi, M. Rippke, K. Lindenau, A. Spannenberg, M. Lamac, F. Reiss, T. Beweries, *Chem. Eur. J.* **2025**, e202500857.
[4] L. Jia, X. M. Yang, A. Ishihara, T. J. Marks, *Organometallics* **1995**, *14*, 3135-3137.

Bifunctional Group 4 Metallocenes: Postcoordinative Functionalisation for Tuning Amine Borane Dehydropolymerisation Catalysts

M. Greiner[1], F. Reiß[1*], T. Holtrichter-Rößmann[2], T. Beweries[1]

[1]Leibniz Institute for Catalysis, Albert-Einstein-Strasse 29a, 18059 Rostock, Germany
[2]LANXESS Organometallics GmbH, Ernst-Schering-Straße 14, 59192 Bergkamen, Germany
**fabian.reiss@catalysis.de*

The dehydrocoupling of amine boranes is an already known research field to build up polyamineboranes as a new class of materials that is analoguous to polyethylene. The hydrogen evolved during polymerisation could be used as an on-demand hydrogen source or as an *in situ* reducing reagent.[1]
Our group already investigated the structure and mechanisms of dinuclear group 4 metallocene catalysts facilitating this reaction.[2] In this contribution a new type of bifunctional catalysts with a group 4 metallocene core and a Lewis acidic or Lewis basic anchor group is introduced. A variety of these catalysts is easily accessible by the modular buildup from a precusor complex serving as a building block. The feasibility of such postcoordinative functionalisations like hydroboration is already known from litature.[3]
Volumetric measurements and NMR studies indicate that these bifunctional catalyst show a significantly increased activity compared the their unfunctionalised precursors. A possible mechanism explaining these change is *facilitated diffusion* meaning that the introcuced anchor group in second coordination sphere directs the substrate towards the active metallocene centre. This structure-activity relationship is further elucidated by computational studies.

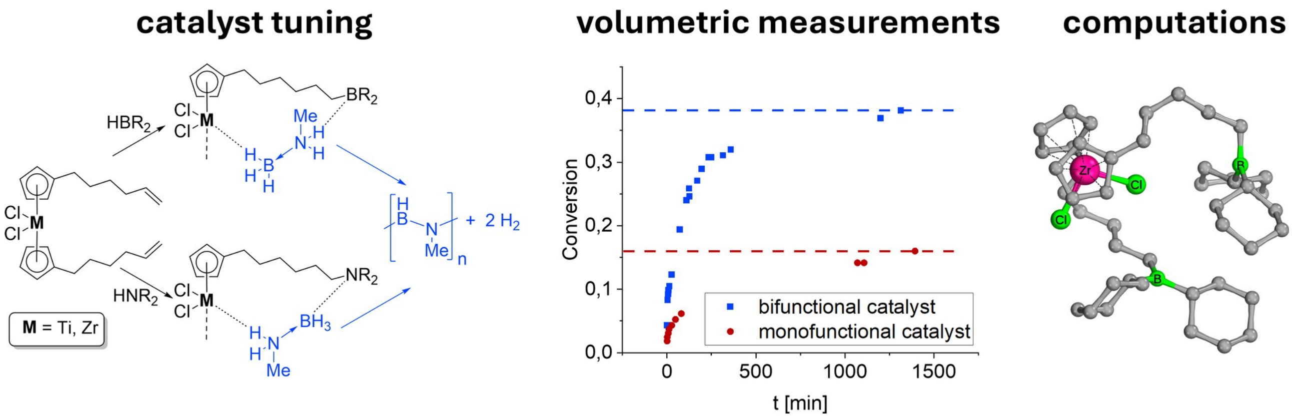

catalyst tuning
volumetric measurements
computations

Figure 1: Modular synthetic approach for group 4 catalysts to tune the dehydrocoupling of amine boranes (left), comparison of activities of a bifunctional group 4 catalyst and its unfunctionalised precursor by volumetric detection of hydrogen generation (middle), semi-empirical approach for isomer sampling (right, xTB-crest).

Keywords: Bifunctional Catalysts, Amine Boranes, Hydrogen, Postcoordinative Functionalisation, Second coordination sphere

Acknowledgments
We would like to thank the German Ministry of Education and Research (BMBF) for financial support (03XP0605C).

References

[1] M. Rippke, X. Tian, F. Reiss, L. Wu, T. Beweries, *Chem. Eur. J.* **2025**, *31*, e202403982.
[2] K. Lindenau, N. Jannsen, M. Rippke, H. Al Hamwi, C. Selle, H.-J. Drexler, A. Spannenberg, M. Sawall, K. Neymeyr, D. Heller, F. Reiß, T. Beweries, *Catal. Sci. Technol.* **2021**, *11*, 4034-4050.
[3] a) G. Erker, R. Aul, *Chem. Ber.* **2006**, *124*, 1301-1310.
b) J. Pinkas, M. Lamač, *Coord. Chem. Rev.* **2015**, *296*, 45-90.

Innovating Polyethylene with Cyclic Side Chains: Synthesis, Structure, and Properties

Jürgen Kranister[1], Alexander Mottl[1], Christian Paulik[1*]

[1]*Institute for Chemical Technology of Organic Materials, Johannes Kepler Universität Linz, Altenberger Straße 69, 4040 Linz, Austria*
[*]*christian.paulik@jku.at*

The incorporation of side chains commonly referred to as short chain branches (SCBs) into the linear backbone of polyethylene (PE) significantly influences key polymer properties such as crystallinity, density, and mechanical performance. Ethylene polymerization via coordinative Ziegler–Natta (ZN) catalysis typically yields highly linear macromolecular structures capable of forming crystalline domains. The introduction of SCBs disrupts this regular packing, thereby reducing the degree of crystallinity. Modulation of the structure and concentration of SCBs enables the tuning of material properties to suit specific applications.[1] Previous investigations have demonstrated that branched comonomers, such as iso-hexene and neo-hexene, exert a greater disruptive effect on crystalline structure compared to their linear analogue, n-hexene.[2] Building on these findings, this study explores the potential of cyclic SCBs characterized by increased steric hindrance to elicit similar or enhanced effects. To this end, three cyclic comonomers (depicted in Figure 1) were evaluated for their feasibility in ethylene copolymerization.

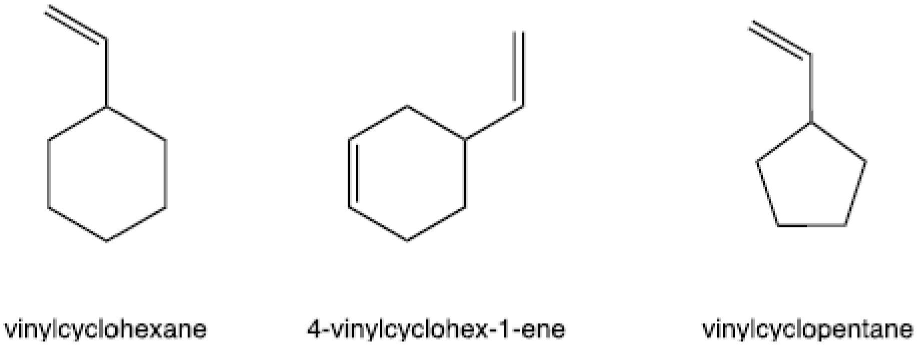


Figure 1 Comonomers used to introduced cyclic SCBs in PE copolymers.

Successful copolymerization of vinylcyclohexane and 4-vinylcyclohexene-1 with ethylene has been previously documented using a variety of catalytic systems, including metallocenes and ZN catalysts.[3],[4] The current study compares the kinetic behavior of these copolymerizations including catalyst activation and deactivation dynamics with those observed in the homopolymerization of ethylene. Additionally, the resulting polymers were characterized in terms of their molecular weight distributions and thermal properties, which are affected by the nature of the incorporated comonomers. Variations in melting temperatures and enthalpies reflect alterations in crystalline content induced by the cyclic side chains.

For comparative purposes, a series of copolymerizations involving ethylene and n-butene was also performed. These conventional copolymers, containing linear and relatively shorter SCBs, serve as reference materials to contextualize the influence of cyclic branching on polymer structure and properties.

Quantitative ^{13}C nuclear magnetic resonance (NMR) spectroscopy confirmed that a minor fraction of the respective cyclic comonomers was successfully incorporated into the polymer backbone, further supporting the structural modifications observed.

References

[1] Simanke, A. G.; Galland, G. B.; Baumhardt Neto, R.; Quijada, R.; Mauler, R. S.; *J. Appl. Polym. Sci.* **1999**, 74, 1194.
[2] Göpperl, L.; Cipullo, R.; Schwarzinger, C.; Paulik, C. *Macromol. React. Eng.* **2023**, *17*, 2300035.
[3] Marques, M.; Yu, Z.; Rausch, M. D.; Chien J. C. W. *J. Polym. Sci.,* Part A: Polym. Chem. **1995**, 33, 2787.
[4] Mani, R.; Burns, C. M. *Polymer* **1993**, 34, 1941.

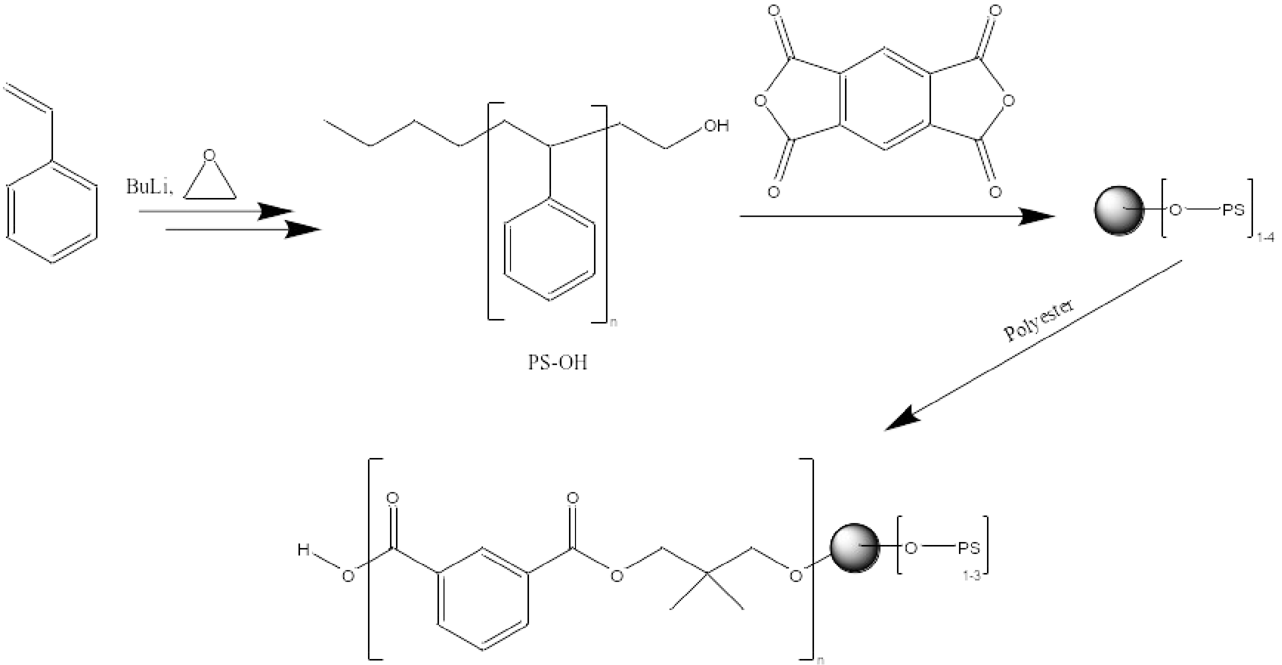
Polystyrene branched Polyesters and their Characterization

C. Schwarzinger*, K.M. Saller

Institute for Chemical Technology of Organic Materials, Johannes Kepler University, Linz, Austria
**clemens.schwarzinger@jku.at*

In order to improve properties of polyester resins (PES) related to polarity, stickiness on non polar substrates, hydrophobicity, etc., we have tried to incorporate polystyrene blocks into such resins. In a first step polystyrene (PS) with terminal hydroxyethyl groups was prepared by ionic polymerization, which was then attached to multifunctional carboxylic acids. At this point multi arm star polymers could be retrieved that were valuable intermediate products for the improvement of polymer characterization techniques based on size exclusion chromatography.

The now functionalized polystyrene chains were then incorporated into precondensed polyesters bearing dedicated functional groups [1] and branched PS-PES systems obtained. This paper reports the first results on synthesis of such polymers and the use of SEC-MALS and MALDI-MS techniques to monitor reaction progress and final structures of these materials [2].



Scheme 1. Synthesis route to polystyrene branched polyesters.

Keywords: polymer synthesis, polyester, MALDI, SEC

References

[1] Saller, K.M..; Hubner, G.; Schwarzinger, C. Introducing free carboxylic acid groups along polyester chains using dimethylolpropionic acid as diol component. *European Polymer Journal* **2023**, *198*, 112442.

[2] Saller, K.M..; Gnatiuk, I.; Holzinger, D.; Schwarzinger, C. Semiquantitative Approach for Polyester Characterization Using Matrix-Assisted Laser Desorption Ionization/Time-of-Flight Mass Spectrometry Approved by 1H NMR. *Analytical Chemistry* **2020**, *92*, 15221-15228.

Design of biobased non-isocyanate polyurethanes

E. Hebda[1*], J. Ozimek, K. Pielichowski

[1] *Cracow University of Technology, Department of Polymer Chemistry and Technology, ul. Warszawska 24, 31-155 Kraków, Poland*
*Corresponding author: *edyta.hebda@pk.edu.pl*

Polyurethanes are the most versatile and common polymer materials. In the synthesis of conventional polyurethanes, ether or ester polyols, diisocyanates and a low molecular weight chain extender are used. The synthesis of these substrates, their subsequent polymerization and recycling of used polyurethanes undoubtedly have a toxic effect on the environment. The very synthesis of diisocyanate, which is obtained from deadly and energy-intensive phosgene, is extremely toxic. Also, the susceptibility of diisocyanate to hydrolysis adversely affects the environment and human life. Due to the growing ecological awareness, the search for an alternative method of PU synthesis began, eliminating the use of isocyanates [1]. A balanced approach is the synthesis of isocyanate-free polyurethanes, which are obtained from cyclic carbonates and diamines. Cyclic carbonates can be obtain with 1,2-diols or can are formed by introducing CO_2 into epoxy compounds, which can be synthesized from renewable raw materials [2].

In this work, CC was synthesized from vanillin alcohol diglycidyl ether (VA) or hydroquinone (HQ). Cyclocarbonylation with carbon dioxide (CO_2) in the presence of tetrabutylammonium bromide (TBAB) catalyst was carried out at 105°C, resulting in the formation of a 5-membered cyclic carbonate. The use of waste and natural substances is consistent with the global efforts to reduce the impact of the chemical industry on the environment [2]. NIPU was obtained by reacting previously synthesized vanillin carbonates and hydroquinone with the long-chain amine polypropylene oxide and 1,12-dodecylamine (DADD). The sample series differed in the ratio of shorter to longer amine. FTIR analysis was used to control the reaction, observing changes in the absorbance of bands originating from carbonate groups (1800 cm^{-1}) and urethane groups (1720 cm^{-1}). The structure of the obtained polyurethanes and the presence of crystalline segments were investigated by WAXD and DSC.

Keywords: NIPU, thermal analysis, non-isocyanate polyurethanes, composites

Acknowledgments
This research was funded by the Polish National Science Centre (Narodowe Centrum Nauki, NCN), under contract number DEC-2022/45/B/ST8/03060.

References

[1] Cornille, A.; Auvergne, R.; Figovsky, O.; Boutevin, B.; Caillol, S. A perspective approach to sustainable routes for non-isocyanate polyurethanes. *Eur. Polym. J.* **2017**, *87*, 535–552.
[2] Fanjul-Mosteirin, N.; Sardon, H.; Fonseca, L.P.; Dove, A.P. Bio-based non-isocyanate poly(hydroxyurethane)s (PHU) derived from vanillin and CO_2. *Mater. Adv.* **2023**, *4*, 2437-2448.

OPTIMIZATION OF THE TAI STRATEGY FOR THE SYNTHESIS OF WATER-SOLUBLE POLYMERS FOR BIOMEDICAL APPLICATIONS

Tania Chopra, Eliška Müllerová, Sachin Gupta, and Vladimír Raus

Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2,
162 06, Prague 6, Czech Republic; raus@imc.cas.cz

Recently, a new synthetic strategy utilizing the copper-catalyzed reversible-deactivation radical polymerization (Cu-RDRP) initiated by the adducts of trichloroacetyl isocyanate (TAI) was introducted.1 This strategy enables the synthesis of unique complex polymeric architectures (e.g. graft copolymers, stars) with unprecedently high chain density. So far, however, the strategy has been applied only to non-polar monomers. Within our current efforts aimed at the preparation of hydrophilic biocompatible polymer-based carriers for biomedical applications, we investigated the applicability of the TAI strategy to the polymerization of water-soluble monomers. In this contribution, the optimization of Cu-RDRP conditions to achieve well-defined polymers will be demonstrated for N-(2-hydroxypropyl) methacrylamide (HPMA) and poly(ethylene glycol) methyl ether methacrylate (PEGMA). Different polymerization parameters, such as temperature, solvent, catalyst and ligand type, or catalytic system stoichiometry, have been varied to attain branched low-dispersity polymers at high monomer conversions. The developed conditions were then applied to synthesize different complex polymeric architectures, e.g., multi-arm polymeric stars based on a β-cyclodextrin core, that will be used for subsequent end-group modification. The synthesized branched polymers were characterized by 1H NMR spectroscopy and size-exclusion chromatography with a triple-detection system.

Acknowledgments: *Tania Chopra thanks the Institute of Macromolecular Chemistry for the financial support of her conference participation.*

References

[1] Gupta S., Janata M., Čadová E., Raus V; Straightforward synthesis of complex polymeric architectures with ultra-high chain density. *Chem. Sci*. **2024**, *15*, 12739-12753.

Influence of Supercritical CO_2 and N_2 on the Viscosity and Solidification Behavior of Polyethylene

J. Eckelt[1], M. Winkler[2], M. Walluch[2], D. Schwarz[2*]

[1]*Wee-Solve GmbH, Mainz, Germany*
[2]*Anton Paar GmbH, Graz, Austria*
[*]*daniela.schwarz@anton-paar.com*

The viscosity of polymer melts plays a critical role in processing efficiency, with high viscosities requiring increased energy input. Supercritical carbon dioxide ($scCO_2$) offers a promising approach to reduce melt viscosity without the need for solvent-based plasticizers [1]. In this study, the rheological behavior of different polyethylene (PE) types was investigated under elevated pressure using a plate-plate pressure cell capable of both rotational and oscillatory measurements.

Flow curves, frequency sweeps and temperature ramps were performed at ambient pressure, 120 bar N_2, and 120 bar $scCO_2$. While N_2 showed no significant impact on melt viscosity, it increased the solidification temperature, depending on the PE type. In contrast, $scCO_2$ acted as a temporary plasticizer, substantially lowering melt viscosity and slightly delaying crystallization. Oscillatory tests proved particularly useful for high-viscosity samples, enabling reliable measurements even near the melting point, provided strain and frequency were carefully adjusted.

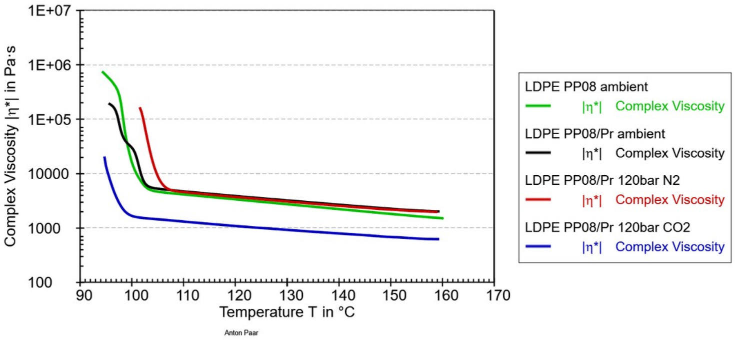


Figure 1: Temperature ramp in oscillation of LDPE at ambient conditions, 120 bar N_2 and 120 bar CO_2

The results highlight the potential of $scCO_2$ in energy-efficient polymer processing and foaming applications, and demonstrate the value of high-pressure rheometry for characterizing pressure-dependent polymer behavior.

Keywords: Polyethylene Viscosity, High-Pressure Rheology, Supercritical CO2, Polymer Crystallization, Plasticization with CO_2

References

[1] Wan, C., Lu, Y., Liu, T., Zhao, L., & Yuan, W. Foaming of low density polyethylene with carbon dioxide based on its in situ crystallization behavior characterized by high-pressure rheometer. *Industrial & Engineering Chemistry Research* **2017**, 61(16), 5334-5345.

Investigating Interface Corrosion in Active Implantable Medical Devices (AIMD) via Diffusion Mechanism

C. Angerer[1*], A. Onken[2], Helmut Schütte[3], Thomas Stieglitz[4], S. Hild[1], T. Doll[2]

[1]*Institute of Polymer Science Johannes Kepler University, Linz, Austria*
[2]*Hannover Medical School, Hannover, Germany*
[3]*Jade University, Wilhelmshafen, Germany*
[4]*Freiburg University IMTEK, Freiburg, Germany*
[*]*christian.angerer@jku.at*

A pinnacle of medical development and innovation are Active Implantable Medical Devices (AIMD), which comprise implantable Cardiac Pacemakers, Neurostimulators or Hearing Devices. These devices have to fulfill strict norms and undergo multiple safety tests. Nevertheless, AIMD have a non-negligible risk of failure caused by the permeation of body fluids and the subsequent diffusion of ions through the protective polymer layer. This process may cause delamination at the polymer-metal interface of the electrode material followed by corrosion, leading to malfunctions and potential harm for the patient [1].

In order to address this problem, a testing system comprised of a wafer coated with a thin platinum layer is crafted. On top, copper indicators are placed, enabling a simple reaction of copper with low molecular weight sulfur components. The entire system is then embedded in highly hydrophobic Sylgard to simulate a protective coating layer. The environmental influence can be varied by adding different solutions made of amino acids, proteins and salts, which in approximation resemble body fluids [1]. A suitable technique to detect the corrosion process on the metal layer is Confocal Raman Microscopy (CRM) which is based on Raman scattering, an inelastic interaction between light and the sample. CRM offers detailed chemical information about the sample combined with high spatial resolution, creating high-resolution Raman images. This enhances the characterization of diffusion and further corrosion mechanisms.

Initial experiments show high permeability of sulfidic components through the Sylgard towards the metal- polymer interface, visualized by a clear color change towards black (Figure 1a). Additionally, Confocal Raman Microscopy provides evidence for the diffusion of sulfides in the polymer and indicates an unequal deposition of CuS. Green areas in Figure 1b illustrate the presence of CuS. To further investigate the diffusion and delamination mechanisms, additional high-resolution Raman Imaging using an optimized testing setup needs to be performed.

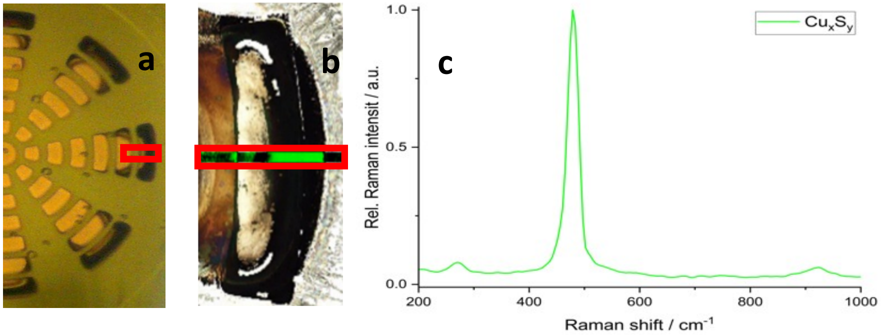


Figure 1: Microscopic image showing the test sample with its indicator structures made of Cu after immersion in potassium sulfide solution. Black areas indicate the formation of CuS (a). The red rectangele illustrates the measurement area for Confocal Raman Microscopy (CRM). Green areas in image (b) indicate the distribution of CuS verified by CRM. The corresponding spectrum is given in image (c) with bands at 265 and 475 cm^{-1}.

Acknowledgments

DFG, Hearing4all

References

[1] Onken A., et.al., Predicting Corrosion Delamination Failure in Active Implantable Medical Devices: Analytical Model and Validation Strategy. *Bioengineering* **2022**, *9(1)*, 10.

Influence of solvent properties on polyethylene-alkane solution viscosity: A torque scaling model

A. Atzenhofer[1], D. Pindrić[1], E.G. Viehböck[1], G. Spiegel[1], C. Paulik[1,2*]

[1]*Competence Center CHASE GmbH, Hafenstraße 47-51, 4020 Linz, Austria*
[2]*Johannes Kepler University, Altenbergerstraße 69, 4040 Linz, Austria*
[*] *christian.paulik@jku.at*

Rheological investigations of polymers offer important insights into processing behavior and viscoelastic properties, which are closely linked to their molecular structure. These findings are essential for tailoring polymeric materials for specific applications. Moreover, understanding these relations can help predict changes in response to external parameters, such as temperature, variations during processing. [1]

The viscosity of polymer solutions is a critical parameter that plays a major role in polymer synthesis, such as solution and bulk polymerization, as well as in manufacturing and dissolution processes.
Solvent supported recycling relies on the dissolution of polymers, followed by purification, and reprecipitation. Viscosity holds significant importance in this process since it influences processability and efficiency in terms of energy consumption. [2]

This work focuses on the development of a torque scaling model for polyethylene-alkane blends.
Utilizing a laboratory scale mixer equipped with a torque sensor, the relationship between the carbon chain length of various alkanes and the corresponding torque measurements is systematically examined. Furthermore, the pursued model shall incorporate the influence of temperature (T) and the amount of solvent (m). The experimental temperatures are chosen below, near and above the melting temperature of polyethylene. An excess amount of solvent is used for the experiments. Ultimately, the model aims to evaluate and predict a relative viscosity shift based on chain length, temperature and solvent concentration.

Keywords: Polyethylene, viscosity, modelling

Acknowledgments

The authors acknowledge financial support through the COMET Centre CHASE, funded within the COMET – Competence Centers for Excellent Technologies program by the BMIMI, the BMWET and the Federal Provinces of Upper Austria and Vienna. The COMET program is managed by the Austrian Research Promotion Agency (FFG).

References

[1] Münstedt, H. Rheological Measurements and Structural Analysis of Polymeric Materials. *Polymers* **2021**, *13*, 1123.
[2] Kol, R.; Nachtergaele, P; De Somer, T., D'hooge, D.R.; Achilias, D.S.; De Meester, S. Toward More Universal Prediction of Polymer Solution Viscosity for Solvent-Based Recycling. *Ind. Eng. Chem. Res.* **2022**, *61*, 10999–11011.

An Open-Source Python-Rust Framework for Monte Carlo Simulation of Linear and Branched Polymer Structures with Computation of Structural Descriptors

Fabian Hofmann[1*], Christian Paulik[2]

[1] *Johannes Kepler University, Institute for Chemical Technology of Organic Materials, Linz, Austria*
[2] *Johannes Kepler University, Institute for Chemical Technology of Organic Materials, Linz, Austria*
**fabian.hofmann@jku.at*

An open-source framework has been developed for the simulation of polymer chain configurations using a Monte Carlo random walk approach, implemented through the integration of Python and Rust. The implementation is influenced by the work of Touloupidis and Albrecht. [1] Linear and branched polymer structures are generated in three-dimensional space, and realistic molecular geometries are preserved by enforcing fixed bond angles and lengths. Steric hindrance is addressed by applying spatial constraints and performing collision detection using spatial hashing techniques. Polymer topologies are represented as graph structures, enabling efficient handling of connectivity and branching. Following chain generation, structural descriptors are calculated to characterize spatial configurations. Through the combination of Rust's computational performance and Python's flexibility, scalable simulations are facilitated and integration into broader computational workflows is streamlined. This tool is intended to support research into polymer structure and the development of structure-property relationships in polymer science.

Keywords: Monte Carlo, polymer chain simulation

References

[1] V. Touloupidis, A. Albrecht, Development of a Monte Carlo Random Walk Model for the Prediction of Linear and Branched Polymer Configuration and Connection to Radius of Gyration and GPC-MALS Experimental Results, Macromolecular Reaction Engineering 16 **2022**. https://doi.org/10.1002/mren.202200002.

Antioxidant and pro-oxidant activity of phenolic stabilizers during photooxidation of polyolefins

V. Gajdošová[1*], I. Šloufová[2], A. Rakitina[1], Z. Starý[1], T. Müller[3], J. Pilař[1], M. Šlouf[1]

[1]*Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, 16206 Praha 6, Czech Republic*
[2]*Charles University, Faculty of Science, Department of Physical and Macromolecular Chemistry, Hlavova 2030, 128 40 Prague 2, Czech Republic*
[3]*Leibniz-Institut für Polymerforschung Dresden e.V. (IPF), Hohe Str. 6, 01069 Dresden, Germany*
[*]*gajdosova@imc.cas.cz*

Phenolic stabilizers are employed in the stabilization of polymers during the processing to prevent thermooxidation [1]. They are also applied in medical applications to protect the polymers against biooxidation (in vivo oxidation) [1,2]. We investigated photodegradation processes in polymer plaques made of bulk polyolefin (HDPE or UHMWPE or COC) prepared by melt-mixing with or without phenolic natural (α-tocopherol) or synthetic (Irganox®1010) stabilizers and spin trapping agent (TTBNB; 2,4,6-Tri-tert-butylnitrosobenzene). The photodegradation was initiated either by non-ionizing radiation (wavelengths corresponding to terrestrial range of solar UV radiation) or ionizing radiation (high-energy electron beam).

In this contribution, we summarize our results concerning the comparison of the degradation processes in selected polyolefin after non-ionizing and ionizing radiation. The samples were characterized IR microspectroscopy, ESR spectroscopy including ESRI imaging, LM and SEM microscopy, and microindentation hardness testing. Both non-ionizing and ionizing radiation have generated polymer radicals in the whole volume of the irradiated samples, albeit by different mechanisms. The low-energy non-ionizing radiation is expected to split C-C bonds indirectly, through the formation of hypothetical chromophores, while high-energy ionizing radiation splits C-C bonds directly. Nevertheless, the resulting alkyl radicals might be assumed to undergo analogous reactions, regardless of their origin. However, our study has demonstrated clearly that the stability/reactivity of the generated radicals (and the concentration of the subsequently generated radical-induced oxidation products) depended on the mechanism of the radical generation together with the dynamics of polymer chains inside the studied polymers, which is closely related to their glass transition temperature. Moreover, the results have documented that the natural phenolic stabilizer exhibited both antioxidant and prooxidant activity depending on the degradation type: (i) antioxidant activity during thermooxidation, (ii) prooxidant activity during exposure to non-ionizing radiation, and (iii) antioxidant activity during exposure to ionizing radiation. The synthetic phenolic stabilizer Irg1010 showed similar, but not entirely identical behavior.

In summary, the activity of phenolic stabilizers depended not only on the degradation type (thermooxidation, non-ionizing or ionizing radiation), but also on type of polyolefin (low-Tg polyethylenes vs. high-Tg COC) and on the exact type of the stabilizer (α-Toc vs. Irg1010). Finally, the addition of TTBNB spin trapping agent enabled us to catch short-living and unstable radicals in HDPE, which could not be detected in the previous studies.

Acknowledgments

The authors acknowledge funding from TN02000020 (TA CR) project.

References

[1] Pilař J.; Šlouf M.; Michálková D.; Šloufová I.; Vacková T.; Dybal J. Pro-oxidant activity of α-tocopherol during photooxidative degradation of polyolefins. ESRI and IR microspectroscopy studies, Polym. Degrad. Stab. 2017, *138*, 55–71.

[2] Bracco, P.; Bellare, A.; Bistolfi, A.; Affatato, S. Ultra-High Molecular Weight Polyethylene: Influence of the Chemical, Physical and Mechanical Properties on the Wear Behavior. A Review. *Materials* **2017**, *10*, 791.

Lowering thermoplastic starch processing temperature by means of acid hydrolysis

Kouka S.[1], Gajdosova V.1, Strachota B.1, Slouf M.1

[1] *Institute of Macromolecular Chemistry CAS, Prague, Czech Republic*

Acid hydrolysis (AH) was investigated as a means to enhance the processability of thermoplastic starch (TPS), a biodegradable and renewable material that ~~often~~ requires relatively high processing temperatures [1]. By~~ partially depolymerizing starch~~ means of partial AH, the goal was to reduce molecular weight in order to lower the melt viscosity and processing temperature, without compromising the homogeneity or mechanical performance of the final product. Starch powder was hydrolyzed for varying durations (0, 15, 30, and 60 minutes), then neutralized, dried, and ~~processed~~ converted to TPS using ~~a~~ our two-step preparation protocol [2]. The impact of hydrolysis on morphology and microstructure was examined using polarized light microscopy (PLM) and scanning electron microscopy (SEM), which revealed progressive disruption of starch granules with increasing AH ~~treatment~~ time. The mechanical and rheological behavior was characterized by dynamic mechanical thermal analysis (DMTA), ~~and~~ microindentation hardness testing (MHI), and oscillatory shear rheometry at 120 °C, showing a gradual increase in stiffness-related ~~parameters~~ properties (G', G'', E_{IT}, and H_{IT}) for more extensively hydrolyzed samples. These trends were consistent with wide-angle X-ray scattering (WAXS) results, indicating increased crystallinity with longer hydrolysis times. Despite this moderate stiffening effect, hydrolyzed starch exhibited significantly reduced melt viscosity and required lower processing temperatures. In situ measurements performed during melt mixing (Fig. 1) confirmed this reduction, supporting the idea that shorter polymer chains formed during hydrolysis acted as an internal lubricant~~s~~. Overall, the study has demonstrate~~s~~d that the controlled acid hydrolysis c~~an~~ould effectively ~~balance ease of processing with~~ decrease the processing temperature while maintaining ~~desirable~~ mechanical properties and homogeneity of the final TPS.~~, making it a promising modification route for thermoplastic starch materials.~~

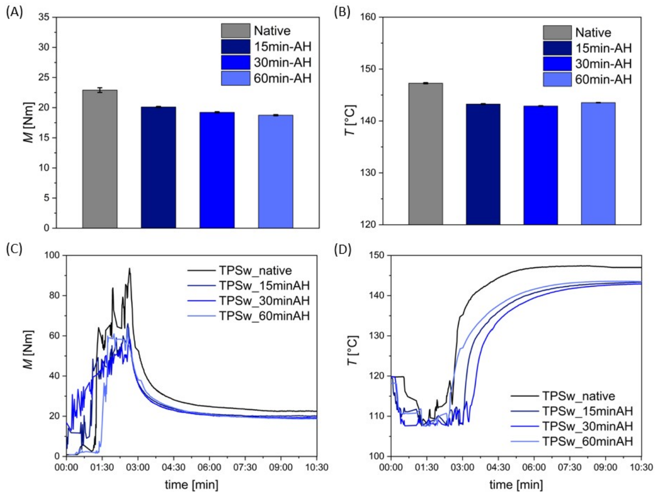


Fig. 1: In-situ measurements of torque moments (a, c) and processing temperatures (b, d) of TPS with different times of acid hydrolysis.

Acknowledgments

Technology agency of the Czech Republic, program NCK2, project TN02000020.

References

1. Huneault, M.A.; Li, H. Preparation and Properties of Extruded Thermoplastic Starch/Polymer Blends. *Journal of Applied Polymer Science* **2012**, *126*, E96–E108.
2. Gajdosova, V.; Strachota, B.; Strachota, A.; Michalkova, D.; Krejcikova, S.; Fulin, P.; Nyc, O.; Brinek, A.; Zemek, M.; Slouf, M. Biodegradable Thermoplastic Starch/Polycaprolactone Blends with Co-Continuous Morphology Suitable for Local Release of Antibiotics. *Materials* **2022**, *15*, 1101.

Multifunctional Biopolymer Blends: Tailoring PLA/PCL Composites for Advanced Applications

E. Ivanov[1*], R. Kotsilkova[1], V. Georgiev[1], T. Batakliev[1], V. Angelov[1]

[1] *Open Laboratory on Experimental Micro and Nano Mechanics (OLEM), Institute of Mechanics, Bulgarian Academy of Sciences, Sofia, Bulgaria*
**ivanov_evgeni@yahoo.com*

This study presents an in-depth investigation of polylactic acid (PLA) and polycaprolactone (PCL) blends, aiming to optimize their structural and functional properties for sustainable and smart material applications. The research integrates advanced rheological, thermal, and mechanical characterization techniques to evaluate phase separation behavior and viscoelastic performance. Polymer blends with varying PLA/PCL ratios were prepared via melt extrusion — a scalable and eco-friendly processing method [1]. Scanning electron microscopy (SEM) revealed morphology transitions from droplet–matrix to co-continuous and phase-inverted structures as the PCL content increased. Rheological measurements highlighted composition-dependent shear-thinning behavior and complex moduli indicative of phase interactions. DMTA analysis showed significant influence of PCL content on the glass transition temperature and mechanical moduli, reflecting changes in thermal and elastic behavior. Differential scanning calorimetry (DSC) confirmed suppressed PLA crystallization and enhanced PCL crystallinity in the blends. Thermogravimetric analysis (TGA) demonstrated that even small additions of PCL significantly improve the thermal stability of PLA. The presence of two distinct degradation stages further confirmed phase separation in immiscible blends. Cole–Cole plots and phase angle analysis offered deeper insight into interfacial dynamics and phase morphology. The combination of these findings highlights the tunable nature of PLA/PCL systems through compositional control. This work bridges current gaps in understanding multiphase biopolymer systems by integrating diverse analytical approaches. The resulting materials exhibit properties ideal for additive manufacturing, shape memory behavior, and other advanced applications. Overall, the study contributes valuable knowledge for designing environmentally friendly, high-performance polymer blends.

Keywords: biopolymer blends, phase separation, rheological characterization, thermal analysis

Acknowledgments
This study was done with the financial support of the European Union—Next GenerationEU within the Project No. BG-RRP-2.011-0001-C01.

References

[1] Ivanov, E.; Kotsilkova, R.; Georgiev, V.; Batakliev, T.; Angelov, V. Advanced Rheological, Dynamic Mechanical and Thermal Characterization of Phase-Separation Behavior of PLA/PCL Blends. *J. Manuf. Mater. Process* **2025**, 9, 1-19.

Graphene-reinforced PVDF Nanocomposites with Enhanced Electrical Conductivity via Controlled 3D Printing

V. Georgiev[1], R. Kotsilkova[1], V. Angelov[1], S. Stoyanova[1], M. Aleksandrova[2], T. Tsanev[2], R. Tomov[2], G. Kolev[2]

[1] *Institute of Mechanics - Bulgarian Academy of Sciences, Sofia, Bulgaria*
[2] *Technical University of Sofia, Dept. of Microelectronics, Sofia, Bulgaria*

This study provides a comprehensive analysis of the thermal and electrical properties of poly(vinylidene fluoride) (PVDF) and its nanocomposite reinforced with 6 weight percent graphene nanoplatelets (GNP). The primary objective is to elucidate how the incorporation of GNP affects the material's overall performance, with particular attention to its suitability for thermal and electronic applications. The research is driven by the growing demand for advanced materials in additive manufacturing, especially for 3D printing technologies that require enhanced thermal stability and electrical conductivity.

Electrical conductivity tests revealed a pronounced influence of the printing orientation on the material's performance. The GNP/PVDF nanocomposite exhibited its highest electrical conductivity, reaching 98 S/m, when printed in a parallel orientation relative to the current flow (3DP 0°). This value decreased to 67 S/m at a 45° orientation and further dropped to 62 S/m when printed at 90°, indicating that the alignment of the material during the printing process plays a critical role in determining its electrical efficiency.

Joule heating experiments further demonstrated the material’s capability for efficient resistive heating. When a voltage of 2 V was applied in the parallel configuration, the composite achieved a maximum surface temperature of approximately 65 °C. Moreover, the repeatability of the heating performance was confirmed through multiple cycles of heating and cooling, with consistent peak temperatures recorded across all trials, suggesting excellent reliability and thermal response consistency.

Heat flow analysis provided additional insights, showing a linear decline in thermal diffusivity as temperature increased. At the same time, thermal conductivity was found to be highest in the parallel orientation due to the more effective alignment of the graphene nanoplatelets along the direction of heat transfer, which facilitated improved thermal pathways.

In conclusion, the findings from this study highlight the significant improvements in thermal stability, orientation-dependent electrical conductivity, and Joule heating efficiency achieved through the addition of GNP to PVDF. These enhanced properties position the GNP-reinforced PVDF nanocomposite as a highly promising material for next-generation applications in 3D printed electronics and thermal management systems.

Keywords: polymer composites, 3D printing, graphene

Acknowledgments

The authors would like to express their sincere gratitude to the Bulgarian National Science Found (BNSF) under Grant No. KP-06-H77/4.

Tensile testing performance and shape memory effect of melt extruded PLA/PCL blends

T. Batakliev[1*], V. Georgiev[1], E. Ivanov[1], V. Angelov[1], R. Kotsilkova[1], Adam Strachota[2]

[1] *Open Laboratory on Experimental Micro and Nano Mechanics (OLEM), Institute of Mechanics, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. Block 4, 1113 Sofia, Bulgaria*
[2] *Institute of Macromolecular Chemistry of the Czech Academy of Sciences, Heyrovského nám. 2, 162 00 Praha 6, Czech Republic*
**Corresponding Author's E-mail address: todorbat@gmail.com*

The current investigation is focused on the mixing of two green polymers at several definite ratios which has resulted in the manufacturing of biodegradable polylactic acid (PLA)/polycaprolactone (PCL) blends with outstanding macromechanical and shape memory properties. A range of non-compatibilized polymer compositions were prepared by using a twin screw melt extrusion technique allowing a homogeneous dispersion of the PCL droplets in the PLA matrix and boosting the interfacial adhesion between the two phases. The macromechanical behavior of the samples was explored by tensile experiments applying three distinct crosshead motion speeds. It has been discovered that the presence of PCL as soft segment contributed to an increment of toughness and elongation at ultimate strength of the polymer composite at expense of the maximum tensile stress and Young's modulus. The strength-stiffness related parameters were found to be more sensitive, in terms of getting to higher values, to the weight content of PLA as hard segment in the polymer blend. Performing of thermally-induced shape memory tests revealed an exceptional reversibility between the temporary and permanent states of the composite materials including impressive shape fixation (R_f) and shape recovery (R_r) rates. SEM analysis of the PLA/PCL compositions unveiled an apparent phase-separated microstructure approving the immiscibility of the two polymers in the blend (Fig. 1).

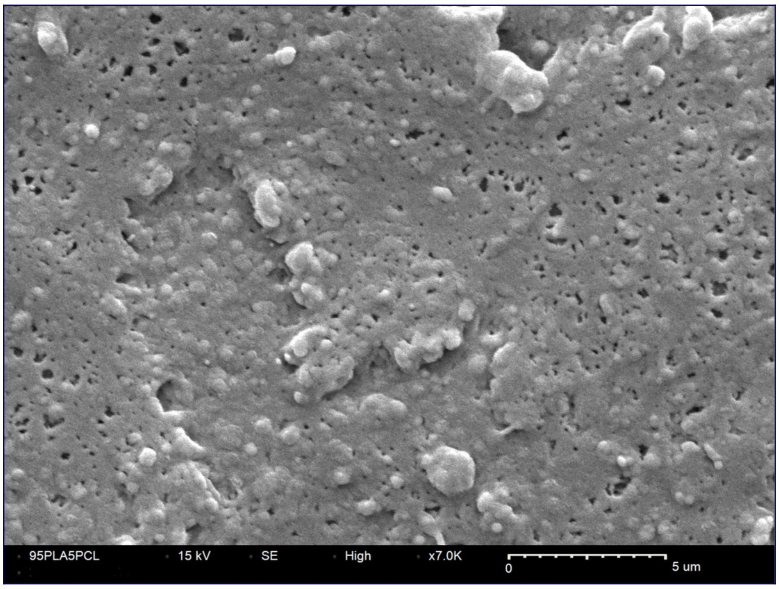


Figure 1. SEM image of melt extruded polymer blend

Keywords: biodegradable polymer blends; tensile testing; shape memory effect

Acknowledgments
This study was done with the financial support of the European Union—Next GenerationEU within the Project No. BG-RRP-2.011-0001-C01. The authors are grateful for the financial contribution from the Bulgarian Academy of Sciences (Bilateral grant agreement between BAS and CAS) under the Project IC-CZ/01/2025-2026.

AFM-Imaging of sectioned 3D-printed Polymer-Polymer Interfaces

D. Schmiedjell[1*], C. Angerer[1], D. Schäffl[1], S. Hild[1]
[1]*Institute of Polymer Science (Johannes Kepler University), Linz, Austria*
[*]*david.schmiedjell@jku.at*

Additive Manufacturing (AM) has rapidly become a prominent technology for applications ranging from high-end uses like aerospace engineering and medicine, to consumer products. One of the most widely used AM techniques is Fused Deposition Modeling (FDM). In FDM thermoplastics are molten and deposited on top of each other in layers. This enables the user to create layer-composite materials allowing optimization of properties such as stiffness and flexibility. [1, 2] However, a major challenge for products created with FDM is the failure of adhesion between print-layers, causing delamination. Adhesion between polymer layers has been described using various mechanisms: physical or chemical bonding, as well as interdiffusion, which is generally considered the most important mechanism [3]. Interdiffusion occurs when two molten polymers are brought into contact. After the initial wetting, mobile polymer chains can move across the interface, creating an interdiffusion region at the polymer interface, which greatly influences the strength of the layer-layer bond [3, 4]. The resulting layer adhesion has been studied extensively on a macroscopic scale, focusing on tensile and bending tests. However, very little research has been done to characterize the layer-layer interface at the microscopic level. Atomic Force Microscopy (AFM) is a microscopy technique based on the interactions between a fine probe tip and the sample surface. It can detect changes in material properties at a nanoscopic resolution. Thus, variation in the composition of the interdiffusion layer can be analyzed due to changes in chemical or mechanical applying the respective AFM techniques, such as phase imaging or contact stiffness.

This study uses AFM techniques to investigate the nature of the contact-region between adjacent layers in layer composites consisting of commonly 3D printed thermoplastics, such as PETG, TPU, and ABS. In order to maximize contact area and optimize conditions for interdiffusion, the polymers were printed on top of each other in parallel lines at elevated bed temperatures. The printed TPU/ABS and TPU/PETG samples were subsequently sectioned using a microtome until a sufficiently smooth surface, perpendicular to the interface, was exposed. The remaining cutting artifacts on the surface were usually well below 100 nm deep.

At first, the polished surfaces are analyzed with regard to topography using the intermittent contact technique. Simultaneous phase imaging can provide the first indications of the formation of an internal diffusion layer. Material sensitive techniques such as friction, stiffness, and adhesion force imaging showed an abrupt change of these properties at the interface, instead of an expected gradual shift from one bulk material to the other. As such it can be said that no significant interdiffusion region could be found in the analyzed samples, suggesting other adhesion mechanisms are dominant in multi-material FDM. Future experiments will investigate the effects of post-print annealing as well as compare results with other techniques such as confocal Raman microscopy.

Keywords: Additive Manufacturing, Atomic Force Microscopy, Material Testing, Composite Materials

References

[1] Rafiee, M.; Farahani, R.D.; Therriault, D. Multi-Material 3D and 4D Printing: A Survey. *Advanced science* **2020**, *7*, 1902307.

[2] Eyri, B.; Gul, O.; Yilmaz, S.; Karsli, N.G.; Yilmaz, T. Characterization of ABS / PETG multi-material composites 3D printed by print-pause-print method. *Polymer Engineering & Sci* **2025**, 1-17.

[3] Leimhofer, C.; Hammer, A.; Roland, W.; Dollberger, S.; Ehrmann, T.; Berger-Weber, G.; Hild, S. Investigation of interdiffusion between compatible polymers under static and co-extrusion processing conditions. *J of Applied Polymer Sci* **2023**, 140.

[4] Yin, J.; Lu, C.; Fu, J.; Huang, Y.; Zheng, Y. Interfacial bonding during multi-material fused deposition modeling (FDM) process due to inter-molecular diffusion. *Materials & Design* **2018**, *150*, 104–112.

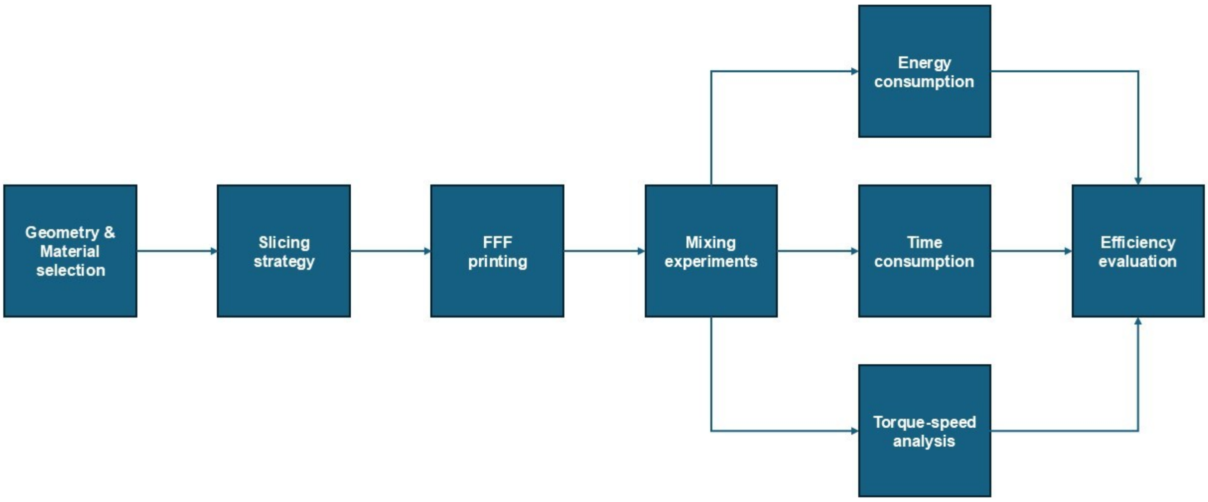
Process Characterization of Additively Manufactured Stirrer Geometries for bioprocessing of non-Newtonian media

Author's names Doris Ostner-Kaineder,[1] Christoph Strasser,[1] Christoph Burgstaller,[1,2]

[1]Transfercenter für Kunststofftechnik GmbH, Additive Manufacturing, Wels, Austria
[2]University of Applied Science Upper Austria R&D-GmbH, Materials, Wels, Austria
**doris.ostner-kaineder@tckt.at*

Conventional methods of blended textiles waste recycling present significant challenges. An alternative strategy involves the biocatalytic separation of waste components through enzymatic hydrolysis of the cellulose fraction. This approach enables the recovery of a processable polyester product and the generation of a glucose-rich solution as a valuable secondary output. Particles in buffer solutions have complex flow behavior which makes it essential to use substrate specific, optimized stirrer geometries to maximize the mixing efficiency. The influencing variables are divided into material-specific (particle size, weight-specific surface area, chemical composition, etc.) and process-specific (stirrer speed, stirrer geometry, stirring strategy, reactor geometry, etc.). Material-specific factors have been previously investigated, which is why this study focused on the process-specific influencing variables, taking mixing efficiency over energy consumption into account.

In this study, various stirrer geometries were manufactured by FFF and characterized for their mixing efficiency. The data was recorded by measuring the motors current and voltage, the torque/speed curve and a computer assisted imaging analysis of mixing. Each geometry was evaluated at varying impeller speeds (20–180 rpm) and solid content (1-3 wt.%) at constant fluid volume of 1.5 liters to assess torque behavior and energy input. The global mixing time was evaluated at 3 wt.% and 180 rpm.


Geometry & Material selection

Slicing strategy

FFF printing

Mixing experiments

Energy consumption

Time consumption

Torque-speed analysis

Efficiency evaluation

Highly efficient reinforcement by titanate (TiNT) nanotubes, achieved by a novel route to their ultra-fine dispersion in epoxy nanocomposites

Silvia Mares Barbosa[1*], Adam Strachota[1], Beata Strachota[1], Ewa Pavlova[1], Magdalena Konefał[1]

[1]*Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, 162 00 Praha 6, Czech Republic*
[*]*(maresbarbosa@imc.cas.cz)*

Titanate nanotubes (TiNTs) offer a cheap alternative to carbon nanotubes (CNTs) as a high-performance fibrous (1D) nanofiller. Very attractive is the TiNT surface covered by OH groups: It offers strong hydrogen bonding and easy chemical modification/functionalization. Moreover, the hydrothermal synthesis of TiNTs [1] is simple and readily scalable, which is favorable for potential industrial applications.

TiNTs were studied mainly in view of their (photo)catalytic, photoelectric, and ion-exchanging properties, combined with bio-compatibility, which opens potential applications in (photo)catalysis, pollutant degradation, membranes, gas- and pH sensors, batteries, dental implants, or drug carriers [2-4].

In view of the excellent strength of TiNTs, their use as reinforcing phase in nanocomposites also was explored. Here, the main challenge was the prevention of TiNT agglomeration. An early solution was the surface-modification of TiNTs, see e.g. [5,6]. A notable reinforcement was achieved in these earlier works, but the effect was smaller than theoretically expected. All the previous studies employed freeze-drying to obtain neat TiNTs (removal of water, which was the solvent during synthesis).

However, the authors observed in their unpublished previous work, that even thoroughly surface-modified TiNTs irreversibly agglomerate after drying. This becomes visible upon their repeated dispersion in water.

In order to systematically eliminate the TiNTs agglomeration, the authors designed a new procedure of TiNTs incorporation into polymer matrixes, which altogether avoids the freeze-drying step: A solvent exchange technique was used in order to transfer precisely controlled amounts of TiNT, from a stable and storable aqueous dispersion into a reasonably stable water-free organic suspension in the monomer(s).

The tested epoxy matrixes were based on diglycidyl ether of bisphenol A (DGEBA), cured by polypropylene oxide α,ω-diamine (MW: 230, 400, and 2000 g/mol). To demonstrate the efficiency of the new approach, TiNT with no surface modification was dispersed as the nanofiller (at 1, 3, and 5 wt.% loading).

Ash analysis confirmed a good control over the filler content, while the transmission electron microscopy (TEM) proved the preservation of the nanotubes, as well as their excellent dispersion, with remarkably suppressed agglomeration.

Albeit the matrix-filler interactions were just physical, namely hydrogen bonding between TiNTs and the polymer chains, they led to an unprecedentedly strong reinforcement of the polymers: The moduli were increased by ca. 1 order of magnitude at the highest TiNT content, as observed by dynamic-mechanical thermal analysis (DMTA). The reinforcement was the highest in the most densely crosslinked matrixes, due to more efficient load transfer.

Keywords: Nanocomposite, epoxy, titanate nanotube.

Acknowledgments

The authors would like to thank the Czech Academy of Sciences, grant No. BAS-25-03 for the financial support of this work, as well as Martina Nevoralová for TGA analyses and Zuzana Kálalová for elemental analyses.

References

[1] Kasuga, T. et al. Langmuir **1998**, 14, 3160−3163.
[2] Bavykin, D. V. et al. Adv. Mater. **2006**, 18, 2807−2824.
[3] Kordas, K. et al. Transl. Mater. Res. **2015**, 2 (1), 015003.
[4] Saker, R. et al. Pharmaceutics **2024**, 16, #635.
[5] Zimmermann, B. et al. Nanotechnology **2014**, 25 (43), #435601.
[6] Beneš, H. et al. Macromolecules **2018**, 51 (15), 5989–6002.

Microplastic Formation During Weathering of Wood Plastic Composites and the Effect of Additives

E. Kuka [1], L.O. Vasiljevs [1,2,*], D. Cirule [1], I. Andersone [1], E. Sansonetti [1], R. Zabarovska [1,2], E. Gulevska [1,3], B. Andersons [1]

[1] Laboratory of Wood Degradation and Protection, Latvian State Institute of Wood Chemistry, Riga, Latvia
[2] Faculty of Chemistry, University of Latvia, Riga, Latvia
[3] Faculty of Natural Sciences and Technology, Riga Technical University, Riga, Latvia
*[*lotars07@gmail.com](mailto:lotars07@gmail.com)*

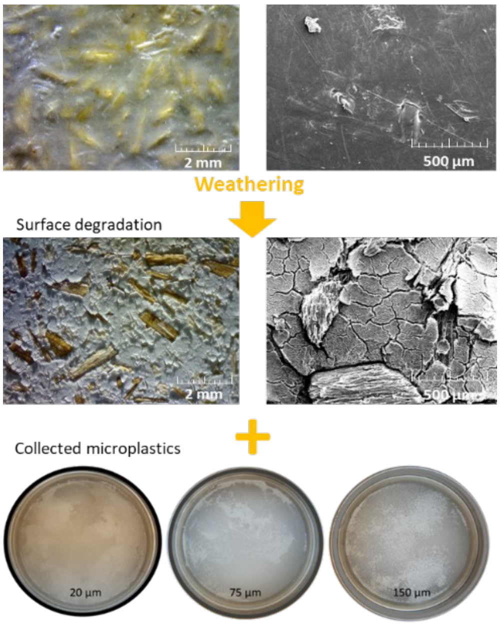


Figure 1: Weathering of wood plastic composite (without additives) and resulting surface degradation with microplastic release collected on sieves.

Wood plastic composites are widely used in construction, automotive, furniture, and consumer products, particularly in North America and Asia. They are also becoming increasingly popular in Europe. The market for WPCs is expected to continue to grow in the coming years, driven by their sustainability, durability, and versatility [1]. However, one important sustainability aspect of these materials has not been studied: microplastics (MPs). The tiny plastic pieces have been recognized as a serious threat by various organisations, and WPCs can be a potential source considering that they are mainly used in outdoor applications where UV radiation can cause sevear degradation [2]. The presented study uses a unique process design specifically developed to quantify the mass of MPs formed during artificial weathering of plastic-based materials. The process is based on a QUV accelerated weathering tester, which was accordingly modified to enable collection of MPs. All WPCs used in the study consisted of recycled polypropylene and wood particles (60:40 by mass). To evaluate if and to what extent additives can affect the release of MPs, five types of additives (coupling agent, antioxidant, pigment, UV absorber and UV stabilizer) were added according to the manufacturer's recommendations. The results showed that without additives, the WPCs released 4.4 g/m^2 of MPs (> 20 µm) during 1 month of artificial weathering. This was due to the surface erosion caused by photodegradation of the plastic matrix, as indicated by both the exposed wood particles and the collected MPs (Figure 1). The formation of MPs was significantly reduced/delayed by the used additives. UV absorber and UV stabilizer were the most effective reducing the amount of MPs by around 80 %. Other additives also had an effect. The improvement was also clearly visible on the surface of the WPCs showing less signs of degradation when analysed by SEM, FTIR and contact angle goniometer. The study reveals that MPs can be released from WPCs, but this process higly depends on the composition.

Keywords: microplastics, wood plastic composites, polypropylene, additives, weathering, degradation, surface erosion, protection.

Acknowledgments

This research is funded by the Latvian Council of Science project MicroWPC, project No lzp-2022/1–0639.

References

[1] Maximize Market Research (**2024**), Wood Plastic Composites Market – Global Industry Analysis and Forecast (2023-2029).

[2] Vasiljevs, L.O., Zabarovska, R., Gulevska, E., Cirule, D., Sansonetti, E., Andersone, I., Andersons, B., Kajaks, J., Kuka, E. Changes in Wood Plastic Composite Properties After Natural Weathering and Potential Microplastic Formation, *Forests* **2024**, 15, 2102.

Synthesis and applications of metallaboroxine polymers as hydrophobic thin films

R. Jambor[1], M. Srb[1], M. Novák[2], Š. Podzimek[2]

[1] *Department of General and Inorganic Chemistry, Faculty of Chemical Technology,*
University of Pardubice, Czech Republic, Studentská 573, 532 10 Pardubice 2, Czechia
[2] *Institute of Chemistry and Technology of Macromolecular Materials, , Faculty of Chemical Technology,*
University of Pardubice, Czech Republic, Studentská 573, 532 10 Pardubice 2, Czechia

In the current context of green chemistry, there is a growing pressure to find new non-fluorinated alternatives of hydrophobic polymers and thus seeking of new hydrophobic polymers is thus hot topic.[1] Here we present synthesis and applications of new polymers based on metallaboroxines. These materials were found as good film forming materials and thus these polymers were used for the preparation of thin layer by spin coating at Si, SiO_2 and polyethylene surfaces. The layers were characterized by the help of SEM, VASE, XRF, UV-VIS spectroscopy and finally their WCA were determined.

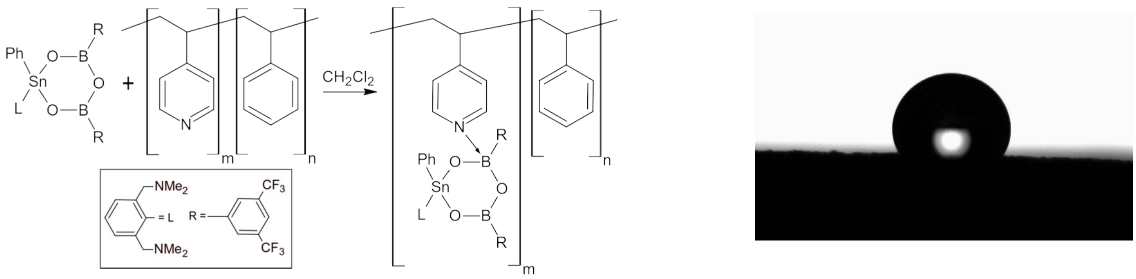


Figure 1 Example of new metallaboroxine based hydrophobic polymer with WCA 125°

Keywords: heteroboroxines, thin layers, hydrophobicity

Acknowledgments

We are grateful for the support of this research by the Czech Science Foundation (GA23-06548S).

References

[1] Li X., Li B., Li Y., Sun J., Chem. Engineering J. 404: 126504-126512, 2021

Hydrophobic heteroboroxine-polydimethylsiloxane thin layers

M. Srb[1], R. Jambor[1], M. Novák[2], Š. Podzimek[2]

[1] *Department of General and Inorganic Chemistry, Faculty of Chemical Technology,*
University of Pardubice, Czech Republic, Studentská 573, 532 10 Pardubice 2, Czechia
[2] *Institute of Chemistry and Technology of Macromolecular Materials, , Faculty of Chemical Technology,*
University of Pardubice, Czech Republic, Studentská 573, 532 10 Pardubice 2, Czechia

Polydimethylsiloxanes (PDMS) can form hydrophobic thin layers with water contact angles (WCAs) of up to 115°. We modified aminopropyl-terminated polydimethylsiloxanes (with four different molar masses) using gallium- and tin-based heteroboroxines via a Schiff base coupling reaction. The resulting compounds were spin-coated onto three substrates (silicon, glass, and polyethylene), and their hydrophobicity was evaluated by WCA measurements.

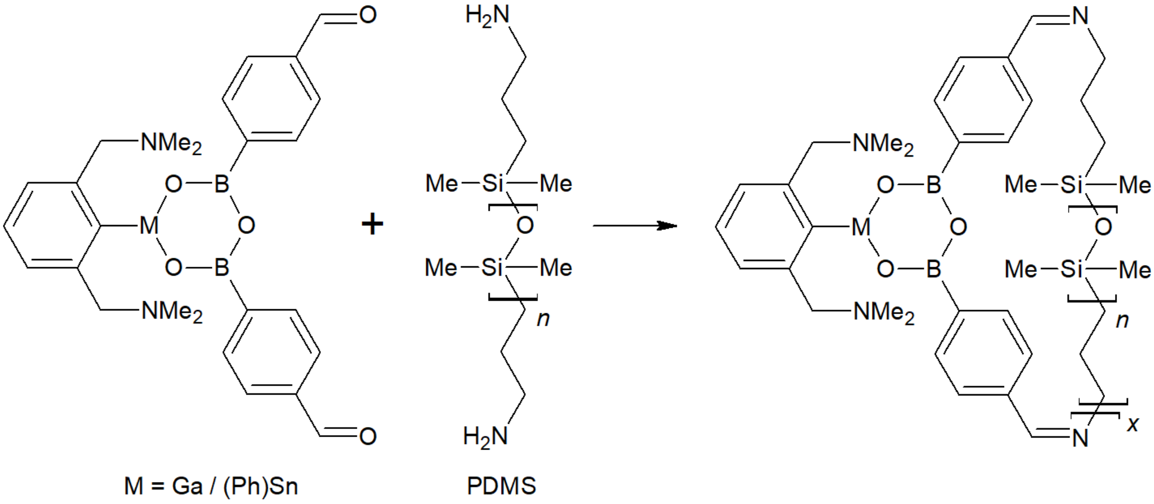


Figure 1 Preparation of heteroboroxine-polydimethylsiloxane polymers

Table 1 Selected WCAs on heteroboroxine-PDMS thin layers on three substrates spin-coated from CH_2Cl_2 solution with concentration 50 g.l^{-1}

M	M$_w$ (PDMS)	silicon substrate	glass substrate	polyethylene substrate		M	M$_w$ (PDMS)	silicon substrate	glass substrate	polyethylene substrate
—	1000000	113°	107°	104°		—	1000000	113°	107°	104°
Ga	900	97°	100°	120°		Sn	900	101°	104°	125°
Ga	3000	105°	102°	118°		Sn	3000	130°	128°	130°
Ga	5000	116°	117°	134°		Sn	5000	109°	108°	126°
Ga	27000	112°	111°	130°		Sn	27000	107°	115°	125°

Keywords: heteroboroxines, thin layers, hydrophobicity

Acknowledgments

We are grateful for the support of this research by the Czech Science Foundation. (GA23-06548S).

Tracking of polymer brush functionalization at the nanoscale

Anna Kiełbasa[1,2]*, Aswathy Sajeevan[1], Szczepan Zapotoczny[1]
[1]*Faculty of Chemistry, Jagiellonian University, Gronostajowa St 2, PL30387 Krakow, Poland*
[2]*Doctoral School of Exact and Natural Sciences Jagiellonian University, Prof. St. Łojasiewicza St 11, PL30348, Cracow, Poland*
**anna.kielbasa@doctoral.uj.edu.pl*

Surface-grafted polymer brushes are utilized in a variety of biomedical applications, including enzyme immobilization, controlled drug release and delivery, biosensing, bioimaging, and enhancing cell adhesion and proliferation. Their effectiveness stems from their highly ordered three-dimensional architecture, the conformational freedom of the surface-grafted macromolecules, and a high density of functional groups, which allow for further modification and bioconjugation.[1],[2]

Creating advanced biomaterials based on polymer brushes often requires the strategic attachment of various functional groups through a multi-step process. To accurately position these functional groups within layers that are only a few dozen nanometres thick, optimized synthetic conditions are necessary, as well as precise instrumental techniques capable of monitoring modifications at the nanoscale. This can be accomplished by combining several complementary microscopic and spectroscopic methods.

This work aims to highlight the effectiveness of employing techniques such as atomic force microscopy (AFM), scattering-type infrared scanning near-field optical microscopy (sSNOM), grazing-angle infrared spectroscopy (GA-FTIR), and spectral ellipsometry (SE) in a complementary manner. Collectively, these methods will offer invaluable insights into the modification chemistry of polymer brushes, setting the stage for the development of advanced structures for biomedical applications.

Keywords: polymer brushes, AFM, sSNOM

Acknowledgments

The research has been supported by a grant from the Priority Research Area Research Support Module under the Strategic Programme Excellence Initiative at Jagiellonian University.
Research funded by the Polish Science Fund within the framework of the Virtual Research Institute.

References

[1] Qu, Z.; Xu, H.; Gu, H. Synthesis and Biomedical Applications of Poly ((meth) acrylic acid) Brushes. *ACS Applied Materials & Interfaces* **2015**, *7*(27), 14537-14551.

[2] Kiełbasa, A;, Kowalczyk, K.; Chajec-Gierczak, K.; Bała, J.; Zapotoczny, S. Applications of surface-grafted polymer brushes with various architectures. *Polymers for Advanced Technologies* **2024**, *35*(4), e6397.

Riboflavin – naturally derived photocatalyst for polymer nanobrushes synthesis

J. Bała[1, 2*], I. Zaborniak[3], S. Zapotoczny[1], P. Chmielarz[3], K. Wolski[1]

[1]*Department of Physical Chemistry and Electrochemistry, Jagiellonian University, Cracow, Poland*
[2]*Doctoral School of Exact and Natural Sciences, Jagiellonian University, Cracow, Poland*
[3] *Department of Physical Chemistry, Rzeszow University of Technology, Rzeszow, Poland*
[*] *justyna.bala@doctoral.uj.edu.pl*

Atom transfer radical polymerization (ATRP) is one of the most effective, widely used and versatile RDRP (reversible deactivation radical polymerization) techniques for the synthesis of complex functional polymeric materials with a wide range of properties, including polymer brushes. However, in its classical approach, it is mediated by transition metals, whose toxic residue contamination remains a challenge in the context of material purification and utilization, especially in microelectronic and biomedical applications. Developing more environmentally friendly techniques without compromising precise, controlled synthesis of well-defined polymers with tailored and diverse topologies contributed to the discovery of organocatalyzed ATRP (O-ATRP). This light-induced technique uses organic-based photocatalysts to mediate polymerization *via* an ATRP mechanism. It is very promising in terms of the scalability and preparation of complex three-dimensional patterned polymer surfaces under mild reaction conditions. Currently, considerable attention in O-ATRP is focused on the development of efficient, low-cost and widely available photocatalysts.

In this work, we demonstrate the use of naturally derived riboflavin (RF) and modified riboflavin molecule (modRF) as a photocatalyst in surface-initiated O-ATRP for the synthesis of polymer brushes from flat model substrates. During the research, a series of visible light-mediated (λ_{max} = 450 nm) polymerizations were performed in a simple, cost-effective, and environmentally friendly approach. Reaction setup includes only three components – monomer, photocatalyst and solvent. Due to the poor solubility of RF in organic solvents, the substitution of hydroxyl groups in the ribitol tail was performed. The obtained in this way modRF photocatalyst made it possible to limit side reactions during SI-O-ATRP while preserving the photoredox properties similar to unmodified RF. A significant advantage of the proposed method is ppm-level concentrations of photocatalyst, which are sufficient to obtain polymer brushes. It is also worth emphasizing that initiation efficiency could be enhanced by changing the structure of the surface-tethered initiator, which consequently improves the polymer layers in terms of thickness and quality. The obtained materials were characterized by Ellipsometry, Atomic Force Microscopy (AFM) and Grazing-Angle Fourier-Transform Infrared Spectroscopy.

Keywords: polymer brush, photocatalyst, O-ATRP, riboflavin

Acknowledgments
The authors would like to acknowledge the National Science Centre in Poland for the financial support within the SONATA BIS 10 project (nr UMO-2020/38/E/ST4/00046).

Poster/ Poly(γ-benzyl-L-glutamate) based nanofibrous membranes as scaffolds for RPE cell cultivation

M. Souibgui[1]*, V. Cimrová[1], J. Hodan[1], O. Pop-Georgievski[1], Z. Moravkova[1], Y. Nemesh[2], Z. Ellederová[2], V. Proks[1], H. Studenovska[1]*

[1]Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovský Sq 2, Prague 6, 162 00, Czech Republic
[2]Institute of Animal Physiology and Genetics, Czech Academy of Sciences, Rumburská 89, Liběchov, 277 21, Czech Republic
**souibgui@imc.cas.cz, studenovska@imc.cas.cz*

This study focuses on the development of ultrathin electrospun membranes made from poly(γ-benzyl-L-glutamate) (PBLG) designed to support the growth of retinal pigment epithelial (RPE) cells.[1] The fabricated PBLG-based nanofibrous membranes (PBLG-NfMs) possess an average thickness of around 5.1 µm, with fibers averaging 0.5 µm in diameter, exhibiting isotropic orientation, high porosity, and large pore sizes. These structural characteristics were specifically tailored to optimize nutrient diffusion and enhance cell survival. The membranes also demonstrated excellent optical clarity and mechanical robustness, ensuring their suitability for potential surgical applications. To improve cellular attachment, the surface of the membranes was functionalized with fibronectin. In vitro culture of RPE cells on these membranes revealed favorable outcomes, including high cell viability, adhesion, and proliferation. Immunostaining results confirmed the preservation of the epithelial phenotype, with expression of key markers such as zonula occludens-1 (ZO-1) for tight junction formation, and RPE65 for RPE-specific metabolic function. These findings underscore the potential of PBLG-NfMs as an effective biomaterial for retinal tissue engineering.

Keywords: Poly(γ-benzyl-L-glutamate), Electrospinning, Nanofibrous membrane, Fibronectin, Cells cultivation, Tissue engineering.

Acknowledgments
The work was supported by the European Regional Development Fund (Grant No. CZ.02.01.01/00/22_008/0004562 Project "Excellence in Regenerative Medicine").

References

[1] Souibgui, M.; Morávková, Z.; Georgievski, O. P.; Hodan, J.; Thottappali, M. A.; Cimrová, V.; Dvořáková, J.; Proks, V.; Studenovska, H. Ultrathin electrospun nanofibrous membranes based on poly(γ-benzyl-L-glutamate). The Journal of Chemical Physics 2024, 161 (23). DOI: 10.1063/5.0238633.

Characterisation of hydrogels with agomelatine as a coating for 3D printed transdermal drug delivery systems

A.B. Nowicka[1*], T. Banaszek[1], W. Kuczko[2], R. Wichniarek[2], D. Tomczak[3], M. Wojtyłko[4], A. Froelich[4], B. Jadach[4], T. Osmałek[4], M. Szybowicz[1]
[1]Faculty of Materials Engineering and Technical Physics, Poznan University of Technology, Poznan, Poland
[2]Faculty of Mechanical Engineering, Poznan University of Technology, Poznan,Poland
[3]Institute of Chemical Technology and Engineering, Poznan University of Technology, Poznan, Poland
[4]Department of Pharmaceutical Technology, Poznan University of Medical Sciences, Poznan, Poland
******ariadna.nowicka@put.poznan.pl*

Agomelatine (AGM) is an atipical antidepressant drug approved for use in the European Union in 2009.
It acts on melatonin and serotonin receptors. The drug is effective in both the acute and continuation phases of depression treatment and is also used in the treatment of anxiety disorders [1]. Currently, AGM is only administered in tablet form and has a low bioavailability <5% [2]. Recently, the concept of using a transdermal route of administration has emerged to increase the bioavailability of AGMs [3,4]. The use of the transdermal route prevents drug degradation in the gastrointestinal tract and first-pass effects in the liver and may maintain therapeutic levels of the drug [3]. Microneedles can be used to deliver the drug to the dermis, where it can enter the systemic circulation through small vessels and make drug delivery more efficient [5].
Raman spectroscopy is a nondestructive, highly sensitive analytical technique that does not require special preparation of the sample. This makes it an increasingly popular tool in the pharmaceutical industry used e.g. to identify active substances, excipients and polymorphic forms, as well as for the distribution of substances in the final drug formulation [6].
The main aim of the present study was to characterise two types of gels (with and without ethanol) for application to the skin. Differences between ethanol gels and AGM-containing suspensions were noted [7]. Micro-needle systems obtained using various 3D printing techniques will also be presented.

Keywords: agomelatine-loaded hydrogels, Raman spectrtroscopy, 3d printing, microneedel

Acknowledgments
The work was performed as a result of the research project no.2021/42/E/NZ7/00125 (ID: 526262) financed by the National Science Centre (Poland)

References

[1] Demyttenaere, K. Agomelatine: A narrative review. *European Neuropsychopharmacology*, **2011**, 21, S703-S709.
[2] Green, B. Focus on agomelatine. *Curr. Med. Res. Opin*. **2011**, 27, 745–749.
[3] Said, M.; Elsayed, I.; Aboelwafa, A.A.; Elshafeey, A.H. Transdermal agomelatine microemulsion gel: Pyramidal screening, statistical optimization and in vivo bioavailability. *Drug Deliv***. 2017**, 24, 1159–1169.
[4] Shinde, M.; Bali, N.; Rathod, S.; Karemore, M.; Salve, P. Effect of binary combinations of solvent systems on permeability profiling of pure agomelatine across rat skin: A comparative study with statistically optimized polymeric nanoparticles. *Drug Dev. Ind. Pharm*. **2020**, 46, 826–845.
[5] Wojtyłko, M.; Froelich, A.; Jadach, B.; Szybowicz, M.; Nowicka, A.; Osmałek, T. Chapter 8 - 3D printed microneedle patches for painless drug delivery, Editor(s): Dimitrios A. Lamprou, Dimitrios G. Fatouros, *Fundamentals and future trends of 3D printing in drug delivery*,Academic Press, **2025**, 185-206.
[6] Shah, K.C.; Shah, M.B.; Solanki, S.J.; Makwana, V.D.; Sureja, D.K.; Gajjar, A.K.; Bodiwala,K.B.; Dhameliya,T.M. Recent advancements and applications of Raman spectroscopy in pharmaceutical analysis, *Journal of Molecular Structure*, **2023,** 1278,134914.
[7] Wojtyłko, M.; Nowicka, A.B.; Froelich, A.; Szybowicz, M.; Banaszek, T.; Tomczak, D.; Kuczko, W.; Wichniarek, R.; Budnik, I.; Jadach, B.; Kordyl, O., Białek, A., Krysztofiak, J., Osmałek, T., & Lamprou, D. A. Characteristics of Hydrogels as a Coating for Microneedle Transdermal Delivery Systems with Agomelatine. *Molecules* **2025**, 30, 322.

Mechanical Properties of Photocurable Resin with Added Solvents

D. Tomczak[1], W. Kuczko[2], A. B. Nowicka[3], T. Osmałek[4], M. Wojtyłko[4], R. Wichniarek[2],
M. Szybowicz[3]

[1]Institute of Chemical Technology and Engineering, Poznan University of Technology, Berdychowo 4,
60-965 Poznan, Poland
[2]Faculty of Mechanical Engineering, Poznan University of Technology, Piotrowo 3,
61-138 Poznan, Poland
[3]Faculty of Materials Engineering and Technical Physics, Poznan University of Technology, Piotrowo 3,
60-965 Poznan, Poland
[4]Chair and Department of Pharmaceutical Technology, Poznan University of Medical Sciences, Rokietnicka 3,
60-806 Poznan, Poland
**dorota.tomczak@doctorate.put.poznan.pl*

Products obtained by VAT photopolymerisation 3D printing have many advantages, such as speed of production, possibility of obtaining complex shapes, high resolution or low price. The masked stereolithography technique (MSLA), one of the VAT 3D printing methods, makes it possible to obtain complex parts in terms of both geometry and chemical composition, thanks to the use of liquid resin. With the selection of suitable substances, it is possible to obtain composite materials [1], including composite elements used in pharmacy with controlled release of an active pharmaceutical ingredient (API) [2]. Due to the diverse properties of available APIs, it is often necessary to use cosolvents to incorporate the API into the resin, such as alcohols or acetone. The presence of cosolvents affects the properties of the finished products, including mechanical properties [3]. The aim of this work was to compare the effects of two different alcohols, ethanol and isopropanol, which can be used as cosolvents on the properties of acrylic-urethane resin, including hardness and tensile strength. For this purpose, samples were prepared from pure resin, with the addition of 10% ethanol and 10% isopropanol. The samples obtained were subjected to a static tensile test, whereby the elastic modulus, tensile strength and relative elongation were determined. Hardness was determined using a Shore D hardness tester. The samples were tested one week after manufacture. The results obtained show a deterioration in the mechanical properties of the samples with solvent addition, but they are still satisfactory in terms of potential applications. It was shown that the properties of samples with ethanol addition are slightly better than those of samples with isopropanol at a solvent content of 10%. The study therefore opens up new avenues of research related to the use of different cosolvents allowing the introduction of a wide range of APIs into photocurable resins to obtain controlled-release composites.

Keywords: Masked Stereolitography, Photopolymerisation, Cosolvent, Solvent, Mechanical Properties, Active Pharmaceutical Ingredient

Acknowledgments
The work was performed as a result of the research project no. 2021/42/E/NZ7/00125 (ID: 526262) financed by the National Science Centre (Poland).

References

[1] Shah, D.M.; Morris, J.; Plaisted, T.A.; Amirkhizi, A.V.; Hansen, C.J. Highly filled resins for DLP-based printing of low density, high modulus materials. Addit. Manuf. 2021, 37, 101736.
[2] Lim, S.H.; Kathuria, H.; Bin Amir, M.H.; Zhang, X.; Duong, H.T.; Ho, P.C.L.; Kang, L. High resolution photopolymer for 3D printing of personalised microneedle for transdermal delivery of anti-wrinkle small peptide. J. Control. Release 2021, 329, 907–918.
[3] Tomczak, D.; Kuczko, W.; Nowicka, A.B.; Osmałek, T.; Szybowicz, M.; Wojtyłko, M.; Wichniarek, R. Evaluation of the Effect of Ethanol on the Properties of Acrylic-Urethane Samples Processed by Vat Photopolymerization. Appl. Sci. 2024, 14, 5875.

Thermosensitive Poly (N-isopropylacrylamide) Hydrogel for Wound Healing Dressing

M. Q. Yang, Y. H. Ho, K. C. Cheng

Department of Chemical Engineering and Biotechnology,
National Taipei University of Technology, Taipei, 106, Taiwan
**gordon@mail.ntut.edu.tw*

Thermosensitive poly (N-isopropylacrylamide) (PNIPAM) hydrogels were synthesized via a polymerization process initiated by a hydrogen peroxide-ascorbic acid redox system. This redox pair triggers polymerization under mild conditions, ensuring that the hydrogel maintains its bioactivity. In our study, PNIPAM was blended with various additives, including sodium alginate, chitosan particles, and theophylline, to assess how these components influence the material's viscoelastic properties. The mixtures were evaluated using dynamic mechanical analysis (DMA) in shear mode, which allowed us to characterize the temperature-dependent behavior of both the solution and the resulting hydrogel. One particular sample, designated 100N5A-GT, was formulated with a weight ratio of PNIPAM, sodium alginate, theophylline, and phosphate-buffered solution of 7.6:0.4:0.43:92, respectively. At a lower temperature of 20°C, the complex viscosity of the formulation was measured at approximately 1.77 Pa·s. This relatively low viscosity suggests that the material exists in a liquid state, making it suitable for injection. However, as the temperature increased to 35°C, the complex viscosity rose sharply to 264 Pa·s. This marked increase indicates a transition from a liquid to a gel state, which is ideal for in situ formation of a wound-healing dressing upon application to the skin. This thermally induced phase transition was further confirmed using cloud point measurements and the inversion tube test, both of which corroborated the temperature sensitivity. Additionally, spectrophotometric analysis was employed to monitor the release profile of theophylline from the hydrogel. The results revealed that the incorporation of chitosan particles significantly slowed the release rate of theophylline, suggesting that chitosan plays a crucial role in modulating drug delivery from the hydrogel matrix.

Keywords: N-isopropylacrylamide； sodium alginate, theophylline, injectable wound dressing, thermosensitive hydrogel

Acknowledgments
We thank the Ministry of Science and Technology of Taiwan for their financial support of this study under Contract: MOST 111-2221-E-027-010.

References

[1] Arafa, A. A., Nada, A. A., Ibrahim, A. Y., Zahran, M. K., & Hakeim, O. A. Greener therapeutic pH-sensing wound dressing based on Curcuma Longa and cellulose hydrogel. *European Polymer Journal* **2021**, 110744.

[2] Ahmad, N. In vitro and in vivo characterization methods for evaluation of modern wound dressings. *Pharmaceutics* ***2022,*** 15(1), 42.

[3] Rezvani Ghomi, E., Niazi, M., & Ramakrishna, S. The evolution of wound dressings: From traditional to smart dressings. *Polymers for Advanced Technologies* ***2023***, 34(2), 520-530.

Lithium phthalocyanine - molecular oxygen sensor

Elena Tomsik[1], Zulfiya Cernochova1[1*], Magdalena Scheibe[2], Krzysztof Tadyszak[1*]

1. *Institute of Macromolecular Chemistry, Czech Academy of Sciences, Prague, Czech Republic*
2. *J. Heyrovsky Institute of Physical Chemistry, Czech Academy of Sciences, Prague, Czech Republic*

[*]*Corresponding Author's E-mail address tadyszak@imc.cas.cz, cernochova@imc.cas.cz*

Lithium phthalocyanine is a dissolved oxygen sensor [1]. The primary field of application is the measurement of dissolved oxygen in tissues, tumors, 3D cell cultures (e.g., spheroids), or cells. Sensors are biocompatible and stable in biological conditions, being insoluble in water, which makes them an ideal system for long-term monitoring of oxygen levels.

Molecular oxygen sensors for dissolved oxygen (pO_2) are crucial for biological and medical applications. Changes in oxygen levels can be a marker of general inflammatory processes, misbuilding of blood vessels, poor diffusion geometry, and other severe abnormalities in tissues (e.g., tumors). Additionally, medical treatment can be dependent on pO_2 levels, for example, radiological anticancer therapy.

The principle of operation is based on the detection of magnetic field fluctuations caused by the O_2 molecules around the radical. Such fluctuations cause EPR line broadening, which can be calibrated and quantified for EPR oximetry.

Keywords: Lithium phthalocyanine, oxygen sensor, EPR, radicals

Acknowledgments

We acknowledge the fnancial support from the Ministry of Education, Youth and Sports of the Czech Republic (grants # LM2023053 and LUAUS24272) and the Czech Academy of Sciences, Strategy AV21 (research program "Breakthrough technologies of the future-sensors, digitization, arti)cial intelligence, and quantum technology", research topic "New correlative techniques for biological analysis and imaging and synthetic polymer materials"), and from the project New Technologies for Translational Research in Pharmaceutical Sciences/NETPHARM, project ID CZ.02.01.01/00/22_008/0004607, for fnancial support.

References

[1] Tomsik, E., Cernochova, Z., Scheibe, M., & Tadyszak, K. (2025). Lithium phthalocyanine (γ-structure) as a molecular oxygen sensor. *RSC Advances*, *15*(5), 3738–3748. https://doi.org/10.1039/d4ra08335k

Hierarchically porous polyHIPE carriers for the immobilization of lactase

M. Paljevac, D.Pečar, P. Krajnc*

University of Maribor, Faculty of Chemistry and Chemical Engineering, PolyOrgLab, Smetanova 17,
SI-2000 Maribor, Slovenia
*Corresponding Author's E-mail address: *peter.krajnc@um.si*

Porous polymer monoliths are increasingly used in a variety of separation processes, including stationary phases for various chromatographic techniques, high-throughput bioreactors, thermoplastic microfluidic devices, and as solid supports for enzyme immobilization and catalytic reactions. Among the monomers used for the preparation of such monoliths, glycidyl methacrylate (GMA) and methyl methacrylate (MMA) are the most widely used. GMA is particularly attractive due to its reactive structure, which combines a polymerizable methacrylate group with an epoxy functionality suitable for post-polymerization modifications.

Several templating methods have been developed for the preparation of porous, cross-linked poly(GMA) monoliths. One very effective method is the polymerization of the continuous phase of a high internal phase emulsion (HIPE), which results in materials with highly interconnected, open-cell porous structures. HIPEs are emulsions consisting of two immiscible liquids, where the internal (dispersed) phase has a volume fraction of more than 74%, exceeding the maximum packing density of uniform spheres. The resulting polyHIPE materials typically have a structure characterized by large voids formed by the droplets of the internal phase and smaller interconnected pores (windows) between them [1].

Poly(GMA) with reactive epoxy groups and adjustable porosity offer an excellent platform for the immobilization of enzymes. Various immobilization mechanisms have been explored, including direct covalent binding, surface activation with crosslinkers such as glutaraldehyde, and non-covalent interactions such as hydrogen bonding and electrostatic forces. Porous structures are particularly advantageous as they provide a larger surface area and facilitate the stabilization of enzymes in the architecture of the material [2].

β-Galactosidase, a versatile enzyme with important applications in the food, pharmaceutical and biotechnology industries, is mainly used for lactose hydrolysis in milk production, supporting the development of lactose-free products. It also plays a role in the synthesis of prebiotic oligosaccharides, bioactive compounds and specialty sugars. Its broad specificity and operational stability have led to extensive research on its immobilization on various supports [3].

In this work, β-galactosidase was immobilized on hierarchically porous polyGMA supports prepared by the emulsion-templating method (polyHIPE). Two immobilization strategies were compared: direct covalent binding and surface activation by glutaraldehyde. Immobilization of β-galactosidase on highly porous poly(GMA) by glutaraldehyde activation resulted in higher enzyme loading (0,43 mg/100 mg polymer) and a significantly improved catalytic performance with optimal activity at pH 6.5 and 35°C compared to direct binding without activation. In flow reactors, complete lactose conversion was achieved at 0.5 $\mathrm{mL\cdot min^{-1}}$, while higher flow rates reduced efficiency.

Keywords: polyHIPE, glycidyl methacrylate, immobilized enzymes, glycoside hydrolase enzyme

Acknowledgments

The financial support of the Slovenian Research Agency (ARIS) via programmes P2-0006 and P2-0414 is gratefully acknowledged.

References

[1] Paljevac, M.; Podgornik, A.; Kotek, J.; Jeřabek, K.; Krajnc, P. Influence of topology of highly porous methacrylate polymers on their mechanical properties. *Macromolecular Materials and Engineering* **2018**, *18*, 1-8.

[2] Kimmins, S.D.; Wyman, P.; Cameron, N.R. Amine-functionalization of glycidyl methacrylate-containing emulsion-templated porous polymers and immobilization of proteinase K for biocatalysis. *Polymer* **2014**, *55*, 416–425.

[3] Pečar, D.; Zečević, K.; Goršek, A. The Immobilization of β-Galactosidase on Glass Fiber Rolls. *Catalysts* **2023**, *13*, 1503-1515.

Encapsulation of Resveratrol in Poly(ε-caprolactone)-Poly(methacrylic acid) Copolymeric Micelles for Oral Delivery

L. Radeva[1*], K. Kamenova[2], S. Konstantinov[1], P. D. Petrov[2], K. Yoncheva[1]

[1]*Faculty of Pharmacy, Medical University of Sofia, Sofia, Bulgaria*
[2]*Institute of Polymers, Bulgarian Academy of Sciences, Sofia, Bulgaria*
[*]*l.radeva@pharmfac.mu-sofia.bg*

The application of nanosized drug delivery systems such as polymeric micelles in medicine is of a particular interest since they could provide targeted drug delivery, increased solubility and stability of the loaded substance as well as enhanced bioavailability and pharmacological effects [1, 2]. The natural polyphenol resveratrol exerts anrioxidant and anti-inflammatory effects, however, its poor aqueous solubility hinders its application [3, 4]. Therefore, its encpasulaition in nanoparticles could be considered an appropriate strategy. Taking this into consideration we developed novel micellar copolymeric carrier for resveratrol based on poly(methacrylic acid) and poly(ε-caprolactone) (PMAA-b-PCL-b-PMAA). Atom transfer radical polymerization (ATRP) of tert-butyl methacrylate (t-BMA), initiated from a bifunctional PCL macroinitiator, followed by hydrolysis of t-BMA groups, was applied for sythesizing central PCL hydrophobic block and two outer PMAA hydrophilic blocks amphiphilic block copolymer. The micelles were then obtained via self-assembly of the copolymer in aqueous media. The critical micelle concentration (CMS) was found to be 0.076 g/L and the system was characterized with mean diameter of 102 nm. Resveratrol was loaded via the solvent evaporation method at a mass ratio between the drug and the polymer 1:15. Encapsulation efficiency of 72% and loading degree of 67 µg/mL were achieved. The mean diameter of the loaded micelles was lower, namely 78 nm. TEM confirmed the small size and showed spherical shape of the micelles. The in vitro release tests showed burst release followed by sustained release which was slightly faster in media with pH=6.8 in comparison with pH=1.2. This was in agreement with the founding that the micelles aggregated in the acidic media due to protonation of the PMMA chains. Kinetic analysis showed that the release in the buffer with pH=6.8 followed first order kinetic while the process in the slightly acidic medium correlated with the Higuchi model. More importantly, 100% resveratrol was released from the system for 24 h in comparison with the free drug which showed dissolution of only 10% for the same period. Albumin denaturation assay confirmed the anti-inflammatory activity of both encapsulated and free resveratrol. In vitro co-culture model of inflammation revelaed that only pretreatment with the encpasulated resveratrol at 5 and 10 µM concentrations showed anti-inflammatory effect. Therefore, the PMAA-b-PCL-b-PMAA triblock copolymer micelles could be considered appropriate carriers for the oral delivery of the hydrophobic polyphenol resveratrol.

Keywords: polymeric micelles, resveratrol, anti-inflammatory activity

Acknowledgments
This research was funded by the European Union-NextGenerationEU, through the National Recovery and Resilience Plan of the Republic of Bulgaria, Project BG-RRP-2.004-0004-C01.

References

[1] Kawabata, Y.; Wada, K.; Nakatani, M.; Yamada, S.; Onoue, S. Formulation Design for Poorly Water-Soluble Drugs Based on Biopharmaceutics Classification System: Basic Approaches and Practical Applications. *Int. J. Pharm.* **2011**, *420*, 1–10.
[2] Suchaoin, W.; Bernkop-Schnürch, A. Nanocarriers Protecting toward an Intestinal Pre-Uptake Metabolism. *Nanomed.* **2017**, *12*, 255–269.
[3] Yang, G.; Chang, C.-C.; Yang, Y.; Yuan, L.; Xu, L.; Ho, C.-T.; Li, S. Resveratrol Alleviates Rheumatoid Arthritis via Reducing ROS and Inflammation, Inhibiting MAPK Signaling Pathways, and Suppressing Angiogenesis. J. *Agric. Food Chem.* **2018**, *66*, 12953–12960.
[4] Robinson, K.; Mock, C.; Liang, D. Pre-Formulation Studies of Resveratrol. *Drug Dev. Ind. Pharm.* **2015**, *41*, 1464–1469.

Evaluation of polyvinylpyrrolidone and sodium alginate as carriers of solid dispersions with curcumin

K. Yoncheva[1*], K. Grigorova[1], M. M. Zaharieva[2], I. Spassova[3], D. Kovacheva[3], H. Najdenski[2]

[1]Faculty of Pharmacy, Medical University of Sofia, 1000 Sofia, Bulgaria
[2]The Stephan Angeloff Institute of Microbiology, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
[3]Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
[*]Corresponding Author: kyoncheva@pharmfac.mu-sofia.bg

The incorporation of hydrophobic drugs into solid polymer dispersions is a modern method for increasing their water solubility [1-2]. In this regard, the incorporation of curcumin into solid polymer dispersions can be considered as an alternative approach to improve its solubility and pharmacological effects in vivo. In the present study, polyvinylpyrrolidone (PVP) and sodium alginate (ALG) were selected as carriers of polymer dispersions. Both types of the dispersions were prepared via solvent evaporation method at three ratios between curcumin and the respective polymer, in particular 1:1, 1:20 and 1:50 (wt/wt). For both polymers the optimal ratio was 1:25. However, the results showed significantly higher solubility of curcumin after formulation in PVP-solid dispersion compared to ALG-solid dispersion. X-ray diffraction analyses revealed complete transformation of crystalline curcumin into an amorphous state in both types of the dispersions. Therefore, the transformation of curcumin into an amorphous state was not the only mechanism by which PVP-dispersion affected its solubility. Further, the release process of curcumin from the PVP-dispersion in phosphate buffer (pH 7.0) showed a complete release within 20 minutes, while the pure curcumin did not dissolve within the same time. The following studies compared the ability of the PVP-solid dispersion of curcumin and pure curcumin to inhibit a biofilm of *Staphylococcus aureus* (methi cillin resistant, MRSA). Microscopic studies showed a more pronounced inhibition of the MRSA biofilm when treated with curcumin incorporated into the PVP-solid dispersion compared to the pure drug. The inhibition of the biofilm by low concentration of curcumin in the PVP-dispersion (11.4 µM) was comparable to the effect of pure curcumin in 100 µM concentration. Thus, polyvinylpyrrolidone appeared as a very effective carrier for formulation of solid dispersion of curcumin that ensured better biopharmaceutical and antimicrobial properties of the drug.

Keywords: curcumin, polyvinylpyrrolidone, sodium alginate, antibacterial activity

Acknowledgments

This research was funded by the European Union-NextGenerationEU, through the National Recovery and Resilience Plan of the Republic of Bulgaria, Project BG-RRP-2.004-0004-C01.

References

[1] Sareen, S.; Mathew, G.; Joseph, L. Improvement in solubility of poor water-soluble drugs by solid dispersion. *Int J Pharm Investig.* **2012**, *2*, 12-17.
[2] Alshehri ,S.; Imam, S.S.; Hussain, A.; Altamimi, M.A.; Alruwaili, N.K.; Alotaibi, F.; Alanazi, A.; Shakeel, F. Potential of solid dispersions to enhance solubility, bioavailability, and therapeutic efficacy of poorly water-soluble drugs: newer formulation techniques, current marketed scenario and patents. *Drug Deliv.* **2020**, *27,* 1625-1643.

Cross-Linked Poly(methyl methacrylate) Nanocomposites, Synthesis, Characterization, and Antibacterial Effects

Nazeeha S. Alkayal [1],* and Mashail A. Al Ghamdi [2]

[1] Chemistry Department, Faculty of Science, King Abdulaziz University,
P.O. Box 80203, Jeddah 21589, Saudi Arabia
[2] Biological Department, Faculty of Science, King Abdulaziz University,
P.O. Box 80200, Jeddah 21589, Saudi Arabia
* Correspondence: nalkayal@kau.edu.sa

Abstract:

Polymer networks were synthesized using the condensation method between PMMA and melamine as cross-linkers. CuO nanoparticles (NPs) and activated carbon (AC) were used as a filler. The final products PMMA/Mel, PMMA/Mel-CuO, and PMMA/MelAC were tested for antibacterial activities against *E.coli* and *S. aureus.* The chemical structure and composition, thermal properties, and surface morphology of the new PMMA/Melbased nanocomposites were investigated by various techniques. The XRD and EDX results showed the successful incorporation of CuO NPs and AC into the polymer matrix. Also, the thermal stability of the PMMA/Mel polymer was significantly enhanced after adding CuO nanoparticles. This finding showed that the PMMA/Mel-CuO and PMMA/MelAC nanocomposites have greater activity against both bacteria than PMMA/Mel. The PMMA/Mel-CuO and PMMA/Mel-AC polymers showed high activity against *S. aureus* bacteria, with inhibition zones of 22.6 mm and 11.3 mm, respectively. This confirms that small-sized nanoparticles have an effective role in killing bacterial cells.

Keywords: cross-linked PMMA; melamine; CuO nanoparticle; activated carbon; antibacterial; *E. coli*; *S. aureus*

References

Alkayal, N.S.; Al Ghamdi, M.A. Cross-Linked Poly(methyl methacrylate) Nanocomposites' Synthesis, Characterization, and Antibacterial Effects. *Polymers* **2025**, *17*, 269. https://doi.org/10.3390/polym17030269

Polymeric materials: from nanoparticles to tissue implants

Ye. Tazhbayev[1]*, A. Galiyeva[1], A. Daribay[1], U. Toleuov[1]

[1]*Buketov Karaganda University, Karaganda, Kazakhstan*
**Corresponding Author's E-mail address:* tazhbaev@mail.ru

Polymers are increasingly used in various medical applications from drug delivery to artificial implants in tissue engineering. Drug delivery using nanoparticles is indeed one of the most promising applications of polymers [1-2]. Our group is developing ways to produce polymeric nanoparticles for the delivery of anticancer and anti-TB drugs. Both diseases are urgent and a great danger to mankind. Below we present some of our research results.

Table 1 – Nanoparticles with anti-tuberculosis drugs

Biopolymer	Medicinal product	Loading capacity	Results of the study
Polystyrene	Capreomycin sulphate		Synthesis of polymeric nanoparticles was carried out by chain polymerisation, the average size of the obtained NPs was 173 nm.
Polyethylcyanoacrylate	Capreomycin sulphate	76,3 %	Inclusion of capreomycin sulphate in the matrix of polyethylcyanoacrylate allows to increase the drug half-life by 3 times, thus prolonging the effect of the drug. The polymeric particles had an average size of 132-550 nm.
Polylactide-co-glycolide	Isoniazid (INH)	76 %	PLGA-INH colloidal nanoparticles were developed by double emulsion, nano-deposition and emulsion methods. The average size is up to 200 nm, narrow particle size distribution.
Polylactide (PLA)	INH, Vitamin C	INH: 72 %, VitC: 83 %	PLA-INH-VitC nanoparticles were synthesised for the first time by double emulsion method. Inhibit the growth of isoniazid-resistant mycobacteria.
PLA	Streptomycin	50 %	The size of polylactic acid nanoparticles is 310 nm. The yield of NPs is 82.5 %.
Serum albumin (HSA and BSA)	INH	82 %	Nanoparticles of albumin with INH were obtained. Narrow size composition, high degree of binding. MIC - 2.5 µg/ml.
HSA	INH, Rifampicin (RIF)	INH: 27 %, RIF: 44 %	The LVs with INH and RIF were 216.7±3.7 nm in size and had a ζ-potential of -26.7±1.5.
HSA	RIF	86 %	NCs with RIF were obtained by the Taguchi method. The average size is 190.7±2.3 nm, ζ-potential is -22.7±0.3.
HSA	p-aminosalicylic acid		PASC LVs were obtained by desolvation method. Drug loading into empty albumin wafers.
BSA **Polyethylene glycol (PEG)**	INH	46 %	PEG fragments and amino groups of albumin. PEG-BSA-INH NPs were obtained, size 226.9±1 nm.

The final choice of a suitable polymer, particle size and production method depends firstly on the biocompatibility of the polymer, secondly on the physicochemical properties of the drug substance, and thirdly on the therapeutic goal.

Another important problem is osteoarthritis, a joint disease caused by the destruction of the soft tissues of the joint surfaces. This severe disease progresses over time. A possible solution to this problem is the use of 'soft' polymeric materials in endoprostheses, which are able to change their shape when the configuration of the bone articulation changes and, at the same time, retain the mechanical properties necessary to stiffen the joint. The elastic properties of hydrogels can be dramatically improved by creating 'double' meshes, which are two interpenetrating polymer meshes with different properties. The first mesh is usually formed by a strongly cross-linked and rigid polymer, and the second one by a weakly cross-linked and flexible polymer. In this work, we combined biocompatible and biodegradable mesh materials, which had previously been used independently, to create a high-strenght dual mesh for producing a personalised biomedical product using 3D printing technology.

References

[1] Araujo, L.; Löbenberg, R.; Kreuter, J. Influence of the Surfactant Concentration on the Body Distribution of Nanoparticles. *Journal of Drug Targeting* **1999**, 7(5), 295–302.

[2] Jin, P.; Liu, L.; Chen, X.; Cheng, L.; Zhang, W.; Zhong, G. Applications and Prospects of Different Functional Hydrogels in Meniscus Repair. *Front. Bioeng. Biotechnol.* **2022**, 10, 1082499.

MOLECULARLY IMPRINTED POLYMER FOR SELECTIVE SORPTION OF TORASEMIDE

Dragana Mutavdžić Pavlović[1*], Kristina Tolić Čop[1], Anđela Skelin[1]

[1]*Faculty of Chemical Engineering and Technology, University of Zagreb, Trg Marka Marulića 19, 10000 Zagreb, Croatia*
[*]*dmutavdz@fkit.unizg.hr*

The development of novel materials and analytical techniques has increased the sensitivity of detection and analysis of various emerging contaminants (EC) such as pharmaceuticals, which are already recognized as micropollutants in various areas of the environment. In environmental analysis, molecularly imprinting technology, in which synthetic polymers sensitive to specific molecules are synthesized, has attracted considerable attention. The most commonly used polymerization technique in the preparation of molecularly imprinted polymers (MIP) is bulk polymerization, in which a monomer unit, a template molecule, a crosslinking agent and an initiator dissolved in a suitable porogen are mixed in a batch [1]. After a 24-hour of reaction at 60 °C and subsequent washing of the template, the MIP formed was mechanically ground into small particles with specific cavities matched to the dimensions of the template. Torasemid (TOR), a diuretic drug, was selected as the molecule of interest for which MIP was prepared and tested by sorption experiments. Preliminary experiments involved DFT calculations of the binding interactions between TOR and various monomer units, where the optimized interaction between torasemide and methacrylic acid was achieved in a 1:3 ratio. Based on the computational predictions, different MIPs were prepared by changing the amount of substance of the template and monomer to experimentally determine the material with the best performance. The MIP with the highest mass of TOR added to the polymerization mixture showed the best sorption and extraction performances; therefore, it was further characterized (BET and SEM analysis) and tested by sorption kinetic studies, the effect of contact time, initial concentration of TOR, mass of sorbent and ionic strength. To determine the selectivity of MIP for TOR, the same experiments were performed in parallel for non-molecularly imprinted polymers (NIP). For both types of sorbents, sorption equilibrium was reached after 24 hours, and the experimental data best fitted the pseudo-second-order model (R^2>0.99). By changing different reaction parameters, the sorption behaviour of both polymers followed a similar trend, highlighting the increased sorption affinity of MIP for the elimination of TOR from aqueous media.

Keywords: torasemid, molecularly-imprinted polymer, non-molecularly imprinted polymer, sorption

Acknowledgments

This study was supported by the Croatian Science Foundation under the project number HRZZ-IP-2022-10-4400 entitled Development of molecularly imprinted polymers for use in analysis of pharmaceuticals and during advanced water treatment processes (MIPdePharma).

References

[1] Huang, DL.; Wang, RZ.; Liu, YG; et al. Application of molecularly imprinted polymers in wastewater treatment: a review. *Environ Sci Pollut Res* **2015**, 22, 963–977.

Development of Biocompatible Porous Hydrogels via Aqueous Two-Phase System: A Comparative Study of Poly(ethylene oxide), Polysarcosine, and Glucomannan

A.E. Morán, J. Dvořáková, A. Golunová, V. Proks*
Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, 162 06 Prague 6, Czech Republic
moran@imc.cas.cz

Hydrogels have become essential in tissue engineering applications like injectable systems and 3D bioprinting due to their biocompatibility and ECM-mimicking properties. Their porous, interconnected structure supports cell growth, nutrient transport, and cell migration—key features for replicating native ECM function [1]. Various of fabrication strategies have been explored to achieve such porosity in hydrogels. Among these strategies, aqueous two-phase systems (ATPS) have gained attention as a biocompatible method. ATPS involves forming of two immiscible aqueous phases, that can be precisely controlled through polymer concentration, molecular weight, and solution viscosity. In this approach, one polymer forms the hydrogel matrix via crosslinking, and the second phase functions as a pore-forming agent. This second phase is typically removed after gelation because it does not interact with the hydrogel matrix [2]. Polyethylene oxide (PEO) is commonly used as a pore-forming agent for hydrogels due to its water solubility, low toxicity, and minimal interference with crosslinking, enabling the formation of well-defined pore structures [3]. However, its reported immunogenicity has led to the search for safer alternatives. In this study, we explore aqueous two-phase systems (ATPS) using polysarcosine and glucomannan as alternative porogens, comparing them with PEO. We assess how each affects hydrogel porosity, phase separation, and suitability for biological applications.

A biocompatible ATPS was developed for the fabrication of porous hydrogels using polysarcosine and glucomannan. The construction of the porous hydrogel involved the use of methacryloyl and tyramine functionalized polymers, including hyaluronic acid methacryloyl (HA-MA), poly(N^5-2-hydroxyethyl-L-glutamine) methacryloyl (PHEG-MA), hyaluronic acid tyramine (HA-TYR), and a combination of HA-MA with PHEG-MA. The polymer precursors were photocrosslinking under the blue light using Ru(II) complex/$(NH_4)_2S_2O_8$ or Riboflavin/L-Arginin as photoinitiators. The resulting hydrogels were analyzed based on several factors, including the gelation time, gel yield, swelling, pore size, and morphology. The findings of this study underscored the efficacy of the ATPS system as a more compatible approach to producing porous hydrogels for biocompatible applications.

Keywords: Hydrogels,Two phase systems , biocompaility.

References

[1] Zhang, C., Liu, X., Gong, J., & Zhao, Q. (2023). Liquid sculpture and curing of bio-inspired polyelectrolyte aqueous two-phase systems. Nature Communications, 14(1), 2456.

[2] Hwang, C. M., Sant, S., Masaeli, M., Kachouie, N. N., Zamanian, B., Lee, S. H., & Khademhosseini, A. (2010). Fabrication of three-dimensional porous cell-laden hydrogel for tissue engineering. *Biofabrication*, *2*(3), 035003.

[3] Ying, G. L., Jiang, N., Maharjan, S., Yin, Y. X., Chai, R. R., Cao, X., ... & Zhang, Y. S. (2018). Bioprinting: Aqueous Two-Phase Emulsion Bioink-Enabled 3D Bioprinting of Porous Hydrogels (Adv. Mater. 50/2018). *Advanced Materials*, *30*(50), 1870382.

Synthesis of new degradable 2-hydroxyethyl methacrylate hydrogels for biomedical applications

H. Macková[1], M. Dušková-Smrčková[1], Z. Morávková[1], Š. Kubinová[2,3], D. Horák[1]
[1]*Institute of Macromolecular Chemistry CAS, Prague, Czech Republic*
[2]*Institute of Physics CAS, Prague, Czech Republic*
[3]*State Institute for Drug Control, Prague, Czech Republic*

The research of degradable hydrogel materials with high water content and mechanical properties similar to tissues is crucial for the development of new drug delivery systems, tissue engineering, medical devices, and biomedical healthcare sensors. Specifically, synthetic hydrogels based on polymethacrylates are cost-effective and widely used in medical applications. Moreover, they can be easily modified. We offer the synthesis of degradable hydrogels based on a copolymer of 2-hydroxyethyl methacrylate and zwitterionic 2-methacryloyloxyethyl phosphorylcholine via reversible addition-fragmentation chain transfer polymerization (RAFT). Two synthesis strategies were used and compared. First, low-molecular-weight water-soluble copolymers containing 2-(acetylthio)ethyl methacrylate were synthesized, and then hydrogels were formed by a polymer-analogous reaction involving the deprotection of thiol groups with triethylamine, which was followed by disulfide bond formation using 2,2′-dithiodipyridine or 6,6′-dithiodinicotinic acid. The second strategy involved preparing hydrogels by block RAFT polymerization using the degradable crosslinker bis(2-methacryloyloxy)ethyl disulfide. Finally, to make the hydrogels attractive for cell attachment, interpenetrating or semi-interpenetrating networks with water-soluble collagen I were prepared using both strategies. Optionally, collagen crosslinkers, such as genipin or dithiobis(succinimidyl propionate) were used to improve the mechanical properties of the resulting hydrogels. All hydrogels containing reductively degradable disulfide bridges were compared in terms of their compositions, degradability, and mechanical properties.

Keywords: HEMA, degradable, disulfide, hydrogel

Acknowledgments: This work was supported by the Czech Science Foundation (No. 25-16155S).

Design and synthesis of a DASA-based photoswitchable probe for lipid membrane analysis

Vít Guiglielmo Mišurec[1*], Jan Petrášek[2], and Martin Hrubý[1]

[1]*Institute of Macromolecular Chemistry CAS, Praha, Czechia*
[2]*Institute of Experimental Botany CAS, Praha, Czechia*
[*]*vg.misurec@gmail.com*

We present a photoswitchable molecular probe capable of reporting on the lipidic architecture of biological membranes. Built upon the Donor–Acceptor Stenhouse Adduct (DASA) platform, this probe is expected to respond dynamically to its environment, with switching kinetics sensitive to local lipid density and membrane affinity. In model membrane systems, we predict that densely packed lipid phases significantly alter the rate and efficiency of the photoisomerization process. These results suggest a mechanistic correlation between membrane structure and photochemical behavior, positioning DASAs as promising tools for studying membrane heterogeneity and dynamics *in situ*. This work bridges responsive molecular design with functional biological imaging applications.

Acknowledgments

We acknowledge the financial support from the Ministry of Education, Youth and Sports of the Czech Republic (grants # LM2023053 and LUAUS24272) and the project New Technologies for Translational Research in Pharmaceutical Sciences/NETPHARM, project ID CZ.02.01.01/00/22_008/0004607, co-funded by the European Union.

References

[1] Reyes, C. A.; Karr, A.; Ramsperger, C. A.; Talim G. K., A.; Hye Joon Lee; Picazo, E. Compartmentalizing Donor–Acceptor Stenhouse Adducts for Structure–Property Relationship Analysis. *J. Am. Chem. Soc.* **2025**, *147* (1), 10–26. DOI: 10.1021/jacs.4c14198.

[2] Doroudgar, M.; Morstein, J.; Becker-Baldus, J.; Trauner, D.; Glaubitz, C. How Photoswitchable Lipids Affect the Order and Dynamics of Lipid Bilayers and Embedded Proteins. *J. Am. Chem. Soc.* **2021**, *143* (25), 9515–9528. DOI: 10.1021/jacs.1c03524.

Polymeric materials: from nanoparticles to tissue implants

Ye. Tazhbayev[1]*, A. Galiyeva[1], A. Daribay[1], U. Toleuov[1]

[1]*Buketov Karaganda University, Karaganda, Kazakhstan*
**Corresponding Author's E-mail address:* tazhbaev@mail.ru

Polymers are increasingly used in various medical applications from drug delivery to artificial implants in tissue engineering. Drug delivery using nanoparticles is indeed one of the most promising applications of polymers [1-2]. Our group is developing ways to produce polymeric nanoparticles for the delivery of anticancer and anti-TB drugs. Both diseases are urgent and a great danger to mankind. Below we present some of our research results.

Table 1 – Nanoparticles with anti-tuberculosis drugs

Biopolymer	**Medicinal product**	**Loading capacity**	**Results of the study**
Polystyrene	Capreomycin sulphate		Synthesis of polymeric nanoparticles was carried out by chain polymerisation, the average size of the obtained NPs was 173 nm.
Polyethylcyanoacrylate	Capreomycin sulphate	76,3 %	Inclusion of capreomycin sulphate in the matrix of polyethylcyanoacrylate allows to increase the drug half-life by 3 times, thus prolonging the effect of the drug. The polymeric particles had an average size of 132-550 nm.
Polylactide-co-glycolide	Isoniazid (INH)	76 %	PLGA-INH colloidal nanoparticles were developed by double emulsion, nano-deposition and emulsion methods. The average size is up to 200 nm, narrow particle size distribution.
Polylactide (PLA)	INH, Vitamin C	INH: 72 %, VitC: 83 %	PLA-INH-VitC nanoparticles were synthesised for the first time by double emulsion method. Inhibit the growth of isoniazid-resistant mycobacteria.
PLA	Streptomycin	50 %	The size of polylactic acid nanoparticles is 310 nm. The yield of NPs is 82.5 %.
Serum albumin (HSA and BSA)	INH	82 %	Nanoparticles of albumin with INH were obtained. Narrow size composition, high degree of binding. MIC - 2.5 μg/ml.
HSA	INH, Rifampicin (RIF)	INH: 27 %, RIF: 44 %	The LVs with INH and RIF were 216.7±3.7 nm in size and had a ζ-potential of -26.7±1.5.
HSA	RIF	86 %	NCs with RIF were obtained by the Taguchi method. The average size is 190.7±2.3 nm, ζ-potential is -22.7±0.3.
HSA	p-aminosalicylic acid		PASC LVs were obtained by desolvation method. Drug loading into empty albumin wafers.
BSA **Polyethylene glycol (PEG)**	INH	46 %	PEG fragments and amino groups of albumin. PEG-BSA-INH NPs were obtained, size 226.9±1 nm.

The final choice of a suitable polymer, particle size and production method depends firstly on the biocompatibility of the polymer, secondly on the physicochemical properties of the drug substance, and thirdly on the therapeutic goal.

Another important problem is osteoarthritis, a joint disease caused by the destruction of the soft tissues of the joint surfaces. This severe disease progresses over time. A possible solution to this problem is the use of 'soft' polymeric materials in endoprostheses, which are able to change their shape when the configuration of the bone articulation changes and, at the same time, retain the mechanical properties necessary to stiffen the joint. The elastic properties of hydrogels can be dramatically improved by creating 'double' meshes, which are two interpenetrating polymer meshes with different properties. The first mesh is usually formed by a strongly cross-linked and rigid polymer, and the second one by a weakly cross-linked and flexible polymer. In this work, we combined biocompatible and biodegradable mesh materials, which had previously been used independently, to create a high-strenght dual mesh for producing a personalised biomedical product using 3D printing technology.

References

[1] Araujo, L.; Löbenberg, R.; Kreuter, J. Influence of the Surfactant Concentration on the Body Distribution of Nanoparticles. *Journal of Drug Targeting* **1999**, 7(5), 295–302.
[2] Jin, P.; Liu, L.; Chen, X.; Cheng, L.; Zhang, W.; Zhong, G. Applications and Prospects of Different Functional Hydrogels in Meniscus Repair. *Front. Bioeng. Biotechnol.* **2022**, 10, 1082499.

Sustainable Lithium-Ion Batteries: New Strategies for Aqueous Cathode Production

Hannah Dworzak-Oberherber[1], Felix Leibetseder[1], Klaus Bretterbauer[1]

[1]*Institute for Chemical Technology of Organic Materials, Johannes Kepler University Linz, Austria*
[*]*hannah.dworzak@gmail.com*

Due to the ongoing climate crisis, the modern world continues to experience an ever-growing demand for reliable and high-performance energy storage systems. Lithium-ion batteries (LIB) based on high-nickel layered metal oxides represent the current state of the art for applications requiring high energy densities, such as electric vehicles. At present the LIB cathode production still relies on PFAS-emitting fluorinated polymers processed with toxic N-methyl pyrrolidone. Attaining greener processes, improved recyclability, and achieving an overall transition to sustainability requires the adoption of water-soluble polymers and aqueous processing.

Whilst in theory, water-soluble electrode binders have been developed, the combination with high-nickel active materials still poses several problems. The most crucial consequence of adding the active material into an aqueous electrode slurry is the subsequent increase in pH due to Li^+-ion leaching and formation of lithium hydroxide. This causes corrosion of the aluminum current collector and decreases the battery lifetime. Researchers and industry have previously tried to mitigate this by adding acids to the electrode slurry, which appears beneficial in controlling this effect. [2]

This research presents an alternative strategy to solve the “pH problem” of aqueous cathode processing for LIB, aiming to reduce the need for additional acidic additives. Specialty monomers, polymers, and a novel reactive coating process are combined to improve the electrode manufacturing. Processing of the electrode slurry systems and reactive coating tests were conducted. The behaviour of the active cathode material (NMC) in water is studied in-depth by examining influencing factors such as pH, lithium ion leaching, and other crucial processing parameters. These combined results seek to reduce and optimize process steps and enable a new energy-saving and environmentally friendly method for producing electrodes for sustainable LIBs.

Keywords: Lithium-ion batteries, aqueous processes, cathodes, polymeric binders, sustainable electrode binders

References

[1] Hofmann M.; Kapuschinski M.; Guntow U.; Giffin G.A. Implications of Aqueous Processing for High Energy Density Cathide Materials: Part I. Ni-Rich Layered Oxides. *J. Electrochem. Soc* **2020**, *167*, 140512.
[2]Tolchard J.R.; Vullum P.E.; Arstad B.; Wagner N.P. New insights into orthophosphoric acid assisted rapid aqueous processing of NMC622 cathodes. *RSC Sustain*. **2023,** *1*, 378-387.

Chitosan: a promising material for the prevention of lead leakage in perovskite photovoltaic cells

R.M. Duarte[1]*, S.T. Saraiva[1], A.C. Fonseca[1]

[1] CEMMPRE, ARISE, *Department of Chemical Engineering, University of Coimbra, Coimbra, Portugal*

**rubenmendesduarte@gmail.com*

The global energy transition into renewable sources is becoming a pressing topic with new technologies being researched and entering the market. However, some of these new technologies still present some challenges. Photovoltaic power is one of the fastest growing sources of electricity and new alternatives to traditional silicon cells have been created [1][2]. Perovskite photovoltaic cells are one of such alternatives; they are promising yet the lead in its structure may leak into the environment when the cells get damaged [3][4]. Due to lead toxicity, this makes perovskite cells less appealing to the public. Until now, fossil based polymers have been used to try to solve this problem but with varying degrees of success. Additionally, their synthesis is still dependant on non-renewable raw materials which is seen as an important disadvantage. Thus, this work aims to take advantage of a bio-based polymer to improve the perovskite structural integrity. This contributes to a decrease in the amount of lead released into the environment if the cell is damaged and exposed to water, all while maintaining the high power conversion efficiency reported for perovskite photovoltaic cells. The base polymer chosen was chitosan due to its ability to interact with heavy metals and its abundance in nature [5]. Yet, it is not soluble in the common solvents used in perovskite manufacturing: dimethylsulfoxide (DMSO) and N,N'-dimethylformamide (DMF). Thus, chitosan was modified to turn it soluble in the desired solvents and also to increase its hydrophobicity, which can further protect the perovskite layer from being dissolved by water [6]. The modified chitosans that were soluble in DMSO or DMF were used to prepare films with perovskite. The films were submerged in water and the amount of lead released from the film was compared with the perovskite film without any polymer. The power conversion efficiency of the photovoltaic cells with the new polymers in the perovskite layer was determined and compared to the one obtained by cells without chitosan.

Keywords: Perovskite, Lead, Modified Chitosan

References

[1] Gnida, P.; Amin, M.F.; Pająk, A.K.; Jarząbek, B. Polymers in High-Efficiency Solar Cells: The Latest Reports. *Polymers* **2022**, *14*(10), 1946.

[2] Pastuszak, J.; Węgierek, P. Photovoltaic Cell Generations and Current Research Directions for Their Development. *Materials* **2022**, *15*(16), 5542.

[3] Solak, E. K.; Irmak, E. Advances in organic photovoltaic cells: a comprehensive review of materials, technologies, and performance. *RSC Advances* **2023**, *13*(18), 12244–12269.

[4] Zhang, H.; Lee, J.-W.; Nasti, G.; Handy, R.; Abate, A.; Grätzel, M.; Park, N.-G. Lead immobilization for environmentally sustainable perovskite solar cells. *Nature* **2023**, *617*(7962), 687–695.

[5] Popa, A.; Visa, A.; Maranescu, B.; Hulka, I.; Lupa, L. Chemical Modification of Chitosan for Removal of Pb(II) Ions from Aqueous Solutions. *Materials* **2021**, *14*(24), 7894.

[6] Khorasani, A.; Mohamadkhani, F.; Marandi, M.; Luo, H.; Abdi-Jalebi, M. Opportunities, Challenges, and Strategies for Scalable Deposition of Metal Halide Perovskite Solar Cells and Modules. *Advanced Energy and Sustainability Research* **2024**, *5*(7).

Self-standing Covalent Organic Framework Membranes for Efficient Osmotic Energy Harvesting

Xi Ma[1], Seema Agarwal[1,2*]

[1] *Macromolecular Chemistry II, Advanced Sustainable Polymers, University of Bayreuth, 95440 Bayreuth, Germany*
[2] *Bavarian Polymer Institute, University of Bayreuth, 95440 Bayreuth, Germany*
[*]*Email: agarwal@uni-bayreuth.de*

Undeniably, fossil fuels have powered modern civilization; however, after two centuries of extraction, global reserves of these non-renewable resources are approaching depletion. In contrast, the Gibbs free energy (ΔG) generated by salinity gradient mixing between seawater and freshwater remains one of the most significant yet underdeveloped renewable energy resources. Membrane-based reverse electrodialysis (RED) enables direct electricity generation from osmotic energy by harnessing the net ion flux driven by concentration gradients across ion-selective membranes. Therefore, developing ion-selective membranes with both high conductivity and high selectivity is particularly critical for efficient osmotic energy harvesting. Covalent organic frameworks (COFs) demonstrate remarkable potential for osmotic energy conversion due to their tunable nanochannel architectures, high porosity, and exceptional chemical stability. Herein, we demonstrate a facile solution-processing strategy for fabricating free-standing, micrometer-thick and crystalline membranes of imine-linked 2D ionic TpPa-$(SO_3H)_X$ COF (X=0.5, 1, 1.5, 2). By systematically tuning the $-SO_3H$ group density via stoichiometric control during COF synthesis, we achieved optimized charge-governed ion selectivity (quantitatively described by cation transference number, 0.943) in the nanochannels. Under salinity gradients mimicking seawater/riverwater conditions (0.5 M/0.01 M, NaCl), the device delivered an exceptional power output density of 24.6 W m^{-2}, representing a 4.9-fold enhancement over commercial benchmarks (5 W m^{-2}).

Keywords: covalent organic framework, self-standing membrane, osmotic energy harvesting, ion.

Electrochemical Stability of Polypyrrol-Based Supercapacitors Containing Acid Blue 25

T. Hix-Janssens*, D. V. Tumacder, P. Bober

Institute of Macromolecular Chemistry, Czech Academy of Sciences, Prague, Czech Republic
**hixjanssens@imc.cas.cz*

Organic dyes, such as Acid Blue 25 (AB) positively influences the electrochemical and morphological properties of polypyrrole (PPy) [1, 2]. These research results can be further used to develop more efficient and flexible supercapacitors. Within this work, electropolymerization of pyrrole occurred on activated carbon cloths in the presence of AB concentrations between 0.625 and 2.5 mM. They were prepared using chronoamperometry with an applied potential of 1.5 V or 2.0 V for 20 min and 15 min, respectively. Calculated areal capacitances between all samples with AB and neat PPy were similar. However, the PPy containing AB showed a higher cyclic stability in both cyclic voltammetry and galvanostatic charge-discharge measurements. With an applied potential of 2.0 V during electropolymerization, the areal capacitance (C_A) after 1000 cycles of PPy decreased by 39% of the original value. In comparison, the C_A of those that included AB during the polymerization process decreased by 12-27%. Additionally, the effect of AB on the morphology of PPy on the carbon cloths was investigated using scanning electron microscopy. Samples containing only PPy showed the typical globular structure, while those containing AB showed the formation of fibrous structures. Increasing the applied potential and the concentration of AB during electropolymerization increased the count of these structures. These results show the promising nature of how organic dyes can positively affect the electrochemical properties of pyrrole to pave the way towards flexible and stable supercapacitors.

Keywords: supercapacitors, polypyrrole, acid blue, chronoamperometry

References

[1] Tumacder D. V., Morávková Z., Konefał M. *et al.*, Materials Research Bulletin. 168:112455, **2023**.
[2] Tumacder D. V., Morávková Z., Bober P., Materials Letters, 308:131295, **2022**.

Conducting polymer-based composite aerogels: synthesis and application for energy storage

P. Bober*, K. A. Milakin, D. Von Tumacder

Institute of Macromolecular Chemistr, Czech Academy of Sciences, Prague, Czech Republic
**bober@imc.cas.cz*

Conducting polymer-based aerogels represent new class of conducting macroporous materials which combine physicochemical properties of the conducting polymer with mechanical properties of a polymer support [1-3]. Polyaniline-poly(*N*-vinylpyrrolidone) aerogels with carbon nanofibers (PANI-CNF-PVP) were prepared via two steps [3]. First, PANI-CNF-PVP cryogels were prepared by oxidative cryopolymerization of aniline in water:isopropanol medium in the presence of various amounts of dispersed CNF (0.05–2.5 mg ml^{-1}). Second, prepared cryogels were converted to aerogels by freeze-drying. The effect of CNF incorporation on the resulting properties of aerogels were investigated by SEM, specific surface area, and electrical conductivity measurement. Additionally, the electrochemical performance (cyclic voltammetry, GCD, EIS) was explored in the assessment of potential synergistic interaction between the components of the aerogels and application for energy storage. Symmetrical supercapacitor with PANI–CNF–PVP aerogel as the electrode material was assembled. The device reached gravimetric capacitance of 213 F g^{-1} with energy and power densities of 30 Wh kg^{-1} and 1000 W kg^{-1}, respectively, and showed 95% cycling stability after 1000 cycles.

Keywords: conducting polymers, aerogels, supercapacitors

References

[1] Minisy, I. M.; Acharya, U.; Veigel, S.; Morávková, Z.; Taboubi, O.; Hodan, J.; Breitenbach, S.; Unterweger, C.; Gindl-Altmutterc, W.; Bober, P. Sponge-like polypyrrole-nanofibrillated cellulose aerogels: synthesis and application. *Journal of Materials Chemistry C* **2021**, *9*, 12615-12623.

[2] Bober, P.; Minisy, I. M.; Morávková, Z.; Hlídková, H., Hodan, J.; Hromádková, J.; Acharya, U. Polypyrrole aerogels: efficient adsorbents of Cr(VI) ions from aqueous solutions. *Gels* **2023**, *9*, 582:1-16.

[3] Milakin, K. A.; Tumacder, D. Von; Taboubi, O.; Acharya, U.; Hromádková, J.; Lhotka, M.; Pop-Georgievski, O.; Bober, P. Double-porous polyaniline-based cryogels with carbon nanofibers for supercapacitors. *ACS Applied Energy Materials* **2024**, *7*, 3354-3365.

Exciton Management in Supramolecular Polymers for Advanced Optoelectronic Applications.

M. A. Thottappali[1], Y. Panthi[1], A. Pandey[1], A. Chernyshev[2], J. Zedník[2], J. Vohlídal[2], J. Pfleger[1]

[1]Institute of Macromolecular Chemistry CAS, Prague, Czech Republic.
[2]Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Prague, Czech Republic;

Effective management of excitons relies on understanding the excited-state dynamics upon photoexcitation. This study explores the excited-state dynamics in a coordination polymer, $[CoU]_n$, formed through the self-assembly of 3,6-di(2,2′:6′,2″-terpyridin-4′-yl)-9-phenylcarbazole (U) with cobalt (II) (Co^{2+}) ions[1], in which the coordinated terpyridine (tpy) groups adopt a perpendicular arrangement around the Co^{2+} ions. The coordination alters the optical and electronic properties, like the energy band gap, and affects the exciton lifetime and dynamics [2]. Using femtosecond transient absorption spectroscopy, we analyzed metal - ligand charge transfer states and their impact on exciton dissociation and charge separation.

While comparing the time evolution of the excited-state spectra of the thin films, the $[CoU]_n$ complex exhibits an additional spectral feature compared to the broader transient response of Unimer (U). This suggests the formation of metal-to-ligand charge transfer (MLCT) states, leading to a modified exciton relaxation pathway. [3] The extended lifetime components in the complex imply a stabilized charge-separated state, likely influenced by ligand field effects and counterion interactions, which are crucial for electronic applications.

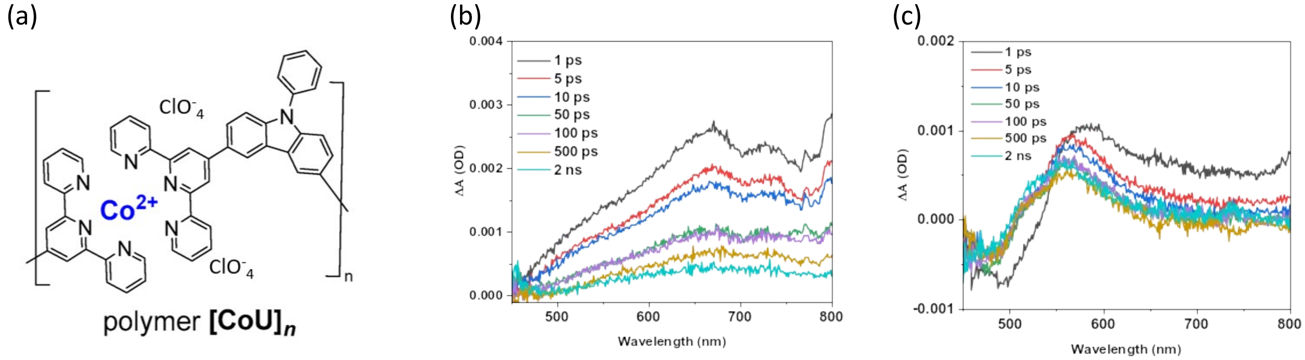


Fig. 1. (a) Scheme of metallo-supramolecular copolymer $[CoU]_n$, (b) Time evolution of transient absorption of thin film of U, (b) Time evolution of transient absorption of thin film of $[CoU]_n$ complex.

Acknowledgments

The work was financially supported by the MEYS of the Czech Republic, project LUAUS24032

References

[1] Pandey, A.; Chernyshev, A.; Panthi, Y.R.; Zedník, J.; Šturcová, A.; Konefał, M.; Kočková, O.; Foulger, S.H.; Vohlídal, J.; Pfleger, J. Synapse-Mimicking Memristors Based on 3,6-Di(tpy)-9-Phenylcarbazole Unimer and Its Copolymer with Cobalt(II) Ions. Polymers 2024, 16, 542.

[2] Owen, M.E.; Carter, E.; Hutchings, G.J.; Ward, B.D.; Murphy, D.M. Influence of Counterions on the Structure of Bis(Oxazoline)Copper(Ii) Complexes; an EPR and ENDOR Investigation. Dalt. Trans. 2012, 41, 11085–11092.

[3] Roy, S.; Roy, S.; Saha, S.; Majumdar, R.; Dighe, R.R.; Jemmis, E.D.; Chakravarty, A.R. Cobalt(II) Complexes of Terpyridine Bases as Photochemotherapeutic Agents Showing Cellular Uptake and Photocytotoxicity in Visible Light. Dalt. Trans. 2011, 40, 1233–1242.

Influence of particle size and quantity in mechanical recycling of silicone rubber

B. Liedl[1*], T. Höftberger[1], C. Burgstaller[1,2]

[1]*Transfercenter für Kunststofftechnik GmbH, Wels, Austria*
[2]*FH Oberösterreich F&E-GmbH, Wels, Austria*
**barbara.liedl@tckt.at*

Silicone rubber is a widely used elastomer, with a broad range of applications across many industries. Injection mouldable liquid silicone rubbers (LSR) are a type of silicone with high production quantities, and hence production waste generated. Although there are chemical recycling approaches for silicones, mechanical recycling is virtually ignored in research. In our study we investigated a mechanical recycling approach of LSRs by introducing ground particles as filler into matrix LSR material (**Figure 1**). We examined the influence of Shore A hardness, degree of shredding, and amount of filler used. Our results reveal good mechanical properties, close to those of the original materials. Even if there are still obstacles to overcome in industrial processes, our study could encourage to consider mechanical recycling of production scraps also for silicones as contribution to waste reduction.

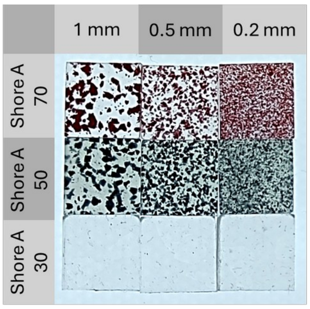


Figure 1: Silicone rubbers of three different Shore A hardnesses filled with 10 wt.% of milled silicone particles.

Keywords: mechanical recycling, liquid silicone rubber, silicone grinding

Acknowledgments
The research is carried out within the project Resilient (Rückgewinnung und Recycling von Silikonen und Thermoplasten aus Mehrkomponentenprodukten und -abfällen mit verbesserten neuen Technologien), subsidised by the province of Upper Austria (FTI – upperVISION2030) under the Grant no. Wi-2023-255271.

The influence of the particle size of silicon rubber particles in the meltfiltartion of Polyethylen

Thomas Höftberger[1*], Barbara Liedl[1*], Christoph Burgstaller[1,2*]

[1]*Transfercenter fuer Kunststofftechnik, Wels, Austria*
[2]*Univercity of Applied science Upper Austria, Wels, Austria (*
**barbara.liedl@tckt.at*

In the modern society there are a lot of applications for a combiantion of a themoplastic material and silicon rubber. The good processabilty of themoplastic materials and the good sealing properties of silicon rubber are one reason for this material combiantion. One of the biggest sources for silicon rubber contaminated themoplastics are pipe lines, with with a pressue valve. This matirial source has approximatly a pollution grade under 1% of silicon rubber. To determine the pollution grade and the influnce on the properties of the themoplast and the influence of melt filtration the folloeing work was carried out. The aim of the work was, to investigate the influnece of the partikel size and the amount of the pollution on the mechanical properties, the influence of meltfiltration on the themal stabiltity of the thermoplast and the influence of the partikel size on the melt filtration behaviour. Therefore 3 model compounds with a silcon rubber shore 50 are produced with 0,1 ,0,5 , 1% polloution with a polyethylen matrix. This compounds were meltfiltrated with a 14/30/150 mesh. The pressue infront of the sieve and behind the sieve where mesured. The melt filtartion where carried out 20 min or til 90 bar are reached infont of the sieve, because of the limits of the filtration setup. The mechanical properties where determined with the compounds and the filterd materials. As a measuremnt method for the pollution the m-tga where choosen, because the matrix can be burned of and around 50% of the silicon rubber stays back. Therefore the m-tga was used to compare the coumpound with the filtrated materials.
The experiments have shown, that the pressure infront of the sieve is higher with bigger particels and if the particels are to big the sieve closes and the process hat to be stopped. The pressure equilibrium with 0,2 and 0,5 mm particels lets assume that a part of the silicon rubber partikels are pushed throuth the sieve.

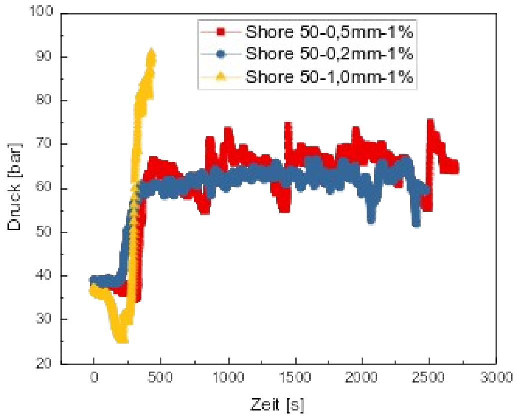


Figure 1: Comparison of the pressure infront of the sieve with 3 diffrnet particel sizes over the processtime

Keywords: recycling, extrusion,rubber

Acknowledgments

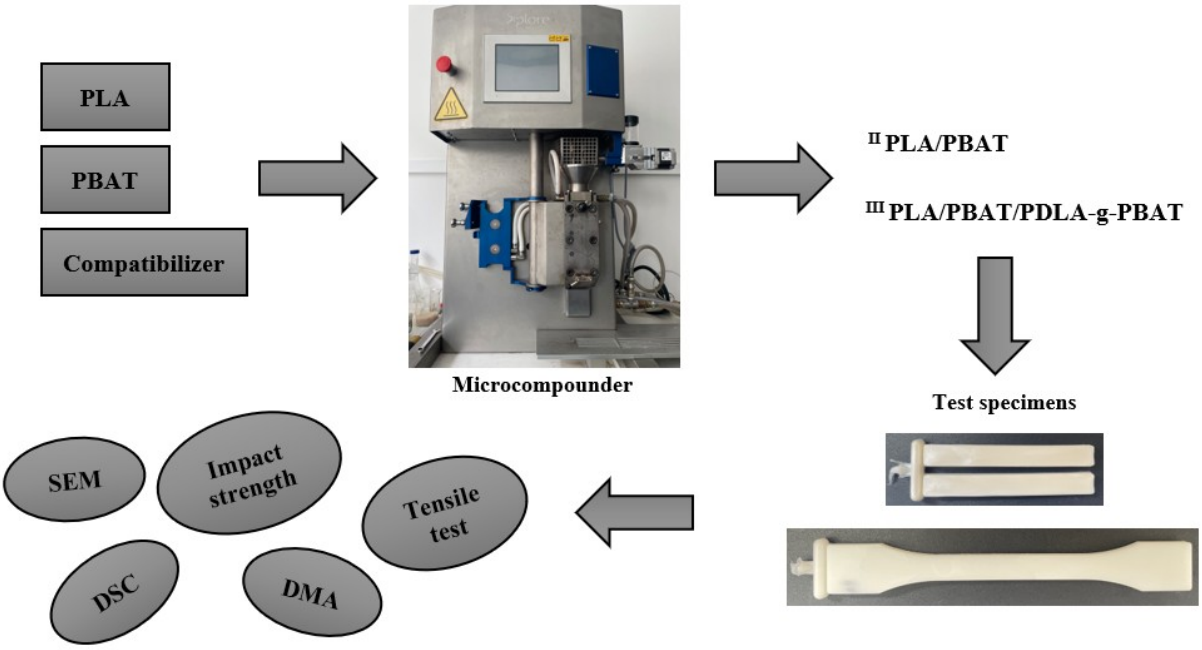
The research is carried out within the project Resilient (Rückgewinnung und Recycling von Silikonen und Thermoplasten aus Mehrkomponentenprodukten und -abfällen mit verbesserten neuen Technologien), subsidised by the province of Upper Austria (FTI – upperVISION2030) under the Grant no. Wi-2023-255271.

Reactive compatibilization of biodegradable PLA/PBAT blends

J. Novák[1*], M. Boruvka[1], J. Gomez-Caturla[2], C. Ngaowthong[3]

[1]*Technical University of Liberec, Liberec, Czechia*
[2]*Universitat Politecnica de Valencia, Alcoy, Spain*
[3]*King Mongkut's University of Technology, Prachinburi, Thailand*
[*]*jan.novak@tul.cz*

The intrinsic brittleness of poly(lactic acid) (PLA) constrains its applicability in scenarios requiring plastic deformation under conditions of increased mechanical stress. To overcome this, a series of poly(lactic acid) (PLA)/poly(butyleneadipate-co-terephtalate) (PBAT) biodegradable blends with a reactively extruded compatibilizer based on PDLA-g-PBAT iniciated by dicumyl-peroxide (DCP) were prepared through melt blending. The influence of processing parameters (reactive extrusion time and temperature etc.) and blend composition on the microstructure development and thermo-mechanical properties was observed. The thermal behavior and crystallinity of PDLLA/PDLA-g-PBAT/PBAT blends were analyzed by differential scanning calorimetry (DSC). Miscibillity and interphase compatibilization were investigated by scanning electron microscopy (SEM). Mechanical properties (charpy impact strength, tensile strength, modulus and elongation at break) were determined using universal tensile and impact testing machine. Measurement of dynamic mechanical analysis (DMA) was realized to underpin the results of mechanical testing, microstructure observation and thermal behaviors.



Graphical abstract

Keywords: PLA, PBAT, biodegradable blends, interphase compatibilization

Synthesis of Functional Polyesters based on Citric Acid

A. Kruglhuber*, C. Bernhard, K. M. Saller

Institute for Chemical Technology of Organic Materials, Johannes Kepler University, Linz, Austria
**annakruglhuber@gmail.com*

Polyesters are highly versatile materials that are of relevance to many different product categories. In view of the current challenges concerning climate change and pollution, they are attractive alternatives to conventional materials. With polyesters, a transition to bio-based and renewable educts has shown to be possible. Also, ester bonds are prone to hydrolysis under the right conditions and several biodegradable polyesters are reported [1]. The focus of the current research project is to synthesize functional polyesters based on citric acid, which is an easily available, cheap and renewable resource.

The chemical structure of citric acid is shown in Figure 1, with its multifunctionality being an interesting feature. In literature, the hydroxy group is reported to be unreactive. Also, the tertiary carboxyl group is described as less reactive than its primary counterparts during esterification. This should enable synthesis of polyester with carboxyl side chains, that are thus available for subsequent functionalization [2]. However, experimental data suggests the latter statement to not be entirely valid. Gelation is observed at a certain reaction time that depends on the monomers and the employed reaction conditions.

During synthesis, the conversion can be monitored by means of nuclear magnetic resonance spectroscopy (NMR). Depending on the utilized diol, reactions of the tertiary COOH group can be observed in ^{1}H and ^{13}C NMR spectra. The molecular weights of the resulting polyester chains as well as branching is investigated via size exclusion chromatography (SEC). Current synthesis procedures lead to broad and multimodal size distributions as shown in Figure 1.

Overall, citric acid-based polyesters can be described as promising materials worth exploring in more detail. With the currently ongoing optimization of their synthesis route and the associated focus on proper characterization, they seem to be viable candidates for biobased and biodegradable special products.

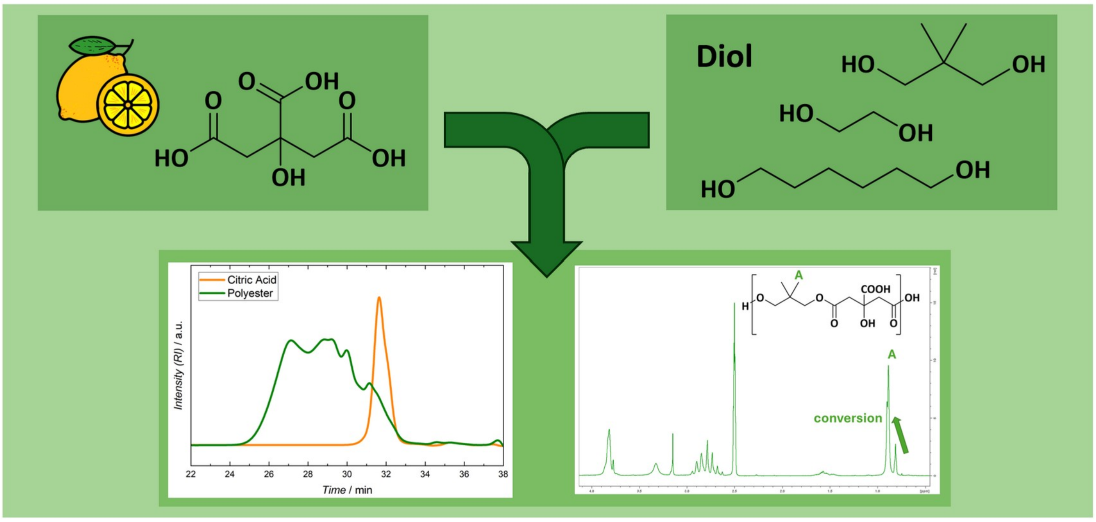


Figure 1: Schematic representation of the synthesis of citric acid-based polyesters.

Keywords: polyester synthesis, citric acid, renewable monomers, functional polyester, biodegradability

References

[1] Olarte-Paredes, A.; Salgado-Delgado, A.M.; García-Fuentes, J.J.; Salgado-Delgado, R.; Cedillo-Valverde, G.; López-Lara, T.; Hernández-Zaragoza, J.B.; Castaño, V.M. Synthesis and characterization of a polyester based on citric acid/ethylene glycol/glycerol. *Journal of Macromolecular Science, Part A* **2021**, *58*(12), 890–898.

[2] Noordover, B.A.; Duchateau, R.; van Benthem, R.A.; Ming, W.; Koning, C.E. Enhancing the functionality of biobased polyester coating resins through modification with citric acid. *Biomacromolecules* **2007**, *8*(12), 3860-3870.

Optimizing the Crosslinking Process of Citric Acid-based Polyesters

C. Bernhard*, A. Kruglhuber, K. M. Saller

Institute for Chemical Technology of Organic Materials, Johannes Kepler University, Linz, Austria
**clemens.bernhard@gmail.com*

The development of bio-based polymers is regarded as a crucial step towards a more sustainable chemical industry by reducing the environmental challenges that come along with traditional petroleum-based plastics. Among a variety of bio-based alternatives, polyesters derived from citric acid, stand out as particularly promising. Citric acid can be industrially produced through fermentation of molasses or corn starch, both of which are renewable resources that reduce the dependence on fossil fuels. These citric acid-based polyesters offer significant advantages over traditional materials, including enhanced recyclability and biodegradability.

Crosslinking of functional polyester precondensates forms a three-dimensional polymer network, which improves mechanical properties and thermal stability. Traditional options such as crosslinking via unsaturated building blocks negatively affect biodegradability by forming very stable C-C bonds. Using the additional carboxylic acid group of citric acid for crosslinking instead provides a network exclusively based on ester bonds which are cleaved during (bio)degradation. Our research aims to optimize this cross-linking process for sustainable polyesters using a variety of different crosslinking agents. By systematically varying reaction parameters such as temperature, reaction time, and oven setup, we obtained materials with different properties and tackled challenges arising during upscaling of the batch process.

Analytical methods, such as Gel Permeation Chromatography (GPC), are used to monitor the reaction progress in the early stages of crosslinking, before obtaining insoluble networks (Fig. 1c). Furthermore, Differential Scanning Calorimetry (DSC) and Infrared Spectroscopy (IR) are employed to obtain a deeper knowledge of the crosslinking reaction. Since citric acid-based polyesters are suitable for various biomedical applications [1], investigating additional parameters such as the gel content, porosity and degradability is essential.

Figure 1: a) Monomers used for polyester synthesis. b) Products of crosslinking condition screenings. c) GPC allows good comparison of polyester crosslinking conditions before obtaining insoluble networks.

Keywords: polyester, crosslinking, bio-based

References

[1] Salihu, R.; Abd Razak, S. I.; Zawawi, N. A.; Abdul Kadir, M. R.; Ismail, N. I.; Jusoh, N.; Mohamad, M. R.; Mat Nayan, N. H. Citric Acid: A Green Cross-Linker of Biomaterials for Biomedical Applications. Eur. Polym. J. **2021**, 146, 110271.

Bio-Based Hierarchically Porous Polymers from Terpenes and Terpenoid Acrylates via High Internal Phase Emulsion Templating

N. Slavič[1], P. Krajnc*

[1]*PolyOrgLab, Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova ulica 17, 2000 Maribor, Slovenia*
**Corresponding author: peter.krajnc@um.si*

The increasing demand for sustainable alternatives to fossil fuel-derived polymers has spurred interest in bio-based monomers, particularly terpenes and terpenoids, due to their natural abundance and inherent polymerisable functionalities [1],[2]. In this research, two complementary approaches were employed to develop hierarchically porous polymers (polyHIPEs) using terpene-based monomers via high internal phase emulsion (HIPE) templating. In the first part of the study, the terpenoids tetrahydrogeraniol, citronellol, and nopol were modified by using acryloyl chloride, resulting in the synthesis of terpenoid acrylates. These bio-derived acrylates served as the organic (monomer) phase in the formulation of HIPEs containing an 85% aqueous phase. The acrylate terpenoids in the organic phase were crosslinked with trimethylolpropane triacrylate (TMPTA) to form the polyHIPEs. A crosslinking degree of 5 and 10 mol% was used to investigate the feasibility of polyHIPE synthesis. While both crosslinking degrees facilitated the formation of polymers, only the 10 mol% systems exhibited the characteristic interconnected porous morphology. The primary pore diameters for tetrahydrogeraniol acrylate and citronellyl acrylate-based polyHIPEs were measured at 15.6 and 16.5 µm, respectively, whereas nopol acrylate-based polyHIPEs displayed a smaller average pore size of 5.6 µm. The second part of the study focused on the direct polymerization of the terpenes limonene, carvone, and myrcene, combined with multifunctional acrylate comonomers – TMPTA and pentaerythritol tetraacrylate (PETA). This strategy enabled the successful synthesis of poly(limonene-co-TMPTA), poly(limonene-co-PETA), poly(carvone-co-TMPTA), poly(carvone-co-PETA), poly(myrcene-co-TMPTA), and poly(myrcene-co-PETA) polyHIPEs. The terpene and acrylate ratios were varied to study the incorporation of the terpenes into the polyHIPE and the effects on the morphological properties. While the synthesis of terpene-based polyHIPEs was successful, the degree of limonene and carvone incorporation reduces when the content thereof in the HIPE mixture is increased. The obtained polyHIPEs exhibited primary pore sizes between 5.51 and 11.63 µm, and specific surface areas ranging from 2.7 $m^2 g^{-1}$ to approximately 300 $m^2 g^{-1}$. This combined study demonstrates the versatility of both terpenoid acrylates and unmodified terpenes as promising, renewable building blocks for the production of hierarchically porous polymers. Moreover, it highlights the potential of limonene and carvone in the synthesis of polyHIPEs, reinforcing the role of plant-derived monomers in the development of sustainable polymeric materials.

Keywords: Terpenes, Terpenoids, PolyHIPEs, Bio-sourced monomers, Porous polymers, High internal phase emulsions

Acknowledgments

This work was supported by the Slovenian Research Agency (ARRS) through the research programme P2-0006.

References

[1] Cywar R. M., Rorrer N. A., Hoyt C. B., Beckham G. T., Chen E. Y. X. Bio-based polymers with performance-advantaged properties. *Nat. Rev. Mater.* **2022**, 7, 83-103.

[2] Della Monica F., Kleij A. W. From terpenes to sustainable and functional polymers. *Polymer Chemistry* **2020**, 11, 5109-5127.

Bio-Inspired Photo-Crosslinking of Casein with Riboflavin Phosphate and Tannic Acid for Enhanced Colorant Retention in Sustainable Cosmetic Applications

Hyun Jong Lee[1*]

[1]*Gachon University, Seongnam, Republic of Korea*
[*]*hjlee2@gachon.ac.kr*

With increasing consumer demand for sustainable cosmetics, developing eco-friendly systems that maintain performance remains challenging. This research introduces a novel approach utilizing photo-responsive biopolymers to enhance water-soluble colorant stability in cosmetic applications. We developed an innovative platform based on casein protein films crosslinked through a riboflavin phosphate (RFP)-mediated photoreaction, with tannic acid (TA) as a natural polyphenolic reinforcement agent [1].

The fabrication process involved a systematic optimization of casein concentration, RFP content, and TA incorporation, followed by blue light irradiation (450-490 nm) to induce protein crosslinking. Structural characterization through FTIR spectroscopy confirmed successful crosslinking via formation of dityrosine bonds, while SEM analysis revealed a networked porous architecture conducive to controlled dye retention. Rheological assessment demonstrated that TA-modified films exhibited significantly improved mechanical properties, with up to 40% increase in storage modulus compared to unmodified counterparts.

The biocompatibility of these films was validated using NIH/3T3 fibroblasts, with cell viability consistently above 90% at all tested concentrations. When applied to human skin models, the photo-crosslinked films containing a model water-soluble red dye demonstrated remarkable color retention under standardized wash conditions, maintaining 85% of original color intensity after 8 hours compared to 32% for non-irradiated controls. The addition of TA provided supplementary improvement in durability through secondary interactions with both the protein matrix and encapsulated colorants.

This study establishes a foundation for development of next-generation sustainable color cosmetics by bridging principles from biomaterials science with cosmetic technology. The versatility of this platform allows for potential expansion to various colorants and active ingredients, offering promising opportunities for dermal delivery systems beyond decorative cosmetics. Our findings demonstrate that biomimetic, photo-responsive protein films represent an effective and environmentally conscious approach to addressing the persistent challenge of water-soluble dye retention in cosmetic applications.

Keywords: Photo-crosslinked casein, Riboflavin phosphate, Sustainable color cosmetics

Acknowledgments

This work was supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government (MSIT) (RS-2025-00518281, RS-2021-NR060117).

References

[1] Hong, M.J.; Lee, Y.; Kyung, S.J.; Choi, J.; Lee, H.J. Sustainable and durable color cosmetics: riboflavin phosphate-mediated photo-crosslinked casein films with tannic acid. *Biomaterials Science* **2024**, *12*, 6136-6147.

The Synthesis and Characterization of Tulipalin A based Hydrogels

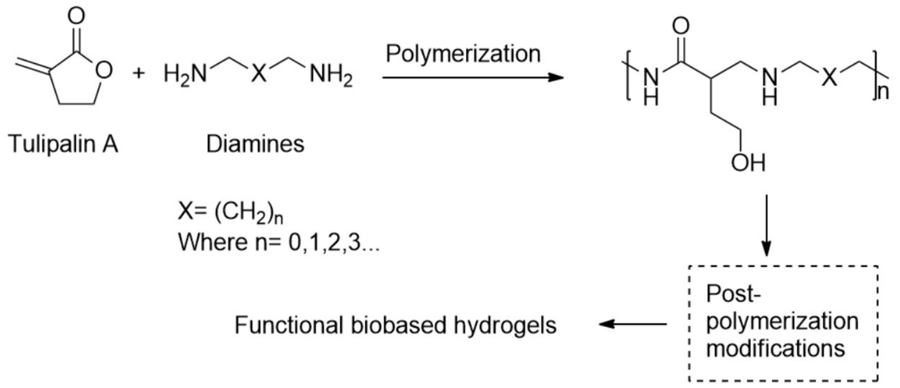
Muhammed Muhsin Puzhakkalakath[1]*, Sambit Kumar Lenka[1], Jaroslav Mosnacek[1]

[1]*Polymer Institute of SAV, Bratislava, Slovakia*

**upolmupu@savba.sk*

Poly(amidoamine)s or PAAs are polymers synthesised through the reaction of carbonyl group with amines. These types of polymers can be modified based on the application requirements; one such example is hydrogel synthesis.[1] Hydrogels are three-dimensional hydrophilic polymer networks extensively swollen with water.[2] They have many applications and are highly beneficial. One of the major disadvantages of these PAAs are their fossil-based origins. One such way to avoid those is to use biobased or renewable monomers for the polymerization. Renewable monomers sourced from plants and bio-feedstocks can be used as a suitable substitute for the synthesis of chemicals, building blocks, and biopolymers in this context.[3]

In the present work, novel hydrogels were synthesized by post-modification of a bio renewable Tulipalin A (α-methylene-γ-butyrolactone or MBL)- based polymer. This involves the polyaddition step-growth polymerization of MBL and diamines, resulting in the formation of poly(amidoamine)s (PAAs), followed by post-polymerization modifications into hydrogels. Prepared hydrogels with various compositions were investigated for their swelling, morphology, cytotoxicity, mechanical, and thermal properties.



Keywords: Renewable Monomer, Polyaddition, Poly(amidoamine)s, Biobased Hydrogels

Acknowledgments

The authors thank for support to FUR4Sustain project, Grant Agency VEGA through project VEGA 2/0153/25 and SRDA grant agency through project APVV-23-0534.

References

[1] Kollár, J.; Danko, M.; Pippig, F.; Mosnáček, J. Functional Polymers and Polymeric Materials from Renewable Alpha-Unsaturated Gamma-Butyrolactones. *Frontiers in Chemistry* **2019**, *7.*

[2] Ahmed, E. M. Hydrogel: Preparation, Characterization, and Applications: A Review. Journal of Advanced Research **2015**, *6 (2)*, 105–121.

[3] Morales, A.; Labidi, J.; Gullón, P.; Astray, G. Synthesis of Advanced Biobased Green Materials from Renewable Biopolymers. *Current Opinion in Green and Sustainable Chemistry* **2021**, *29*, 100436.

Terpene-Based Thiol–Ene PolyHIPEs: Sustainable Routes to Tunable Porous Polymer Networks

Amadeja Koler[1], Peter Krajnc[1]
[1] Faculty of Chemistry and Chemical Engineering, University of Maribor, Maribor, Slovenia

In the pursuit of sustainable alternatives to fossil-derived polymers, terpenes have emerged as a promising class of renewable, bio-based monomers.[1,2] These naturally occurring hydrocarbons—found predominantly in plants, especially in essential oils—exhibit considerable structural diversity and functional group reactivity, making them attractive candidates for the synthesis of advanced polymeric materials.

In this study, porous polymer networks were synthesized by thiol–ene photopolymerization using terpene myrcene, a multifunctional thiol (trimethylolpropane tris(3-mercaptopropionate)) and ethylene glycol dimethacrylate (EGDMA). High internal phase emulsions (HIPEs)[3] were used as templates and allowed the formation of highly porous polymers (polyHIPEs[4,5]) with a porosity of up to 80%. By systematically varying the terpene content (9–40 mol%) and the ratio of thiol to alkene functional groups, the resulting polymer morphology could be precisely controlled. Lower terpene concentrations (10-20 mol%) in combination with an excess of alkene functional groups led to the formation of well-defined, open-cell polyHIPE structures with interconnected pores. In contrast, a higher terpene content (40 mol%) and a stoichiometric thiol:alkene ratio of 1:1 promoted the formation of bicontinuous morphologies.
The materials were characterized by scanning electron microscopy (SEM) for morphology analysis and elemental analysis to evaluate polymerization efficiency. The surface area was determined by nitrogen adsorption/desorption using the Brunauer–Emmett–Teller (BET) method.
A novel approach using thiol–ene polymerization for the synthesis of myrcene-based polyHIPE materials is presented, marking a significant departure from the conventional free-radical polymerization methods commonly used for polyHIPE synthesis. Thiolene polymerization is particularly advantageous for polyHIPEs as it offers superior structural uniformity, improved mechanical properties and the ability to precisely modulate the chemical and physical properties of the material. The results highlight the potential of terpene-based monomers in the development of tunable, porous polymeric materials and demonstrate their applicability in areas such as separation, catalysis and biomedical engineering.

Keywords: Thiol-ene polymerization, terpene, myrcene, polyHIPEs,

References

[1] F. Della Monica, A.W. Kleij, From terpenes to sustainable and functional polymers, *Polym. Chem.* **2020**, 11, 5109–5127.
[2] M.E.G. Mosquera, G. Jim, V. Tabernero, J. Vinueza-vaca, C. Garc, K. Kosalkov, A. Sola-landa, C. Acosta, R. Alonso, M.Á. Valera, Terpenes and Terpenoids : Building Blocks to Produce Biopolymers, *Sustain. Chem.* **2021**, 2, 467–492.
[3] N.R. Cameron, High internal phase emulsion templating as a route to well-defined porous polymers, *Polymer.* **2005**, 46, 1439–1449.
[4] I. Pulko, P. Krajnc, High Internal Phase Emulsion Templating – A Path To Hierarchically Porous Functional Polymers, *Macromol. Rapid Commun.* **2012**, 33, 1731–1746.
[5] I. Pulko, P. Krajnc, Porous Polymer Monoliths by Emulsion Templating, *Encycl. Polym. Sci. Technol.* **2017**, 1–28.

Fabrication of Thermally Stable Enzyme Complexes for Enhanced Polymer Biodegradation and Their Application in Melt Extrusion Processes

Jeong Je Seo[1,2], In Woo Nam[1], Byoung-Sun Lee[2], Yeong Og Choi[1*]

[1]*Textile Innovation R&D Department, Korea Institute of Industrial Technology, Ansan, South Korea*
[2]*Department of Fiber System Engineering, Dankook University, Yongin, South Korea*
[*]*yochoi@kitech.re.kr*

The growing accumulation of plastic waste, particularly microplastics, has intensified the demand for environmentally sustainable recycling technologies.[1] Enzymatic biological recycling presents a promising alternative, enabling polymer degradation under mild, non-toxic conditions with low energy input.[2] However, a major challenge remains in applying enzymes directly to conventional plastic manufacturing processes, such as melt extrusion, which involve high-temperature environments beyond the stability range of most enzymes.

In this study, a commercially available enzyme was immobilized through physical adsorption onto porous supports and entrapment within a polymeric matrix to enhance its thermal stability, enabling its application in polymer melt extrusion processes for improved biodegradability. The enzyme-immobilized composites were blended at a specific ratio into melt extrusion processes such as film casting and fiber spinning to fabricate biodegradable polymer films and fibers. The resulting materials exhibited significantly enhanced biodegradability, experimentally confirming that the enzyme retained its catalytic activity even under the high-temperature conditions of melt processing due to the immobilization.

Keywords: Enzyme Immobilization, Biodegradation, Biological Recycling, Melt Extrusion

Acknowledgments: *This research was funded by Global Industrial Technology Cooperation Program, Ministry of Trade, Industry and Energy (P0028353)*

References

[1] Kyriakopoulos, G. L.; Zorpas, A. A.; Inglezakis, V. J.; Rodríguez-Barroso, R. The silent invaders: microplastic accumulation, impacts, and monitoring approaches. *Toxics*, **2025**, 13.3: 192.

[2] Rahmati, F.; Sethi, D.; Shu, W.; Lajayer, B. A.; Mosaferi, M.; Thomson, A.; Price, G. W. Advances in microbial exoenzymes bioengineering for improvement of bioplastics degradation. *Chemosphere*, **2024**, 355: 141749.

Fabrication and Optimization of Electrospun Porous PLA Nanofiber Membranes for Advanced Filtration Application

Hyo Jung Kim[1,4], Hyo Kyoung Kang[2], Hyun Ju Oh[3], Byoung-Sun Lee[4] and Yeong Og Choi[1*]

[1]*Textile Innovation R&D Department, Korea Institute of Industrial Technology, Aansan, Korea*
[2]*Carbon and Light Materials Application Group, Korea Institute of Industrial Technology, Jeonju, Korea*
[3]*Department of Organic & Nano Engineering, Hanyang University, Seoul, Korea*
[4]*Department of Fiber System Engineering, Dankook University, Yongin, Korea*
+*Corresponding Author: yochoi@kitech.re.kr*

Air pollution has emerged as a critical environmental issue due to rapid industrialization. Particulate matter (PM), a major air pollutant, poses serious health risks as it can lead to respiratory and cardiovascular diseases. This has led to growing demand for high-performance air filtration systems. However, most commercial filters are made of non-biodegradable polymers such PP, PE, and PET, which contribute to environmental pollution during incineration. As a sustainable alternative, polylactic acid (PLA), a biodegradable polymer, has recently gained attention as a promising material for eco-friendly filter applications [1].

Porous fiber structures offer significant advantages in filtration due to their unique morphology. Their large specific surface area provides a greater number of active sites for the physical adsorption of airborne particles [2]. Additionally, compared to conventional smooth-surfaced fibers, porous fibers typically have lower packing density, which reduces air resistance and thus lowers the pressure drop across the filter.

In this study, we fabricated porous PLA nanofiber membranes using the electrospinning process. The pore morphology was controlled by adjusting key processing parameters such as solvent ratio, applied voltage, and humidity. The resulting porous PLA membranes exhibited higher surface area and broader pore size distribution than their smooth counterparts, leading to superior filtration performance. These results indicate that the porous PLA filters are expected to be applied as eco-friendly and high-performance filtration materials.

Acknowledgments
This research was funded by Global Industrial Technology Cooperation Program, Ministry of Trade, Industry and Energy (P0028353)

References

[1] Vatanpour, V.; Dehqan, A.; Pazireh, S.; Zinandli, S.; Azinatazadeh, A.A.; Koyuncu, I. Polylactic acid in the fabrication of separation membranes: A review. *Separation and Purification Technology* **2022**, *296*, 121423.
[2] Russo, F.; Castro-Muñoz, R.; Santoro, S.; Galiano, F.; Figoli, A. A Review on Electrospun Membranes for Potential Air Filtration Application. *Journal of Environmental Chemical Engineering* **2022**, *10*(6), 108452.