EUPOC 2023

Dynamic Polymer Networks

14-18 May 2023, Bertinoro (FC), Italy

Co-Chairs

Filip Du Prez
(Ghent University)

Eric Drockenmuller
(Université de Lyon 1)

Organized by

UNIVERSITÉ DE LYON

GHENT UNIVERSITY

Under the auspices of

epf European Polymer Federation

Supported by

AIM
Associazione Italiana
di Scienza e Tecnologia delle Macromolecole

Acknoledgments

VITRIMAT

SHAREBOT

RSC Applied Polymers

Polymer Chemistry

Booklet of Abstracts

INDEX

PLENARY LECTURES

Index

ORAL CONTRIBUTIONS

Index

POSTER CONTRIBUTIONS

ABSTRACTS

INVITED LECTURES

PL 1

DYNAMIC NETWORKS AS A ROUTE TO ACCESS PLURIPOTENT MATERIALS

STUART J. ROWAN

Pritzker School of Molecular Engineering and Department of Chemistry, University of Chicago (USA) – Email: stuartrowan@uchicago.edu

Abstract

The concept of a pluripotent material is best explained by analogy to stem cells, which are pluripotent as they can give rise to different cell types. Thus, a pluripotent "stem" plastic has the capability of being converted into different classes of plastic material. Limited access to materials in resource-scarce areas (at sea, in space, on the battlefield) present challenges in which the concept of pluripotent plastics is an attractive one. The question, therefore, is "how can we design pluripotent materials? As part of our work in dynamic covalent polymers[1-7] we have been exploring the use room temperature dynamic covalent bonds to develop new classes of dynamic materials[8] and have explored their use to access pressure sensitive adhesives[9] and stress adaptive dense suspensions[10]. This talk will focus on new work aimed at combing this class of dynamic materials with tempering or training procedures to allow access to a wide range of material properties from a single "pluripotent" source.

References

[1] Michal, B.T.; Jaye, C.A.; Spencer, E.J.; Rowan, S.J. "Inherently Photo-Healable and Thermal Shape-Memory Polydisulfide Networks" *ACS Macro Lett.* **2013**, *2*, 694-699. DOI: 10.1021/mz400318m

[2] Michal, B.T.; Spencer, E.J.; Rowan, S.J. "Stimuli-responsive Reversible Two-Level Adhesion from a Structurally Dynamic Shape Memory Polymer" *ACS Appl. Mater. Interfaces* **2016**, *8*, 11041-11049. DOI: 10.1021/acsami.6b01251.

[3] Zhang, L.; Chen, L.; Rowan, S.J. "Trapping Dynamic Disulfide Bonds in the Hard Segments of Thermoplastic Polyurethane Elastomers" *Macromol. Chem. Phys.* **2017**, *218*, 1600320 (1-10). DOI: 10.1002/macp.201600320.

[4] Zhang, L.; Rowan, S.J. "The effect of sterics and degree of crosslinking on the mechanical properties of dynamic poly(alkylurea-urethane) networks" *Macromolecules,* **2017**, *50*, 5051-5060. DOI: 10.1021/acs.macromol.7b01016.

[5] Cudjoe, E.; Herbert, K.M.; Rowan, S.J. "Strong, Rebondable, Dynamic Cross-linked Cellulose Nanocrystal Polymer Nanocomposite Adhesives" *ACS Appl. Mater. Interfaces* 2018, *10*, 30723-30731 DOI: 10.1021/acsami.8b10520.

[6] Chen, L.F.; Zhang, L.H.; Griffin, P.J.; Rowan, S.J. "Impact of Dynamic Bond Concentration on the Viscoelastic and Mechanical Properties of Dynamic Poly(alkylurea-co-urethane) Networks" *Macromol. Chem. Phys.* **2020**, *221*, 1900440. DOI: 10.1002/macp.201900440.

[7] Kato, R.; Mirmira, P.; Sookezian, A.; Grocke, G.L.; Patel, S.N.; Rowan, S.J. "Ion-Conducting Dynamic Solid Polymer Electrolyte Adhesives" *ACS Macro Lett.* **2020**, *9*, 500-506. DOI: 10.1021/acsmacrolett.0c00142.

[8] Herbert, K.M.; Getty, P.T.; Dolinski, N.D.; Hertzog, J.E.; de Jong, D.; Lettow, J.H.; Romulus, J.; Onorato, J.W.; Foster, E.M.; Rowan, S.J. "Dynamic reaction-induced phase separation in tunable, adaptive covalent networks" *Chem. Sci.,* **2020**, *11*, 5028-5036. DOI: 10.1039/D0SC00605J.

[9] Herbert, K.M.; Dolinski, N.D.; Boynton, N.R.; Murphy, J.G.; Lindberg, C.A.; Sibener, S. J.; Rowan, S.J. "Controlling the morphology of dynamic thia-Michael networks to target pressure sensitive and hot melt adhesives", *ACS Appl. Mater. Interfaces* **2021**, *13*, *27471-27480.* DOI: 10.1021/acsami.1c05813

[10] Grayson L Jackson, G.L.; Dennis, J. M.; Dolinski, N. D.; van der Naald, M.; Kim, H.; Eom, C; Rowan, S. J.; Jaeger, H. M. "Designing Stress-Adaptive Dense Suspensions using Dynamic Covalent Chemistry" *Macromolecules,* ***2022,*** *55, 15, 6453–6461. DOI:* 10.1021/acs.macromol.2c00603

PL 2

MOLECULAR ENGINEERING IN FOUR DIMENSIONS: A MECHANISTIC APPROACH TO REPROCESSABLE ELASTOMERS

JULIA A. KALOW

Northwesern University, Evanston, IL 62021 (USA) – Email: jkalpw@northwestern.edu

Abstract

In dynamic covalent polymer networks known as vitrimers, the topology is reconfigured through associative exchange reactions. These materials hold promise as repairable and recyclable thermosets and elastomers. The Kalow Lab combines physical organic approaches and mechanical characterization to interrogate the relationship between the molecular exchange chemistry and flow in reprocessable elastomers. These studies are enabled by the use of crosslinks that exchange via a catalyst-free conjugate addition/elimination pathway. We find that stiffness and stress relaxation rate can be decoupled and independently modulated by synthetically tuning the cross-linker and prepolymer backbone, respectively. Our studies reveal the importance of internal catalysis in accelerating exchange reactions, which has inspired our design of switchable cross-linkers.

PL 3

CATALYTICALLY CONTROLLING THE MATERIAL FLOW IN DYNAMIC POLYMER NETWORKS

ELISABETH ROSSEGGER[1], DAVID REISINGER[1], THOMAS GRIESSER[2], SANDRA SCHLÖGL[1]

[1]*Polymer Competence Center Leoben GmbH, Roseggerstrasse 12, 8700 Leoben (Austria) – Email: sandra.schloegl@pccl.at*
[2]*Institute of Chemistry of Polymeric Materials, Montanuniversitaet Leoben, Otto Glöckel-Strasse 2, 8700 Leoben (Austria)*

Abstract

The use of catalysts is a versatile and convenient approach to control the rate of bond exchange reactions and the related material flow in dynamic polymer networks.[1] In particular, the selection of appropriate catalysts is guided by parameters such as efficiency, (in)solubility, temperature stability as well as long-term performance (e.g. ageing and leaching).

For photocurable resins, the introduction of conventional transesterification catalysts is challenging as they are poorly soluble and compromise on cure rate and pot life, which limits network design and applicable processing techniques. To overcome this drawback, we significantly expanded the toolbox of photocurable monomers suitable for vat photopolymerization 3D printing of dynamic polymer networks (e.g. acrylate and thiol-click systems) by introducing organic phosphates and phosphonates as new transesterification catalysts.[2] To prevent leaching, we employed phosphate and phosphonate derivatives with functional (meth)acrylate groups, which were covalently immobilized within the photopolymer network during the curing reaction. By appropriate network design, we obtained fast curing together with rapid bond exchange reactions and were able to 3D print dynamic thiol-acrylate and acrylate networks with triple-shape memory and thermal mendability.[3]

Following an alternative approach, we explored a novel family of photolatent transesterification catalysts to equip dynamic covalent networks with creep resistance and high bond exchange rates (once activated). We incorporated thermally stable photolatent bases (e.g. quaternary ammonium salts[4] and *N*-substituted derivatives of the amidine base 1,5-diazabicyclo[4.3.0]non-5-ene[5]) in thiol-click networks and realized a local and temporal change in material reflow due to the light-mediated release of strong Brønsted bases. In follow-up studies, we further demonstrated the applicability of various (commercially available) photolatent acids[6] and a newly synthetized photolatent organophosphate[7] for the spatially resolved release of the catalysing species by exploiting the orthogonality between the curing (visible light) and the activation reaction of the catalyst (UV light). Recently, we transferred the concept to thermolatent catalysts, whose activation is not limited by sample geometry and optical transparency of the materials. As proof of principle, the selective activation of dynamic transesterification was shown in fibre-reinforced and highly filled magneto-active thiol-ene polymer composites giving rise to the wide range of potential future applications offered by this concept.

---

[1] F. van Lijsebetten, T. Debsharma, J. M. Winne, F. E. Du Prez, *Angew. Chem.* **2022**, *61*, e202210405.

[2] E. Rossegger, R. Höller, D. Reisinger, J. Strasser, M. Fleisch, T. Griesser, S. Schlögl, *Polym. Chem.* **2021**, *12*, 639.

[3] E. Rossegger, R. Höller, D. Reisinger, M. Fleisch, J. Strasser, V. Wieser, T. Griesser, S. Schlögl, *Polymer* **2021**, *221*, 123631.

[4] D. Reisinger, S. Kaiser, E. Rossegger, W. Alabiso, B. Rieger, S. Schlögl, *Angew. Chem.* **2021**, *60*, 14302.

[5] D. Reisinger, K. Dietliker, M. Sangermano, S. Schlögl, *Polym. Chem.* **2022**, *13*, 1169.

[6] E. Rossegger, K. Moazzen, M. Fleisch, S. Schlögl, *Polym. Chem.* **2021**, *12*, 3077.

[7] C. Dertnig, G. La Guedes de Cruz, D. Neshchadin, S. Schlögl, T. Griesser, *Angew. Chem.* **2022**, *134*, e202210405.

PL 4

DYNAMIC POLYMER NETWORKS VIA TRANS-REACTIONS WITH NEIGHBORING GROUP PARTICIPATIN

HANS HEUTS

Supramolecular Polymer Chemistry Group, Department of Chemical Engineering & Chemistry
and Institute for Complex Molecular Systems, Eindhoven University of Technology,
PO Box 513, 5600 MB Eindhoven, NL
Email: vamvakak@materials.uoc.gr

Abstract

The study of dynamic covalent polymer networks has become a very active field of research over the past decade, with many efforts directed towards the development of novel dynamic chemistries and a better control of the material properties. Our recent efforts have focused on dynamic covalent networks using catalyst-free trans-reactions, in particular in systems based on pyromellitic dianhydride (PMDA)[1,2] and phosphate esters.[3,4] PMDA is a common commercial building block that can be used for dynamic linking in polyesters and was found to be an efficient dynamic cross-linker in diamine systems through an imide-diamide equilbrium, imparting additional stiffness to the networks via supramolecular interactions. Phosphate tri-esters have also been found to be very efficient dynamic linkers and cross-linkers and can undergo transesterification reactions via both associative and dissociative mechanisms, depending on the presence of b-hydroxyl groups. In this presentation, our recent results obtained for these systems will be discussed.

References

[1] H. Zhang, S. Majumdar, R.A.T.M. van Benthem, R.P. Sijbesma, J.P.A. Heuts, "Intramolecularly catalyzed dynamic polyester networks using neighboring carboxylic and sulfonic acid groups" *ACS Macro Letters*, **9**, 272-277 (2020).
[2] Y. Chen, H. Zhang, S. Majumdar, R.A.T.M. van Benthem, J.P.A. Heuts, R.P. Sijbesma, "Dynamic polyamide networks via imide-amide exchange" *Macromolecules*, **54**, 9703-9711 (2021).
[3] S. Majumdar, H. Zhang, M. Soleimani, R.A.T.M. van Benthem, J.P.A. Heuts, R.P. Sijbesma, "Phosphate triester dynamic covalent networks" *ACS Macro Lett.*, **9**, 1753-1758 (2020).
[4] S. Majumdar, B. Mezari, H. Zhang, J. van Aart, R.A.T.M. van Benthem, J.P.A. Heuts, R.P. Sijbesma, "Efficient exchange in a bioinspired dynamic covalent polymer network via a cyclic phosphate triester intermediate" *Macromolecules*, **54**, 7955-7962 (2021).

PL 5

DYNAMIC COVALENT ADDITION-TYPE POLYMER NETWORKS: FROM DESIGNING NETWORKS FROM MOBOMER FOR RECYCLING TO UPCYCLING THERMOPLASTIC POLYETHYLENE INTO REPROCESSABLE CROSS-LINKED OLYETHYLENE

JOHN M. TORKELSON

Department of Chemical and Biological Engineering and Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA
E-mail: j-torkelson@northwestern.edu

Abstract

Dynamic covalent polymer networks, or DCPNs, have been active area of research for roughly two decades. Most research focused on DCPNs has involved networks made by step-growth reactions of functional groups, e.g., polyhydroxyurethane networks made by reaction of cyclic carbonates with amines. However, polymer networks made from addition-type polymerization are also technologically and commercially important. Here, I will describe how simple, catalyst-free, one-step free-radical polymerization reactions can be used to prepare polymer networks from monomer that allow for full recovery of cross-link density after multiple, melt-state reprocessing steps. They key is to employ simple cross-linkers in the reaction that have two or more polymerizable carbon-carbon double bonds and a moiety that undergoes dissociative dynamic chemistry at elevated temperature but remains robustly covalently bonded at intended use conditions. My research group has studied and/or developed four such simple cross-linkers, and I will describe the utility and any limitations of each cross-linker. I will also discuss the implications of the dissociative nature of these dynamic covalent cross-linkers for the temperature dependence of the rubbery plateau modulus and the activation energies associated with elevated-temperature stress relaxation and viscous creep. Finally, I will describe how we can employ these simple cross-linkers to upcycle virgin or spent thermoplastic polyethylene (PE) into dynamic covalent PE networks. The process conditions employed to make these dynamic covalent PE networks are like those used to make non-reprocessable PE networks from PE with one exception, and that is the addition of a few weight percent of the dynamic cross-linker to the PE being processed with a radical initiator. This method works for virgin and post-consumer low-density PE and high-density PE. This approach could prove to be important in effective upcycling of waste polymers because PE comprises more than one-third of all worldwide polymer production.

References

[1] K. Jin, et al., *Adv. Mater.* **2016**, *28*, 6746.
[2] M. Bin Rusayyis and J.M. Torkelson, *Macromolecules* **2020**, *53*, 8367.
[3] L. Li, et al., *Macromolecules* **2021**, *54*, 1432.
[4] M.A. Bin Rusayyis and J.M. Torkelson, *Polym. Chem.* **2021**, *12*, 2760.
[5] M.A. Bin Rusayyis and J.M. Torkelson, *ACS Macro Lett.* **2022**, *11*, 568.
[6] L.M. Fenimore, et al., *J. Mater. Chem. A* **2022**, *10*, 24726.

PL 6

MODELING AND DESIGNING CATCH BONDS IN POLYMER SYSTEMS

CORNELIS STORM

TUE, The Netherlands
Email: c.storm@tue.nl

Abstract

Catch bonds are physical or chemical bonds whose lifetime increases with increasing load – bonds that become stronger when a force is applied. This counterintuitive behavior is showing up in increasingly many biological protein-protein bonds, and leads to interesting, functional behavior for instance in biological adhesion. I will explain the general physical principles that lead to catch bonding at the single-polymer level, and will suggest some ways in which this behavior can be designed into synthetic systems to produce materials with unique mechanical properties.

PL 7

STIMULI-RESPONSIVE NON-COVALENT POLYMER NETWORKS

CHRISTOPH WEDER
Adolphe Merkle Institute, University of Fribourg, Switzerland
Email: Christoph.weder@unifr.ch

Abstract

Supramolecular polymers are formed by the self-assembly of monomeric units equipped with binding motifs that enable hydrogen bonding, metal-ligand coordination or other directional non-covalent interactions. The reversibility of supramolecular bonds can be exploited to disassemble SPs back into their monomeric species. This can be achieved in a controlled manner by the application of a specific stimulus, such as heat, light or a mechanical force, making supramolecular interactions a versatile design element for the creation of functional polymers with unusual stimuli-responsive properties. In this presentation we will discuss several recent examples of supramolecular polymer networks assembled through hydrogen-bonding motifs or metal-ligand complexes. These non-covalent bonds were used to assemble different types of supramolecular monomers to create a broad range of stimuli-responsive polymers. Functions that can be achieved using this design approach include the ability to heal, (de)bonding on demand, and mechanochromic effects. We also present strategies that allow pushing the mechanical properties of supramolecular polymers towards the range covered by conventional thermoplastics

References

[1] J. Sautaux, F. Marx, I. Gunkel, C. Weder, S. Schrettl "Strong, stiff, and tough supramolecular polymers" *Nature Comms.* **2022**, *13*, 356.
[2] M. Mareliati, L. Tadiello, S. Guerra, L. Giannini, S. Schrettl, S. Weder "Metal-ligand complexes as dynamic sacrificial bonds in elastic polymers" *Macromolecules* **2022**, *55*, 5164-5175.
[3] L.N. Neumann, E. Oveisi, A. Petzold, R. Style, T. Thurn-Albrecht, C. Weder, S. Schrettl "Dynamics and Healing Behavior of Metallosupramolecular Polymers" *Sci. Adv.* **2021**, *7*, eabe4154.
[4] D.K. Hohl, S. Balog, C. Cappelletti, F. Karasu, C. Weder "Crystallizable Supramolecular Polymers - Binding Motif and Processing Matter" *Macromolecules* **2020**, *53*, 9086–9090.

PL 8

SYNTHESIS OF VITRIMERS IN DISPERSED MEDIA

DAMIEN MONTARNAL

[1] *Université de Luon, CPE Lyon, CNRS, Catalyse, Polymérisation, Procédeés et Matériaux, UMR 5128, F-69003 Lyon (France) – Email: damien.montarnal@univ-lyon.fr*

Abstract

Vitrimers aim at combining the benefits of thermoplastics and thermosets by incorporating in polymer networks dynamic covalent crosslinks governed by associative, exchangeable reactions in chemical equilibrium.[1] At high temperatures or in the presence of catalysts, chemical equilibria are fast enough to enable large scale reorganisation and stress relaxation of the network, and as a consequence plastic deformation, reprocessing and welding of the sample. In contrast with dissociative reversible networks that depolymerize at high temperatures, associative vitrimer networks remain crosslinked at all times and display a high melt elasticity and therefore a large adaptability to mould-free (re)processing techniques.

This versatile concept has been successfully applied to different polymer systems by taking advantage of a variety of equilibrated reactions, either textbook or purposely developed.[2,3] Yet, polymerization methodologies and processing of vitrimers are strongly focused on thermosetting formulations, i.e. liquid precursors cured into a dynamic crosslinked network, or modification and functionalization of thermoplastics in the melt.

In view of expanding further the uses and applications of vitrimers, we started to develop syntheses in dispersed media in order to obtain vitrimer nanoparticles that can form films or composites by sintering across particles.[4,5]

We will show a few recent examples involving techniques such as waterborne miniemulsion polymerization or sol-gel synthesis in organic solvents. Horizons opened by these methods will be illustrated, focusing in particular on nanostructured materials or on the synthesis of highly densely crosslinked vitrimers with high Tgs that are not attainable using a direct route.

References

[1] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, Science **2011**, *334*, 965.
[2] M. Guerre, C. Taplan, J. M. Winne, F. E. Du Prez, Chem. Sci. **2020**, *11*, 4855.
[3] A. Jourdain, R. Asbai, O. Anaya, M. M. Chehimi, E. Drockenmuller, D. Montarnal, Macromolecules, **2020**, *53*, 1884.
[4] T. N. Tran, E. Rawstron, E. Bourgeat-Lami, D. Montarnal, ACS Macro Lett. **2018**, *7*, 376
[5] F. Lossada, J. Guo, D. Jiao, S. Groeer, E. Bourgeat-Lami, D. Montarnal, A. Walther, Biomacromolecules **2019**, *20*, 1045.

PL 9

SYNERGISTIC INTERACTIONS OF DYNAMIC COVALENT CHEMISTRY AND ORIENTATIONAL ORDER IN COVALENT ADAPTABLE NETWORKS

TAYLER S. HEBNER[1], ALEXA S. KUENSTLER[1], MATTHEW K. MCBRIDE[1], ALINA M. MARTINEZ[1], TIMOTHY J. WHITE[1], CHRISTOPHER N. BOWMAN[1]

[1] *Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder CO 80309 (USA)*
E-mail: Christopher.Bowman@colorado.edu

Abstract

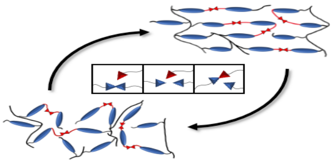


Figure 1. Dynamic bonds enable reprogramming in structural networks.

The ability to impart ordered structure in polymer chains enables functionality such as improved strength, anisotropic mechanical properties, and stimuli-responsive deformations. Structural order within the polymer network is enforced during the initial synthesis of a polymer network. The resulting network retains the programmed orientation and associated properties. However, this leaves minimal opportunities to program secondary network structure due to the permanence of the covalent crosslinks. Therefore, the combination of covalent adaptable networks (CANs) with structurally ordered networks is highly desired as a means to enable *re*structuring the material and enable a broader range of functionality. Here, integration of CANs will be demonstrated in two structural networks: liquid crystalline elastomers (LCEs) and semicrystalline polymers.

In LCEs, anisotropic orientation enables stimuli-responsive deformations. Since CANs rely on external stimuli to activate bond exchange, stimulus orthogonality must be used to ensure that actuation and network reorientation are activated independently. In one approach, LCEs are designed for thermal actuation and photo-activated network reorientation. [1] Using photo-responsive allyl sulfide bonds, the network undergoes secondary programming by mechanically deforming the network and activating bond exchange. The resulting LCE undergoes thermal actuation, exhibiting complex actuated shapes that are not accessible by surface or mechanical alignment alone. Also, LCEs are programmed for photoresponsive actuation using diarylethene and thermally activated thiol-anhydride bond exchange. [2] Further, by incorporating CANs in semicrystalline materials, the range of accessible properties and shapes of semicrystalline materials becomes dramatically expanded. In this work, we use thiol-thioester exchange in thiol-ene based semicrystalline networks to demonstrate catalytic control of crystallization and reprocessing of complex geometries.[3,4]

References

[1] Hebner, T.S., B.E. Kirkpatrick, Anseth, K.S., Bowman, C.N., White, T.J., Surface Enforced Alignment of Reprogrammable Liquid Crystalline Elastomers, *Advanced Science,* 2022, 2204003

[2] Hebner, T.S., Podgórski, M., Mavila, S., White, T.J., Bowman, C.N. Shape Permanence in Diarylethene-Functionalized Liquid-Crystal Elastomers Facilitated by Thiol-Anhydride Dynamic Chemistry, *Angewandte Chemie Int. Ed.,* 2022, e202116522.

[3] Kuenstler, A.S., Hernandez, J.J., Trujillo-Lemon, M., Osterbaan, A., Bowman, C.N, "Vat Photopolymerization Additive Manufacturing of Tough, Fully Recyclable Thermosets", *ACS Appl. Mater. Interfaces,*. 2023, 15, 8

[4] Kuenstler, A.S., Bowman, C.N., "Catalytic Control of Crystallization in Dynamic Networks", *ACS Macro Lett.,* 2023, 12, 2, 133-139

PL 10

POLYMERIC TOPOLOGY ISOMERIZATION NETWORKS

TAO XIE

State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China.
Email: taoxie@zju.edu.cn

Abstract

Bond exchange in typical dynamic covalent polymer networks allows access to various attractive properties including thermoset recycling, self-healing, and shape reconfigurability. For these networks, however, the design intent is that their molecular architectures remain unchanged before and after the bond exchange. An opposite possibility is that the network architecture can be designed to switch to various topological states corresponding to different material properties. We call this latter class of polymer network as Topology Isomerizable Network (TIN). In this talk, I will introduce the basic principle of TIN and show several examples on how TIN can be designed. The concept of TIN paves a way to programmable regulation of network polymers with practical implications for various fields including soft robotics, flexible electronics, medical devices, and 3D/4D printing.

References

[1] W. Miao, B. Yang, B. Jin, C. Ni, H. Feng, Y. Xue, N. Zheng, Q. Zhao Q, Y. Shen, T. Xie T. "An orthogonal dynamic covalent polymer network with distinctive topology transformations for shape- and molecular architecture reconfiguration.." *Angew. Chem. Int. Ed,.* **2022**, *134*, e202109941.
[2] W. Miao, W. Zou, B. Jin, C. Ni, N. Zheng, Q. Zhao, T. Xie. "On demand shape memory polymer via light regulated topological defects in a dynamic covalent network" *Nat. Commun.* **2020**, *11*, 4257.
[3] W. Zou, B. Jin, Y. Wu, H. Song, Y. Luo, F. Huang, J. Qian, Q. Zhao, T. Xie. "Light-triggered topological programmability in a dynamic covalent polymer network." *Sci. Adv.,* **2020**, *6*, eaaz2362.

PL 11

MULTIPLY RESPONSIVE DYNAMIC MATERIALS CONTROLLED BY POLYMER STRUCTURE

DOMINIK KONKOLEWICZ, PHD
Department of Chemistry and Biochemistry, Miami University
Hughes Hall 246, 651 E. High St., Oxford, OH 45045 (USA) –
email d.konkolewicz@miamiOH.edu

Abstract

Polymer materials with precise control over polymer structure has been an underexplored avenue to control dynamic and responsive materials. Incorporating multiple dynamic linkers into polymers with controlled structure offers unique possibilities to add multiple dimensions, of responsiveness, independent of bulk materials properties. Further functionality can be introduced by adding in nanoreinforcements such as carbon nanotubes.

A specific focus of this talk will be the synergies of polymer microstructure, crosslinker chemistry and reinforcement to generate materials with enhanced structure and function.

PL 12

PHASE SEPARATION: AN EFFECTIVE TOOL TO IMPROVE THE PERFORMANCE AND PROCESSABILITY OF VITRIMERS?

RENAUD NIKOLAŸ

Molecular, Macromolecular Chemistry and Materials, ESPCI Paris, CNRS, PSL University,
10 rue Vauquelin, 75005 Paris, France –
Email: renaud.nicolay@espci.psl.eu

Abstract

Vitrimers are chemically crosslinked networks that can rearrange their topology without decreasing their crosslinking density thanks to exchangeable links present in the network.[1,2] As a result, vitrimers can be potentially reshaped and recycled at will, while displaying the superior properties of crosslinked polymers at service temperature.

Very promising materials, vitrimers still display limitations that impact their transition towards industry, such as high viscosity even at elevated temperatures (due to the Arrhenian temperature dependence of the melt viscosity), or moderate creep resistance at working temperatures in the case of low T_g materials.[3,4]

In this lecture, different strategies relying on phase separation will be presented and their efficiencies to simultaneously address these limitations will the discussed in the case of vitrimers relying on dioxaborolane metathesis.[5]

References

[1] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler "Silica-Like Malleable Materials from Permanent Organic Networks." *Science* **2011**, *334*, 965–968. https://doi.org/10.1126/science.1212648.

[2] N. J. Van Zee, R. Nicolaÿ "Vitrimers: Permanently Crosslinked Polymers with Dynamic Network Topology." *Prog. Polym. Sci.* **2020**, *104*, 101233. https://doi.org/10.1016/j.progpolymsci.2020.101233.

[3] M. Guerre, C. Taplan, J. M. Winne, F. E. Du Prez, "Vitrimers: Directing Chemical Reactivity to Control Material Properties." *Chem. Sci.* **2020**, *11*, 4855–4870. https://doi.org/10.1039/D0SC01069C.

[4] A. Breuillac, A. Kassalias, R. Nicolaÿ "Polybutadiene Vitrimers Based on Dioxaborolane Chemistry and Dual Networks with Static and Dynamic Cross-Links." *Macromolecules* **2019**, *52*, 7102–7113. https://doi.org/10.1021/acs.macromol.9b01288.

[5] M. Röttger, T. Domenech, R. van der Weegen, A. Breuillac, R. Nicolaÿ, L. Leibler "High-Performance Vitrimers from Commodity Thermoplastics through Dioxaborolane Metathesis." *Science* **2017**, *356*, 62–65. https://doi.org/10.1126/science.aah5281.

PL 13

PROCESSING AND MANUFACTURING OF DYNAMIC POLYMER NETWORKS FOR SOFT ROBOTIC APPLICATIONS

JOOST BRANCART[1], ELLEN ROELS[1], FRANCESCA FURIA[1], SEPPE TERRYN[2], GUY VAN ASSHE[1]

[1]*Physical Chemistry and olymer Science, Vrije Universiteit Brussels, Pleinlaan 2, 1050 Brussels (Belgium)– Email: joost.brancart@vub.be*
[2]*BruBotics, Vrije Universiteit Brussels and imec, Pleinlaan 2, 1050 Brussels (Belgium)*

Abstract

Dynamic covalent chemistries enable improved (re)processability of polymer networks, in comparison to their permanently crosslinked analogues. In dissociative networks, the crosslink density of the polymer network decreases with increasing time and intensity of the adequate stimulus, such as heat or light, resulting in a change from a solid network to a viscous liquid. In contrast, associative networks do not show this large change in network connectivity. The rate at which a certain functional group can exchange bonds with existing covalent bonds changes upon the increase of the stimulus intensity. Dynamic covalent chemistries have also become very popular to create self-healing materials that are able to reform broken covalent bonds to recover their functional properties, increasing the service lifetime of structures and systems.

The manufacturing of certain products goes hand in hand with dedicated processing techniques. A wide variety of such processing techniques is widely available and can be divided in three main categories: (1) formative manufacturing, (2) subtractive manufacturing and (3) additive manufacturing. On the one hand, materials are designed for optimal processing using one or several processing techniques. On the other hand, certain manufacturing techniques are unavailable for specific material classes. Reactive processing techniques rely on formulations of monomers or prepolymers that undergo a chemical reaction during the shaping process, traditionally resulting in permanently shaped objects. In contrast, thermoplastics can be shaped and reprocessed using thermal methods above their melting point or glass transition temperature.

Thermoreversible or thermally activated covalent adaptable networks can be processed either starting from their monomers and prepolymers through reactive processes or using thermal methods, where the dynamic covalent bonds are activated thermally. They offer a more flexible processability by opening to a wider variety of processing methods, both reactive and thermal. Accurate knowledge of the reaction kinetics and thermodynamics and the structure-processing-property relations enables the design and optimization of the functional properties in view of intended applications and to tailor the processability. The dynamic covalent chemistry, choice of monomers and resulting polymer network architecture determine the (thermo)mechanical properties, thermoresponsive behaviour and (self-) healing capabilities.

The manufacturing of soft robotic systems and sensor integration will be considered based on dynamic covalent chemistries, in particular on the thermoreversible polymer networks. Heating the thermally reversible polymer networks based on the Diels-Alder reaction shifts the reaction equilibrium towards the gradual breaking of the cycloadduct crosslinks, eventually leading to degelation. This reversible gel transition has been employed (1) casting, (2) mouling, (3) welding, (4) extrusion of filaments for the 3D printing and many other methods of manufacturing compliant components for self-healing soft robotic devices.

PL 14

THE SUPRAMOLECULAR ROUTE TO DYNAMIC POLYMER NETWORKS: FROM H-BONDING TO IONOMERS

ENRICO DALCANALE[1], ROBERTA PINALLI[1]

[1]*Department of Chemistry, Life Sciences and Environmental Sustainability University of Parma, Parco Area delle Scienze 17/A 43124 Parma (Italy) – Email: enrico.dalcanale@unipr.it*

Abstract

The merging of polymer science with supramolecular chemistry has created a new, thriving field of research.[1] The positive fallout of this merging is demonstrated by the appearance of supramolecular polymers presenting unique mechanical, electronic, biological and self-healing properties.[2] More recently, non-covalent interactions have been used as dynamic networks to produce reprocessable/recyclable thermosets.[3] Depending on the type of interaction exploited, a wide span of materials properties can be targeted. Aiming at melt-processable materials, requiring limited viscosity at processing temperature, two different routes have been selected for the reversible cross-linking of PE, namely by the exploitation of thermoreversible hydrogen-bonds and electrostatic interactions.

Our first approach to produce PE thermoreversible networks, foresees the formation of multiple H-bonded obtained through the homodimerization of ODIN, a sextuple H-bond donor/acceptor unit, covalently linked to PE-HEMA (the *co*-polymer of ethylene and a small amount of 2-hydroxyethyl methacrylate).[4] Incorporation of ODIN into PE-HEMA results in increased melt strength, greater tensile strength, and improved oxygen barrier properties of the resulting polymer, while retaining adaptability of the polymer network (Figure 1). Cross-linking *via* ODIN motif is still effective after melting of the crystalline lattice, where a rubbery plateau modulus is observed after melting, revealing a remarkably increased melt strength.

In a second, more recent approach, we prepared a new type of PE-based ionomer, which has the dielectric and mechanical properties of XLPE, but can be melt-processed thanks to its dynamic network character.[5] This new type of PE ionomer is obtained via high-pressure/high-temperature free radical copolymerization of ethylene in the presence of small amounts of ion-pair comonomers comprising amino terminated methacrylates and methacrylic acid. The synthesized ionomers feature a crystallinity, melting temperature, rubber plateau modulus and thermal conductivity similar to XLPE but remain melt-processable. Moreover, the preparation of the ionomers is free of byproducts, which readily yields a highly insulating material with a low direct-current (DC) electrical conductivity of 1 to $6 \cdot 10^{-14}$ S m^{-1} at 70 °C and an electric field of 30 V mm^{-1}.

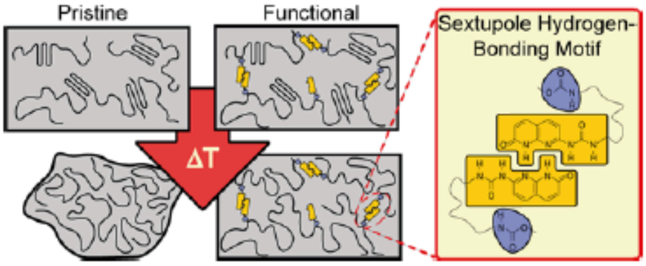


Figure 1. Dynamic cross-linking of PE via ODIN

---

[1] A. Ciferri, (ed.) *Supramolecular Polymers*, Second Edition, Francis & Taylor, New York (2005).

[2] T. Aida, E. W. Meijer, S. I. Stupp, *Science* **2012**, *335*, 813-817.

[3] L. Voorhaar, R. Hoogenboom, *Chem. Soc. Rev.* **2016**, *45*, 4013-4031.

[4] J. Tellers, S. Canossa, R. Pinalli, M. Soliman, J. Vachon, E. Dalcanale, *Macromolecules* **2018**, 51, 7680-7691.

[5] S. D'Auria, A. M. Pourrahimi, A. Favero, P. Neuteboom, X. Xu, M. Bek, R. Kádár, E. Dalcanale, R. Pinalli, C. Müller, J. Vachon, *Adv. Funct. Mater.* under revision.

ORAL CONTRIBUTIONS

OC 1

PLASTICITY ANDREPROCESSING OF DYNAMIC COVALENT POLYMER NETWORKS

NING ZHENG

State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering,
Zhejiang University, Hangzhou 310027, China
Email: zhengning@zju.edu.cn

Abstract

Dynamic covalent polymer network (DCPN) has unique processing properties owing to the reversible bond exchange. The localized movement of polymer segments originating from bond exchange can lead to solid-state plasticity, while long-range chain movement (or macroscopic flow) can result in reprocessing. In this talk, I will first introduce the shaping of rigid and brittle glass by employing the solid-state plasticity of DCPN. The second work is the discovery of a thiourea-based DCPN that can not only be reprocessed but also undergoes selective oxidation, resulting in a significant strengthening of mechanical properties. We believe our approach can expand the scope of material processing and potentially open up applications of DCPN in unexplored territories.

References

[1] H. Feng, N. Zheng*, W. Peng, C. Ni, H. Song, Q. Zhao, T. Xie. "Upcycling of dynamic thiourea thermoset polymers by intrinsic chemical strengthening." *Nat. Commun.*, **2022**, 13, 397.
[2] Y. Xu, Y. Li, N. Zheng*, Q. Zhao, T. Xie*. "Transparent origami glass." *Nat. Commun.*, **2021**, 12, 4261.

OC 2

THERMOREVERSIBLE THIOMALEIMIDE PHOTODIMERS: A NEW CHEMISTRY PLATFORM FOR COVALENT ADAPTABLE NETWORKS

HANNES A. HOUCK

[1]*Department of Chemistry, University of Warwick (UK)*
Email: Hannes.houck@warwick.ac.uk

Abstract

WITHDRAWN

OC 3

(Thermo-)mechanical characterisation of reshapeable Glass-Fibre Reinforced Vitrimers (GFRVs)

VIRGINIA AMFILOCHIOU[1], TAPAS DEBSHARMA[2], FILIP DU PREZ[2], IVES DE BAERE[1], WIM VAN PAEPEGEM[1].

[1]Department of Materials, Textiles and Chemical Engineering, Mechanics of Materials and Structures Group, Ghent University, Technologiepark 46, 9052 Zwijnaarde, Belgium – Email: virginia.amfilochiou@ugent.be, Wim.VanPaepegem@UGent.be
[2]Department of Organic and Macromolecular Chemistry, Polymer Chemistry Research Group, Ghent University, Krijgslaan 281 S4-bis, B-9000 Gent, Belgium

Abstract

Fibre reinforced plastics (FRPs) are widely used in aerospace, wind energy and automotive. However, the end-of-life scheme for such materials is not environmentally friendly or energy-efficient [1]. As the demand for sustainability is increasing there is a growing need for new reprocessable FRPs. Vitrimers are a novel polymer group, discovered in 2011, that couples the reprocessing properties of thermoplastics with the chemical resistance and mechanical performance of thermosets due to their Covalent Adaptable Network (CAN) [2].

In this work, Glass-Fibre Reinforced Vitrimers (GFRVs) were manufactured and investigated by mechanical and thermomechanical testing, as a sustainable alternative to current thermoset systems. All tests were also performed for the thermoset counterpart materials for comparison purposes. Dynamic Mechanical Analysis (DMA) was performed to quantify the T_g of the materials and identify the effect of storage and ageing on their thermomechanical properties. In-plane shear and tensile tests were performed at room and elevated temperature in order to investigate the performance of the materials at a certain temperature range relevant to possible applications (Figure 1). To identify the failure mechanisms and damage propagation of the GFRVs, cyclic loading-unloading shear tests were conducted. Finally, 2 cycles of a thermoforming process, that was improved compared to the previous work performed by this group on vitrimer composites, was applied (Figure 2) and the FRVCs residual properties were measured.

The results showed that even though the thermoset benchmark materials have a slightly better mechanical performance compared to the FRVCs both the vitrimer and thermoset composites exhibit mechanical properties of the same magnitude. Moreover, their properties diminish relative to each other both at elevated temperatures and after ageing, making GFRVs a promising reprocessable alternative to their thermoset counterpart. Finally, the FRVC was successfully thermoformed into an omega-shape free of any delamination or cracking, while the thermoset counterpart specimen fractured when it went through the same process.

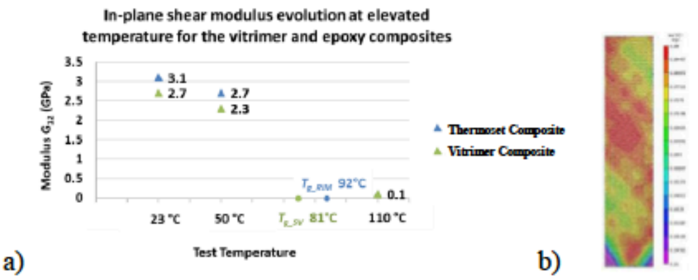


Figure 1: a) In-plane shear modulus evolution at eleveted temperature for the vitrimer and the thermoset composites **b)** example of the shear strain distribution on a SV_GF specimen

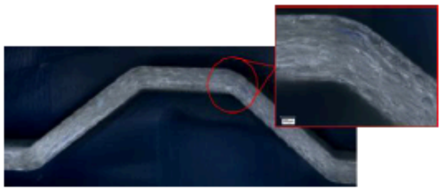


Figure 2: Thermoformed GFRVC in an omega-stifenner shape

[1] Anna, H.-Å. (2005). Model for End of Life Treatment of Polymer Composite Materials. Stockholm: KTH, KTH. p.vi: 104, 124, 129.
[2] Montarnal, D., et al. (2011). "Silica-Like Malleable Materials from Permanent Organic Networks." Science 334(6058): 965-968.

OC 4

STRETCHABLE AND DURABLE INVERSE VULCANIZED POLYMERS WITH CHEMICAL AND THERMAL RECYCLING

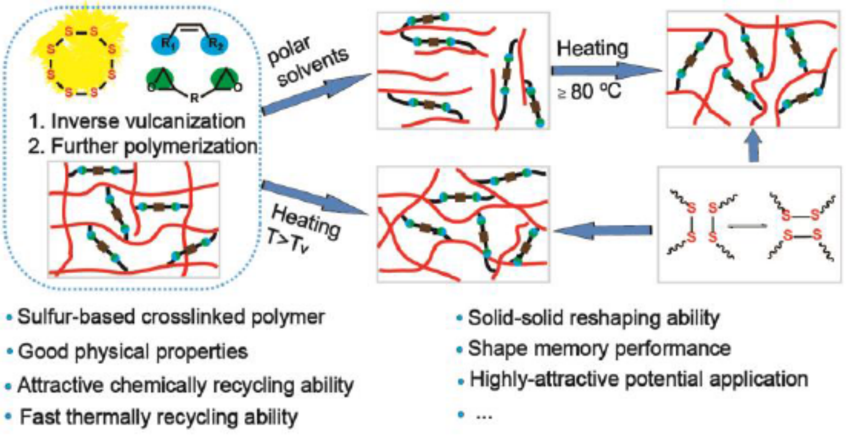
PEIYAO YAN[1], WEI ZHAO[1], SAMUEL J. TORKIN[2], JUSTIN M. CHALKER[2], TARA L. SCHILLER[3], TOM HASELL[1]

[1]Department of Chemistry, University of Liverpool, Liverpool L69 7ZD (UK)
Email: peiyao.yan@liverpool.ac.uk
[2]Institute for Nanoscale Science and Technology, Collee of Science and Engineering,
Flinders University, Bedford Park, South Australia 5042 (Australia)
[3]WMG, University of Warwick, Coventry, CV4 7AL (UK)

Abstract

Basically, this work presents a kind of thermally and chemically recyclable crosslinked sulfur polymer, thanks to presence of sulfur-sulfur dynamic covalent bond, which were made *via* inverse vulcanization. This work has investigated structure-property relationship of the relevant polymeric materials, in order for deep understanding back reason of dynamic properties of the materials. The abstract of this work is illustrated below.)

Inverse vulcanized polymer materials have received considerable attention as a way to use sulfur, an industrial by-product, as a starting material for synthesis. The resulting high-sulfur content polymers have also been investigated because their properties give rise to promising applications such as infrared imaging, energy storage, and heavy metal capture due to their unique structure. However, synthesis of a flexible sulfur polymer network which shows good mechanical properties combining high strength, high elongation, and high toughness is still a significant challenge. Moreover, further exploration of the properties of sulfur polymers to better understand the relationship between the polymers' structure with their performance is still needed. Here, a range of cross-linked sulfur polymers with high tensile elongation and toughness and without losing high strength were successfully synthesized. The obtained cross-linked sulfur polymers show high solvent tolerance in most organic solvents but are demonstrated to be chemically de-cross-linked in polar solvents dimethylformamide, dimethylacetamide, and N-methyl-2-pyrrolidone and can be re-cross-linked after removing the solvent due to the high sulfur ranks present in the polymer network. Despite the significantly improved mechanical properties, highly efficient thermal recycling performance typical of inverse vulcanized polymers was retained. Flexibility and durability, combined with chemical and thermal recycling, could open a new door for wider applications of inverse vulcanized polymers.



- Sulfur-based crosslinked polymer
- Good physical properties
- Attractive chemically recycling ability
- Fast thermally recycling ability
- Solid-solid reshaping ability
- Shape memory performance
- Highly-attractive potential application
- ...

OC 5

EPOXY ACRYLATE RECYCLABLE THERMOSETS WITH A TUNEABLE DROP IN CROSSLINKING DENSITY

STÉPHANIE ENGELEN, FILIP VAN LIJSEBETTEN, RESAT AKSAKAL, JOHAN WINNE, FILIP DU PREZ
Polymer Chemistry Research Group and Laboratory of Organic Synthesis,
Department of Organic and Macromolecular Chemistry, Faculty of Sciences, Ghent University (Belgium)
Email: stephanie.engelen@ugent.be

Abstract

The sustainable development of polymeric materials has become increasingly important due to the depletion of fossil-based resources, as well as an ever-increasing public awareness of problems associated with a petrochemical-based economy. This is driven by the limited availability of crude oil, or by the polluting end-of-life processing of plastic materials. Thus, researchers and companies are looking into renewable alternatives, e.g. raw materials that are not depleting the planet or materials with an increased recyclability or reprocessability.

Undeniably many commercial thermosets that are used in coatings, adhesives, and high demanding applications are making use of epoxies, epoxy acrylates or acrylic resins due to their high chemical resistance and dimensional stability.[1,2] Covalent adaptable networks are networks with the dimensional stability of thermosets but with the intrinsic recyclability of thermoplastics. As a result they offer a solution to the inherent recyclability issues of thermosets.[3,4]

Herein, recyclable epoxy acrylate (EA) thermosets with a tuneable drop in viscosity with up to 3 orders of magnitude (without the need for additives) will be presented. The tuneable material flow results in materials with remarkable reprocessability at high temperatures and desirably, no deformation at lower temperatures. In addition to the readily available EA building blocks used in this work, a bio-based alternative from a vanillin-epoxy will also be discussed.

Acknowledgements

Stéphanie Engelen and Filip Van Lijsebetten would like to thank Research Foundation Flanders (FWO) for the funding of their PhD fellowships (application number: 1SD4821N and 1S49122N).

References

[1] A. J. Kinloch "Mechanics and Mechanisms of Fracture of Thermosetting Epoxy Polymers." Springer, **1985**.
[2] T. Engels "Thermoset adhesives: epoxy resins, acrylates and polyurethanes."Woodhead Publishing Limited **2012**.
[3] W. Denissen, G. Rivero, R. Nicolaÿ, L. Leibler, J. M. Winne, F. E. Du Prez "Vinylogous urethane vitrimers." *Advanced Functional Materials* **2015,** *25*, 2451-2457.
[4] M. Guerre, C. Taplan, J. M. Winne, F. E. Du Prez "Vitrimers: directing chemical reactivity to control material properties." *Chemical Science* **2020**, *11*, 4855-4870.

OC 6

HIGH-THROUGHPUT SYNTHESIS AND REPROCESSING OF VITRIMER-THERMOPLASTIC BLENDS

LILIANA M.A. JOOSTEN[1,2], PHILIPPE CASSAGNAU[1], DAMIEN MONTARNAL[2],
ERIC DROCKENMULLER[1]
[1]Université de Lyon, Université Lyon 1, CNRS, Ingégnierie des Matériaux Polymères, UMR 5223,
F-69003 Lyon (France) - Email: liliana.joosten@univ-lyon1.fr
[2]Université de Lyon, CPE Lyon, CNRS, Catalyse, Chimie, Polymères et Procédés, UMR 5265
F-69003 Lyon (France)

Abstract

Cross-linked polymers are used in a wide range of high performance applications. While they have an outstanding performance, their recyclability is inherently limited to methods that are cost- and energy-intensive and often not desirable in terms of sustainability.[1]

Recently, a new class of materials called covalent adaptable networks (CANs), were introduced.[2] CANs contain dynamic bonds controlled by exchange reactions that are activated by triggers. The bond exchange mechanisms can be classified in dissociative and associative reactions. In dissociative networks a cross-link is broken before it is reformed, whereas in associative networks, also referred to as vitrimers, the bonds are reshuffled via reversible exchange reactions without compromising network integrity.[3] Even in absence of depolymerization, the fast bond reshuffling induces stress relaxation and allow the material to flow and be reshaped. Hence, vitrimers might be key elements in the future recycling of cross-linked materials. In order to allow the implementation of vitrimer production at industrial level, the upscalability of the process needs to be considered already in the design of the material.

In order to bridge the gap between high-throughtput processability and performance during application we have synthesized vitrimer-thermoplastic blends by reactive extrusion.. The mechanical performance of these vitrimer-thermoplastic blends is governed by the morphology resulting from the reactive processing, which can be controlled by carefully selecting the formulation (i.e. chemical nature and composition) and processing parameters. We will present the thermomechanical properties of these new materials and high shear rheology demonstrating excellent (re)processability.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 860911.
(https://www.vitrimat.eu/).

References

[1] D. J. Fortman, J. P. Brutman, G. X. De Hoe, R. L Snyder, W. R. Dichtel, M. A. Hillmyer"Approaches to Sustainable and Continually Recyclable Cross-Linked Polymers" *ACS Sustainable Chem. Eng.* **2018**,*6*,11145−11159.

[2] C. J Kloxin, T. F. Scott, B. J. Adzima, C. N. Bowman "Covalent Adaptable Networks (CANs): A Unique Paradigm in Cross-Linked Polymers" *Macromolecules***2010**,*43*,2643−2653.

[3] G.M. Scheutz, J.J. Lessard, M.B. Sims, B.S Sumerlin"Adaptable Crosslinks in Polymeric Materials: Resolving the Intersection of Thermoplastics and Thermosets" *J. Am. Chem. Soc.* **2019**,*141*,16181-16196.

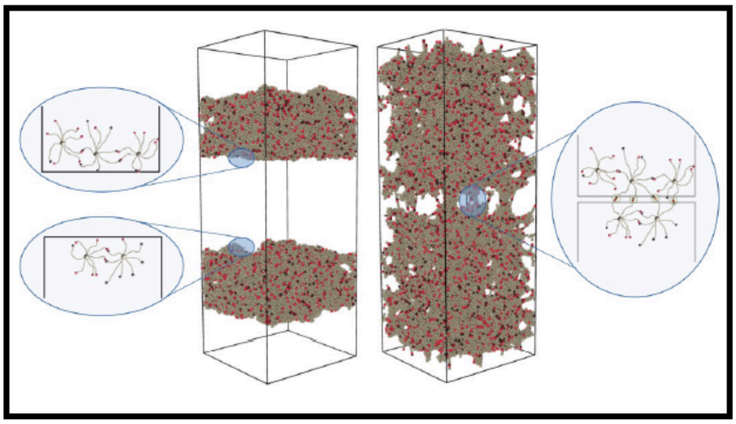
OC 7

DANGLING CHAIN DYNAMICS IN ADAPTIVE POLYMER NETWORKS: SELF-HEALING VITRIMERS AND RENORMALIZED BONDS IN DISSOCIATIVE NETWORKS

WOUTER G. ELLENBROEK[1,2], BART VAN DER HEIJDEN[1], FINN SHERRY[1]
[1]*Department of Applied Physics and Science Education, Eindhoven University of Technology (NL)*
Email: w.g.ellenbroek@tue.nl
[2]*Institute for Complex Molecular Systems, Eindhoven University of Technology (NL)*

Abstract

Adaptive or dynamic polymer networks are a rapidly growing class of materials that are being developed to solve a wide range of societal and industrial problems related to plastic waste.
Vitrimers are already at the forefront of this field because they combine the excellent stability and mechanical properties of covalent networks with the recyclability normally only seen in thermoplastics [1]. In addition, vitrimers have been put forward as excellent self-healing materials. In recent work, we demonstrated, using molecular dynamics simulations of a coarse-grained vitrimer model, the potential of star-polymer-based vitrimers for this purpose [2] (see figure).
Here, we elaborate on these ideas by considering different architectures that should further improve their performance. A crucial ingredient in the understanding of these materials is the way in which the dynamics of the dangling ends in the network regulates the bond-swapping process that drives the self-healing. If time permits, I will discuss how this is related to the dynamics of dissociative networks, where the same dangling end dynamics leads to bond lifetime renormalization [3].



Self-adhesion or self-healing in a model vitrimer [2]. Image by S. Ciarella.

References

[1] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler "Silica-like malleable materials from permanent organic networks", Science 2011, 334(6058), 965-968.
[2] Ciarella, S., Ellenbroek, W.G., "Swap-Driven Self-Adhesion and Healing of Vitrimers", Coatings 2019, 9, 114.
[3] Stukalin, E.B., Cai, L.H., Kumar, N.A., Leibler, L., Rubinstein, M., 2013. "Self-healing of unentangled polymer networks with reversible bonds" Macromolecules 2013, 46, 7525–7541

OC 8

ON THE DEVELOPMENT OF COVALENT ASSOCIATIVE NETWORKS BASED ON POLYCAPROLACTONE

Giacomo DAMONTE[1], Alberto VALLIN[1], Federico FERRETTI[1], Daniele BATTEGAZZORE[2], Arkadiusz ZYCH[3], Athanassia ATHANASSIOU[3], Alberto FINA[2], Orietta MONTICELLI[1]

[1]Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, via Dodecaneso, 16146 Genova (Italy) – Email: giacomo.damonte@edu.unige.it

[2]Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino - sede di Alessandria, viale Teresa Michel, 5, 15121 Alessandria, (Italy)

[3]Smart Materials, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, (Italy)

Abstract

Despite the increasing interest in bioplastics and the promising properties that can be achieved applying dynamic covalent crosslinking to such materials, so far this approach has not been extensively investigated. With this in mind, we have developed novel covalent associative networks (CAN) based on polycaprolactone (PCL), one of the most interesting and widely studied bioplastics, which, although not produced from renewable sources, is considered a biomaterial due to its biodegradability and biocompatibility. In particular, since changing the conformation of the macromolecule, *i.e.*, going from linear to branched or star-shaped, can significantly increase the functionality and allow precise tailoring of CAN properties, *ad-hoc* synthesized star-shaped structures have been considered. Thus, PCL with star-shaped architecture and two different functionalities, hydroxy[1] and acrylic[2], were synthesized to develop two different types of CAN. The synthesized four arms hydroxyl-terminated PCL (PCL-OH) was applied in the development of nanocomposite CAN systems based on reduced graphite oxide (rGO)[3]. The crosslinking reaction was carried out with methylenediphenyl diisocyanate (MDI) to create systems capable of exchanging bonds via transesterification and transcarbamoylation reactions, in the presence of stannous octoate as catalyst. Crosslinking was demonstrated by submerging the samples in a solvent capable of dissolving the star- shaped PCL. These tests showed a significant increase in the crosslinked fraction with increasing temperature and the PCL-OH:MDI ratio. Rheological measurements confirmed the crosslinking of the PCL-OH system, which generated a solid-like behavior depending on the PCL-OH:MDI ratio used. The presence of rGO during crosslinking further led to a huge increase in the viscosity of the melt with a remarkable solid-like behavior, confirming a strong interaction between rGO and crosslinked PCL. Finally, the prepared nanocomposites exhibited self-healing and recyclability properties, thus meeting the requirements for sustainable materials.

For the second CAN system, star-shaped PCL acrylates with 4 and 6 arms (PCL-TA and PCL-HA, respectively), characterized by different molecular weights, and *ad-hoc* synthesized diboronic ester dithiol crosslinker (DBEDT) were used. Crosslinking of the systems, confirmed by swelling tests, resulted in a decrease of crystallinity as well as crystallization temperature due to a reduced chain mobility. Moreover, the measurements of the gel fraction of the samples based on PCL-HA showed a higher crosslinking density than those prepared with PCL-TA, which agrees with DSC results. Finally, the possibility of using this innovative crosslinker, whose synthesis is fast and efficient[4], in the preparation of biobased CAN systems was demonstrated by using it in combination with a monomer derived from cashew nut shell oil, multiepoxidized ethoxylated cardanol.

---

[1] G. Damonte, B. Barsanti, A. Pellis, G.M. Guebitz, O. Monticelli, Eur. Polym. J. 2022, 1765, 111402.

[2] G. Damonte, L. Maddalena, A. Fina, D. Cavallo, A.J. Müller, M.R. Caputo, A. Mariani, O. Monticelli, Eur. Polym. J. 2022, 17115, 111226.

[3] A. Vallin, D. Battegazzore, G. Damonte, A. Fina, O. Monticelli, Nanomaterials 2022, 12. 3744.

[4] A. Zych, J. Tellers, L. Bertolacci, L. Ceseracciu, L. Marini, G. Mancini, A. Athanassiou, ACS Appl. Polym. Mater. 2021, 3, 1135.

OC 9

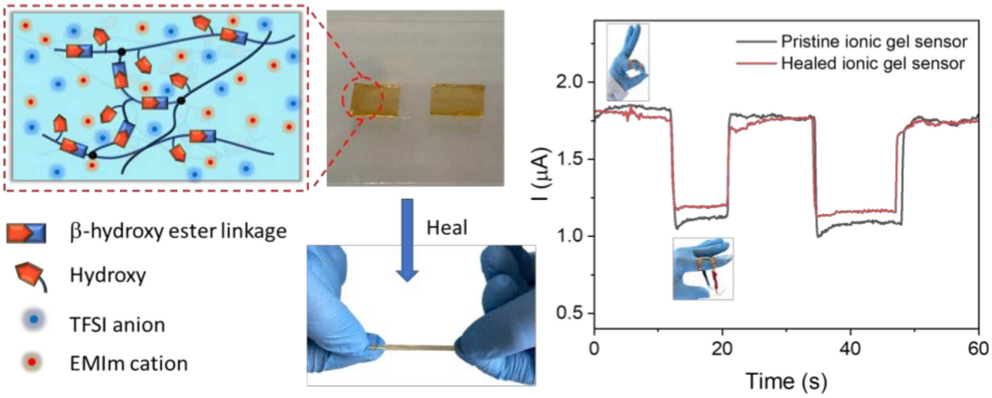
VITRIMER IONOGEL FOR FLEXIBLE STRAIN SENSOR

Khoa V. Bui[1,2], Giao T.M. Nguyen[1], Cedric Vancaeyzeele[1], Frederic Vidal[1],
Chaoying Wan[2] and Cedric Plesse[1]

[1] Laboratoire de Physicochimie des Polymères et des Interfaces, CY Cergy – Paris Université, 5 Mail Gay Lussac 9500 Neuville-sur-Oise (France) – Email : vo-khoa.bui@cyu.fr
[2] IINM, Warwick manufacturing group, University of Warwick, CV4 7AL, Coventry (United Kingdom)

Abstract

Ionogels are organic materials consisting of ionic liquids (ILs) immobilized in a polymer network. They combine the mechanical properties of polymer networks with the ionic conductivity, non-volatility, and non-flammability of ILs. As being conductive, flexible and even stretchable, ionogels have attracted huge attention in the field of wearable electronics or flexible sensors. However, in such applications, ionogels are usually subjected to repeated deformation, making them susceptible to damage. Consequently, imparting these chemically crosslinked ionogels with healing ability is now required to repair and recycle wounded or broken materials and to improve their durability, sustainability and life-span. In this work, we propose to enable the healing and recycling ability of these materials by the introduction of dynamic exchangeble bonds, more specifically by the synthesis of associative covalent adaptable networks, also called vitrimers.[1] The vitrimer ionogels are prepared by introducing dynamic β-hydroxyester linkages within a polyethylene glycol (PEG) network containing 1- Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIm TFSI) ionic liquid. The ionogel are obtained by the in-situ step-growth polymerization between PEG bis(carboxymethylether), trimethylolpropane triglycidyl ether as crosslinker and PEG diglycidylether as chain extender via carboxylic acid – epoxy addition reaction in the presence of various contents of IL. The resulting ionogels with 50 wt. % of EMIm TFSI are soft, stretchable and conductive, with a tensile strength of 100 kPa, a maximum elongation of 300 % and an ionic conductivity of 2.4×10^{-4} S.cm^{-1}. They exhibit strain sensing ability with a great linear correlation between strain and resistance variation, high strain sensitivity (Gauge factor = 2.8 at 100 % strain), and low hysteresis. The β-hydroxy ester generated from the carboxylic acid – epoxy reaction enables network rearrangement, allowing the healing of ionogel after being damaged. The presence of EMIm TFSI in ionogel accelerate the rate of stress relaxation without changing the activation energy of the network rearrangement. The healed ionogel exhibits full recovery of mechanical properties, conductivity and even the strain sensing performance.



[1] Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Science 2011, 334, 965–968

OC 10

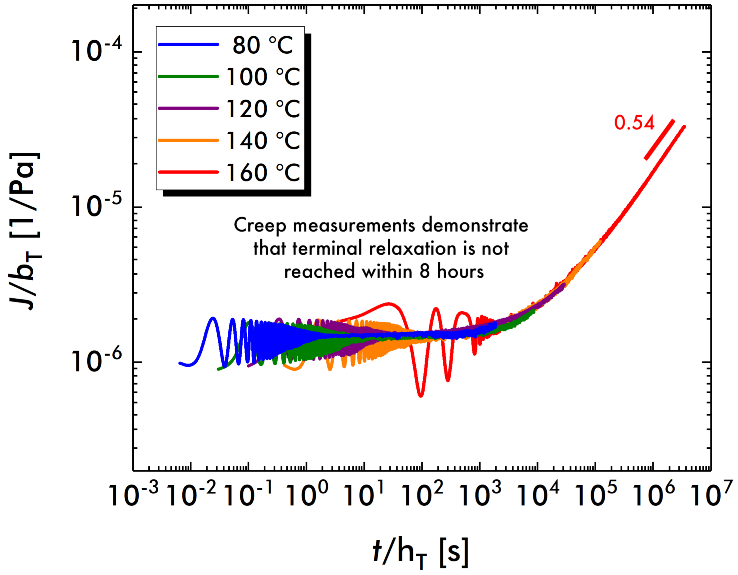
LINEAR RHEOLOGY OF POLYBUTADIENE VITRIMERS

RALM G. RICARTE[1] AND SACHIN SHANBHAG[2]

[1]Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Tallahassee, FL 32310
[2]Department of Scientific Computing, Florida State University, Tallahassee, FL 32306

Abstract

Vitrimers are covalently cross-linked polymer networks that are insoluble in good solvent but processable at high temperatures. These paradoxical traits are enabled by their cross-links, which engage in dynamic associative exchange reactions. Altering the backbone and cross-link chemistry of the vitrimer alters its flow and mechanical behavior. In 2021, Ricarte and Shanbhag utilized the inhomogeneous Rouse model (IHR) to elucidate structure-viscoelasticity relationships for vitrimer melts. Their findings suggested that interplay between chain friction and cross-link exchange governs flow under small-strain conditions. In this work, we experimentally investigate the linear viscoelastic behavior of polybutadiene (PB) vitrimers bearing dioxaborolane cross-links. Vitrimers were synthesized by cross-linking commercial PB (M_n = 6.8 kg/mol and Đ =1.4) with bis-boronic esters *via* a thiol-ene click reaction. Cross-link density was varied from 0.5 to 6 mol%. Linear viscoelasticity was evaluated using small- amplitude oscillatory shear (SAOS), stress relaxation, and creep and recovery measurements. For SAOS, the elastic modulus remains constant while the viscous modulus decreases as angular frequency decreases. For stress relaxation and creep, terminal relaxation is not observed over a period of 8 hrs, even at temperatures of 160 °C. The linear viscoelastic data are compared to the IHR model to gauge the impact of XL mobility and temperature on vitrimer relaxation.



Creep measurements demonstrate that terminal relaxation is not reached within 8 hours

OC 11

N-SULFONYL-URETHANES TO DESIGN POLYURETHANE NETWORKS WITH TEMPERATURE-CONTROLLED DYNAMICITY

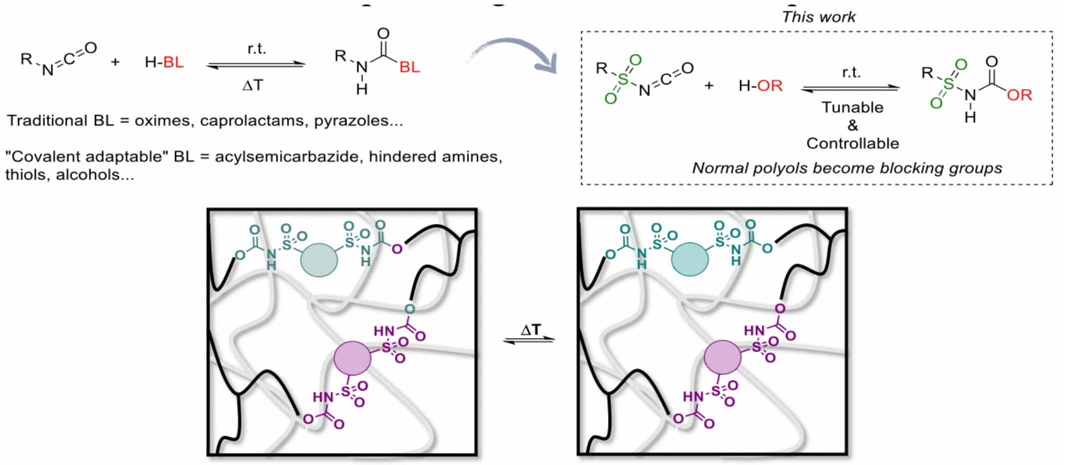
STEPHAN MAES[1], FILIP VAN LIJSEBETTEN[1], JOHAN M. WINNE[2] AND FILIP E. DU PREZ[1]

[1]*Polymer Chemistry Research group, Centre of Macromolecular Chemistry (CMaC) and*
[2]*Laboratory of Organic Synthesis, Department of Organic and Macromolecular Chemistry,*
Faculty of Sciences, Ghent University, Krijgslaan 284-S4, 9000 Ghent, Belgium
E-mail: stephan.maes@ugent.be

Abstract

Polyurethanes (PUs) constitute approximately 31% of all crosslinked materials on the market with applications ranging from foams to coatings[1]. However, (re-)processing of PUs is still hampering because of the energy intensity and inefficiency. At elevated temperatures, urethane linkages can dissociate to regenerate highly reactive isocyanate moieties that swiftly react with all types of nucleophiles[1].

Different strategies improving the control have been suggested, however, the use of blocked isocyanates has been one of the most successful strategies. Typical examples of blocking agents are oximes and caprolactams. Recently, much more common aliphatic thiols and alcohols have gained attention as blocking agent, yet the use of specific catalysts and/or excess of thiol or alcohol are still required[3] On the other hand, changing the steric and/or electronic environments of the dynamic bonds is one of the simplest ways to tune reactivity. Here, we report the introduction of N-sulfonyl urethane bonds (SUs) into PU matrices[4]. Exchange in SUs was observed, while this was not the case for native urethanes under the same conditions. Elastomeric, PU-based covalent adaptable networks with small amounts of SUs were prepared in a straightforward fashion. The presence of these SUs proved to be beneficial for thermomechanical reprocessing of PUs at lower temperatures.



Scheme 1. Schematic representation of blocked isocyanates and the use of alcohols as blocking agent with sulfonyl isocyanates, together with their implementation in covalent adaptable networks.

References.

[1] D.J. Fortman, D.T. Sheppard, W.R. Dichtel, Reprocessing Cross-Linked Polyurethanes by Catalyzing Carbamate Exchange, Macromolecules 2019, 52, 6330–6335.
[2] E. Delebecq, J. Pascault, B. Boutevin, F. Ganachaud, On the Versatility of Urethane/Urea Bonds: Reversibility, Blocked Isocyanate, and Non-isocyanate Polyurethane, Chem.Rev. 2013, 113, 80-118.
[3] X. Chen, S. Hu, L. Li, J.M. Torkelson, Dynamic Covalent Polyurethane Networks with Excellent Property and Cross-Link Density Recovery after Recycling and Potential for Monomer Recovery, ACS Appl. Polym. Mater. 2020, 2, 2093–2101.
[4] S. Maes, F. Van Lijsebetten, J.M. Winne, F.E. Du Prez, submitted.

OC 12

NEW DESIGN OF NANOSTRUCTURED VITRIMER MATERIALS BY MINIEMULSION POLYMERIZATION

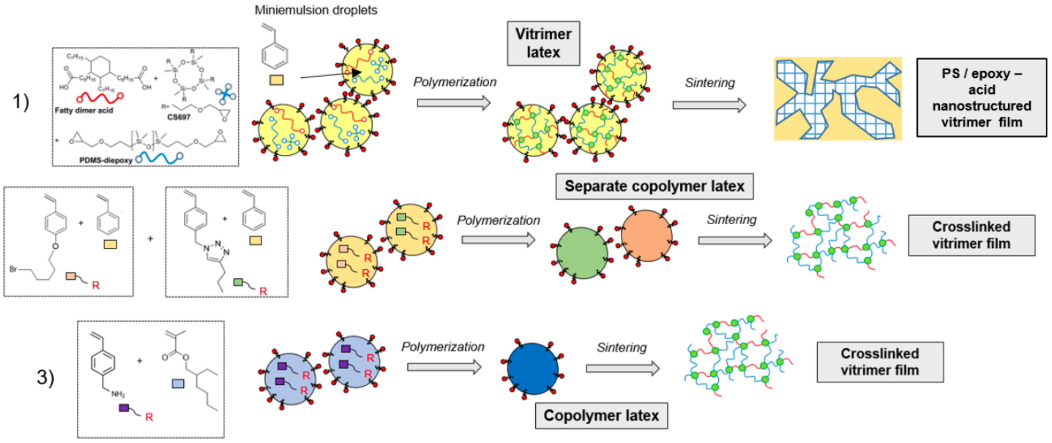
L. GAZZETTA[1], E. BOURGEAT-LAMI[1], D. MONTARNAL1 AND E. DROCKENMULLER[2]

[1]*Catalyse, Polymérisation, Procédés et Matériaux (CP2M), CNRS, Université Lyon 1, ESCPE, Lyon (France)*
[1]*Ingénierie des Matériaux Polymères (IMP), CNRS, Université Lyon 1, Polytech, Lyon (France)*

Abstract

Thermosets are the materials of choice for numerous applications because of their dimensional stability, mechanical properties and chemical resistance. However, as a result of their permanent molecular architecture, thermosets cannot be reshaped, processed or recycled. An attractive chemical strategy to introduce plasticity in cross-linked polymer networks is offered by the introduction of exchangeable chemical bonds, leading to dynamic cross-links such as vitrimers strategy[1]. The main objectives of my thesis was to: i) to develop a new generation of nanostructured vitrimer materials; ii) study and understand the exchange dynamics in these complex systems and iii) study the properties of vitrimers based on in- depth structural and mechanical characterizations. For this purpose, the general strategy was focused on the synthesis of vitrimer nanoparticles or vitrimer films using a miniemulsion strategy[2]. Three distinct systems were studied:

1. Formation of nanostructured vitrimer networks from "epoxy-acid" vitrimer precursors and polystyrene phase using the well-established transesterification exchange reaction in β-hydroxyl ester bonds.
2. Separatesynthesisoflatexesoflinearpolymersthatcontaintriazoleandbromideside-groups, respectively. Upon mixing the complementary latexes and formation of a homogeneous film, interchain reactions into 1,2,3-triazolium forms a dynamic network.
3. Imine-based vitrimer films that relax very quickly at high temperature.



Scheme 1. Global strategy (miniemulsion polymerization) for design of new nanostructured vitrimer materials

References

1. Montarnal, D., Capelot, M., Tournilhac, F. & Leibler, L. Silica-Like Malleable Materials from Permanent Organic Networks. Science 334, 965–968 (2011).
2. Tran, T. N., Rawstron, E., Bourgeat-Lami, E. & Montarnal, D. Formation of Cross-Linked Films from Immiscible Precursors through Sintering of Vitrimer Nanoparticles. ACS Macro Lett. 7, 376– 380 (2018).

OC 13

POLYHYDROXYURETHANE COVALENT ADAPTABLE NETWORKS: LOOKING FOR SUITABLE CATALYST

CAMILLE BAKKALI-HASSANI[1], D. BERNE, P. BRON, V. LADMIRAL, S. CAILLOL

[1]Instiut Charles Gerhardt Montpellier ICGM-CNRS-UM-ENSCM
1919 route de Mende, 34293 Montpellier

Abstract

While transesterification has been largely explored by both organic and polymer chemists, only a few studies comparatively dealt with its “sluggish cousin”, transcarbamoylation.[1] Despite a large potential in polyurethane (PU) and polyhydroxyurethane (PHU) chemistry, designing covalent adaptable network (CAN) using transcarbamoylation [2,3] have been set aside to focus on introducing various dynamic covalent bonds into P(H)U crosslinked networks.[4]

Herein, various bases (DMAP, DBU, TBD, *t*-BuOK) and acids (*p*-TSA, DBTDL) were investigated as potential catalysts for the preparation of PHU covalent adaptable networks (Figure 1). Catalytic systems were first selected for their ability to catalyze cyclic carbonate aminolysis quantitatively (full conversion of cyclic carbonates) with no- or low side reactions (urea formation). Selected PHU networks were fully characterized using thermo-mechanical analysis (TGA, DSC, DMA and tensile test), rheology experiments (stress relaxation, frequency sweep), spectroscopy analysis (ATR-IR), swelling and reprocessing tests. Combining rheology, ATR-IR analysis and model molecular reactions we suggested a catalyst-dependant exchange mechanism in which solely an organotin Lewis acid (DBTDL) was capable to promote transcarbamoylation efficiently with both secondary (major product) and primary alcohol and thus an efficient reprocessing.

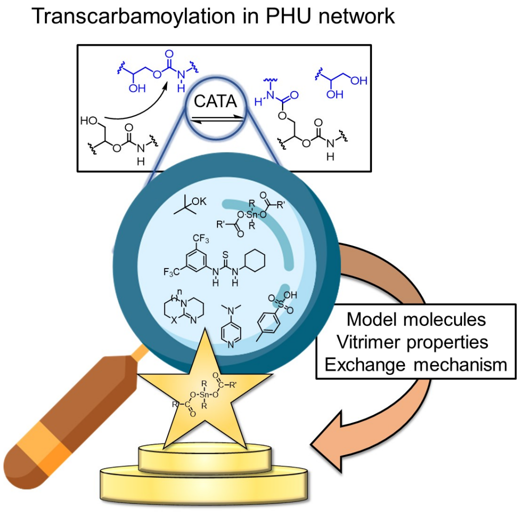


Figure 1. Catalysts employed to control transcarbamoylation in PHU covalent adaptable networks

References

1) C. Bakkali-Hassani et al. *Macromolecules* **2022**, *55* (18), 7974–7991.
2) D. J. Fortman *et al. J. Am. Chem. Soc.* **2015**, *137* (44), 14019−14022.
3) X. Chen *et al. Polym. Chem.* **2017**, *8* (41), 6349−6355.
4) Y. Tao *et al. J. Polym. Sci.* **2022**, DOI: 10.1002/pol.20220625.

OC 14

POLYSTYRENE-BASED MALEIC MONOESTER DISSOCIATIVE NETWORKS

AITOR HERNÁNDEZ TORIBIO, JOHAN M. WINNE, FILIP E. DU PREZ

[1] *Polymer Chemistry Research Group and Laboratory of Organic Synthesis, Department of Organic and Macromolecular Chemistry, Faculty of Sciences, Ghent University, Krijgslaan 281 S4, Ghent B-9000, Belgium. Email: aitor.hernandeztoribio@ugent.be*

Abstract

This study investigates the properties of polystyrene-based maleic monoester[1] (MME) covalent adaptable networks (CANs)[2]. The materials were synthesized using commercially available poly(styrene-ran-maleic anhydride) (PSMA) polymers of high and low molecular weight and widely used diols, which crosslink through dissociative dynamic bonds. Results showed that regardless of the synthesis method used (in-solution or in-bulk), the materials had substantially similar properties, with the exception of slightly improved mechanical properties in the latter case. The simplicity and accessibility of the synthesis of these networks allowed the preparation of a variety of combinations and ratios of these building blocks. This in turn allowed the production of ideal MME systems to study how the rheological, mechanical, and thermal properties of these CANs can be altered and tuned[3] to achieve flow rates and thermal stability suitable for extrusion processing.

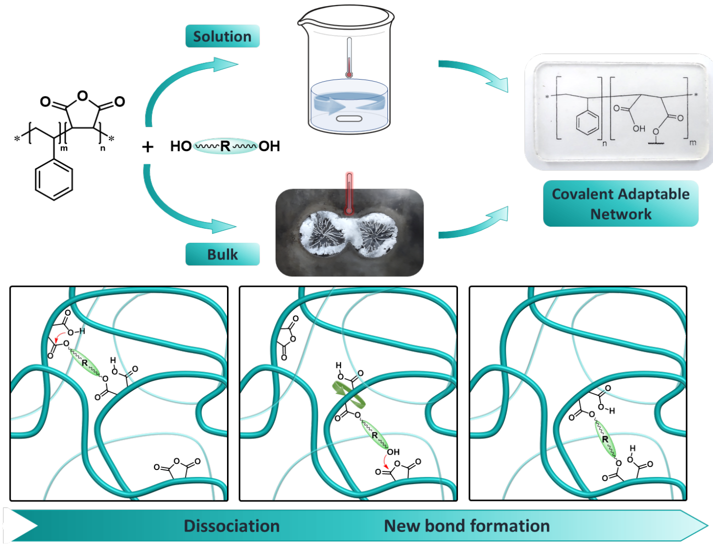


Fig.1: Synthesis methods and schematic representation of dissociative exchanges in MME networks.

Acknowledgements

This project received funding from the European Union’s Horizon 2020 research and innovation program under the Marie Skłodowska–Curie grant agreement No 860911.

References

[1] Delahaye, M.; Winne, J. M.; Du Prez, F. E. “Internal Catalysis in Covalent Adaptable Networks: Phthalate Monoester Transesterification As a Versatile Dynamic Cross-Linking Chemistry”. J. Am. Chem. Soc. 2019, 141 (38), 15277–15287.
[2] Winne, J. M.; Leibler, L.; Du Prez, F. E. “Dynamic Covalent Chemistry in Polymer Networks: A Mechanistic Perspective”. Polym. Chem. 2019, 10 (45), 6091–6108.
[3] Lessard, J. J.; Stewart, K. A.; Sumerlin, B. S. “Controlling Dynamics of Associative Networks through Primary Chain Length. Macromolecules” 2022, 55 (22), 10052–10061.

OC 15

HIGH TG EPOXY VITRIMERS AND COMPOSTES

PAULA FANLO, ALAITZ RUIZ DE LUZURIAGA, NEREA MARKAIDE,
ASIER M. SALABERRIA, ITXASO AZKUNE, ALAITZ REKONDO

CIDETEC, Basque Research and Technology Alliace (BRTA), Po. *Miramón 196,n 20014 Donostia-San Sebastián (Spain)* – Email: pfanlo@cidetec.es

Abstract

Traditional crosslinked aero grade epoxy resins have excellent thermal–mechanical properties and solvent resistance, but are incapable of being recycled, remolded, or repaired. Vitrimers, can be topologically rearranged with the associative exchange mechanism, endowing them with thermoplasticity. Introducing the concept of vitrimers into crosslinked networks to obtain more sustainable thermosets is currently an attractive research topic. While recent research into vitrimers has indicated many advantages over traditional thermosets, an important shortcoming has been identified: susceptibility to creep at service temperature due to the dynamic bonds present in the network. Herein, we want to present low creep aero grade aromatic disulfide epoxy vitrimer with similar thermal and mechanical properties to aero grade epoxy resins while having the ability to be recyclable, repairable, and reprocessable[1].

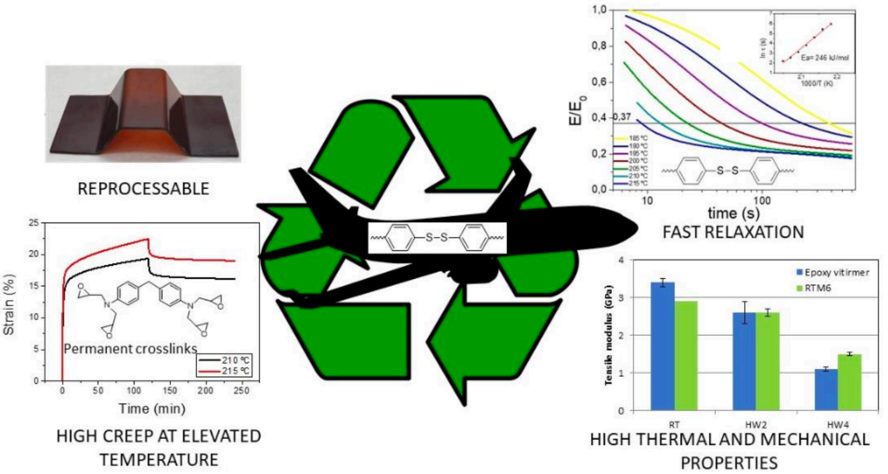


Figure 1. Properties of high Tg epoxy vitrimer.

We demonstrate that aero grade epoxy vitrimer can be designed with reduced creep by the introduction of certain fraction of permanent crosslinks, without having a negative impact in the stress relaxation of the material. The mechanical and relaxation properties were investigated and compared with classical aero grade epoxy resin. A high Tg (175 oC) epoxy vitrimer was obtained which fulfilled all mechanical and thermal specification of aero sector. This work provides a simple network design to obtain aero- grade epoxy resins with excellent creep resistance at elevated temperatures while being sustainable. However, the recyclability of these materials is still something to be improved, because, although permanent bonds are good for some properties, the recyclability of the material is influenced by them. It is known that the more permanent bonds there are, the worse the recyclability. So, the number of these links will be determined by the application and the need we have.

[1] Ruiz de Luzuriaga, A.; Markaide, N.; Salaberria, A. M.; Azcune, I.; Rekondo, A.; Grande, H. J. Polymers 2022, 14, 3180.

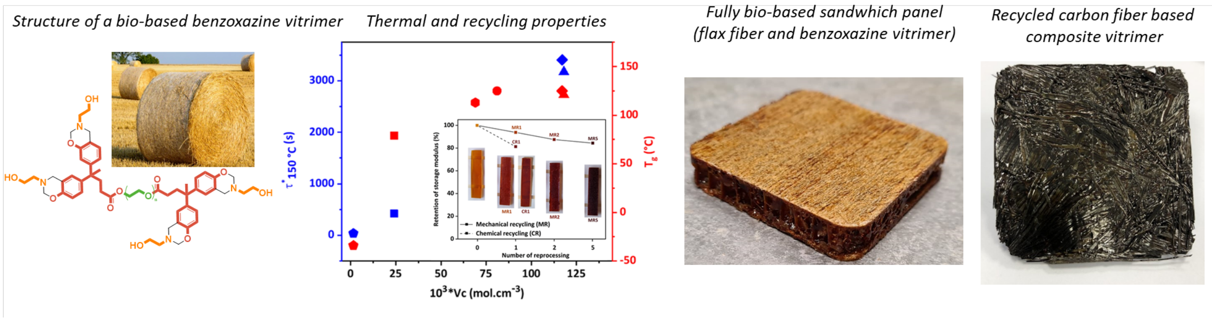
OC 16

EXPLORING THE BENEFITS OF BENZOXAZINES IN THE DESIGN OF VITRIMERS RELYING ON TRANSESTERIFICATION REACTIONS

ANTOINE ADJAOUD[1,2], D. ABDHALLAH BOINA[1], LAURA PUCHOT[1], HENRI PERRIN[1], PIERRE VERGE[1]
[1] Institute of Science and Technology
[2] University of Luxembourg

Over the past few decades, the apogee of industrialization has led to a compelling increase in the consumption of thermosets worldwide, resulting in an abundant source of wastes which cannot be recycled or repaired. To address this issue, reversible dissociative or associative bonds have been inserted within the chemical structure of thermosets to create covalent adaptable networks (CANs), enabling self healability or recyclability [1].

Among the several types of resins, polybenzoxazines (PBZs) emerge as significant for combining traditional thermoset properties with recyclability, healability, and degradability. PBZs are a promising alternative to phenolic and epoxy resins with unique mechanical and thermal properties, such as high glass transition temperature, near-zero shrinkage upon polymerization, and high char yield [2]. They are a monocomponent thermoset with abundant tertiary amines, ideal for trans-esterification reactions. Thanks to the versatile design of their chemical structures, PBZs allows for easy incorporation of esters and aliphatic OH bonds, enabling the formation of highly crosslinked benzoxazines with high Tg (in a range between 100-180 °C), suitable mechanical properties (modulus of no <2.5 GPa and tensile strength of no <40MPa), and constituted of exchangeable bonds allowing for fast recyclability and reshaping (relaxation times at 150 °C are of several 100s seconds). This presentation will highlight the strategies for creating bio-based PBZ vitrimers with such properties using materials like polyethylene glycol, isosorbide, and lignin, and their composites (Fig 1).



Structure of a bio-based benzoxazine vitrimer *Thermal and recycling properties* *Fully bio-based sandwhich panel (flax fiber and benzoxazine vitrimer)* *Recycled carbon fiber based composite vitrimer*

Figure 1. From the left to the right. Example of the structure of a bio-based benzoxazine vitrimer; Overview of thermal and recycling properties; picture of a fully bio-based sandwich; illustration of a recycled carbon-based vitrimer.

Acknowledgement

This research was supported by the Luxembourg National Research Fund (FNR) (C18/MS/12538602)

References

[1] D. Montarnal, M. Capelot, F. Tournilhac and L. Leibler, Science, 2011, 334, 965–968.
[2] H. Ishida, in Handbook of Benzoxazine Resins, ed. H. Ishida and T. Agag, Elsevier, Amsterdam, 2011

OC 17

VITRIMER PHASE TRANSITIONS FROM THE PERSPECTIVE OF ULTRA-SLOW VOLUME CHANGES

ANDREAS KLINGLER, BERND WETZEL, JAN-KRISTIAN KRÜGER

Leibniz-Institut für Verbundwerkstoffe, RPTU Kaiserslautern-Landau, Erwin Schrödinger Straße 58, 67663 Kaiserslautern (Germany) – Email: andreas.klingler@ivw.uni-kl.de

Abstract

The temperature-dependent, macroscopical relaxation behaviour of Vitrimers is of special interest to science and engineering, since it allows to reshape, recycle, and even repair a cross-linked polymer on a molecular level. The molecularly-induced malleability was originally described as a type of second glass transition phenomenon, triggered by temperature and force, and being on the same phenomenological level as a canonical glass transition[1]. The latter one can be best investigated via temperature-induced volume changes[2], because, usually, any kind of molecular change affects the anharmonic interaction potential, and thus the thermal volume expansion coefficient. Hence, shouldn't in this case any kind of Vitrimer inherent dynamic bond exchange reaction also be reflected in changes of the anharmonic interaction potential and thus be captured in temperature-dependent volume changes?

To address this question, hence to investigate if the Vitrimer transition phenomenon indeed couples to the thermal volume expansion under purely temperature-controlled conditions and to discuss the consequences a second canonical glass transition would have, this study describes an investigation of Vitrimer phase transitions by means of ultra-slow, temperature-induced volume changes based on a model Vitrimer system (DGEBA-Pripol1040-Zn-10%). The thermo-optical technique of Temperature-Modulated Optical Refractometry[3] (TMOR), being extraordinary sensitive to volume changes, was used to gain a better understanding of the dynamic and kinetic effects on the glass transition phenomenon[4], as well as the physics of the topology freezing process.

A first glimpse on the results, given in Figure 1, reveal no indication of any kind of relaxation event that might be related to a special molecular rearrangement in the quasi-static thermal volume expansion, beyond the canonical glass transition (jump of β in the data set). Substantiating this finding by dynamic means, TMOR measurements in the frequency range of 1.7 mHz ($\tau = 600s$) remain as well inconspicuous to another relaxation phenomenon. Hence, it seems like as if the dynamic bond exchange reactions stay hidden in the data resolution, or do simply not (sufficiently) couple to the thermal volume expansion.

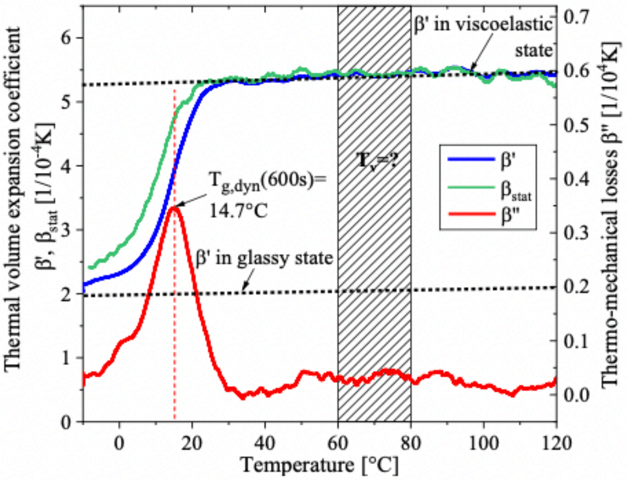


Figure 1: Temperature-induced quasi-static ($\boldsymbol{dT/dt = -0.001K/s}$) and dynamic ($\boldsymbol{\tau = 600s}$) volume changes of DGEBA-Pripol1040-Zn-10%, no external force

[1] Capelot, M. et al., Catalytic Control of the Vitrimer Glass Transition. ACS Macro Lett. **2012**, 1 (7), 789–792.

[2] Kovacs, A. J. et al., Isobaric Volume and Enthalpy Recovery of Glasses. II. A Transparent Multiparameter Theory. J. Polym. Sci. Polym. Phys. Ed. **1979**, 17 (7), 1097–1162.

[3] Müller, U., Krüger, J. K. et al., Temperature Modulated Optical Refractometry: A Quasi-Isothermal Method to Determine the Dynamic Volume Expansion Coefficient. Thermochimica Acta **2013**, 555, 17–22.

[4] Klingler, A. et al., On Volume Changes during Homopolymerization of Polymer Networks Accessed via "Temperature Modulated Optical Refractometry." Thermochimica Acta **2022**, 711, 179185.

OC 18

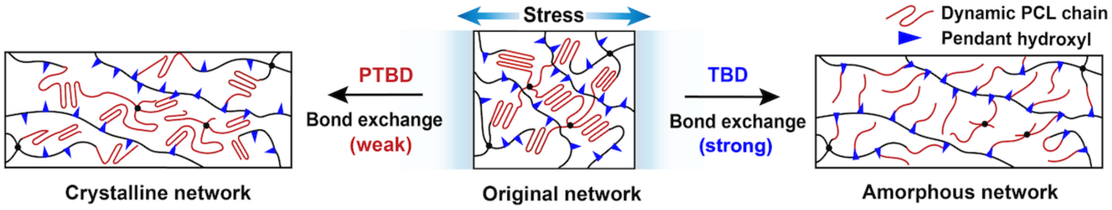
ON-DEMAND CATAYST-REGULATED DISTINCTIVE TOPOLOGICAL TRANSFORMATIONS IN A DYNAMIC COVALENT NETWORK

BO YANG, WUSHA MIAO, HAIJUN FENG, QIAN ZHAO, TAO XIE, NING ZHENG

State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang Universtiy, Hangzhou 310027 (China) – Email: bo_yang@zju.edu.cn

Abstract

Topological transformations in typical dynamic covalent polymer networks do not alter the network architectures, but offer unique adaptabilities including self-healing, reprocessing, and shape reconfigurability[1]. In contrast, topology isomerizable networks allow changing network topologies, leading to programmable physical properties[2]. Combining the two transformation mechanisms into one network would greatly extend the material versatility, but achieving this goal is challenging due to a mechanistic contradiction. We report our successful effort with a dynamic covalent network for which the bond exchange kinetics is regulated by an on-demand catalyst[3]. The network consists of a polycaprolactone backbone, pendant hydroxyls, and a switchable catalyst. The weak alkalinity of the catalyst promotes slow transesterification in polycaprolactone domains, leading to a topological transformation suitable for thermal healing, reprocessing, and shape reconfiguration without changing the polymer properties. Upon UV activation, the catalyst becomes a strong base which induces significant network isomerization due to the rapid transesterification between hydroxyls and polycaprolactone, changing the polymers from crystalline to amorphous. Further spatio- temporal control of the switchable catalyst allows selective programming of both the shapes and properties, which offers potential benefits for emerging applications including flexible electronics and soft robotics.



References

[1] Q. Zhao, W. Zou, Y. Luo, T. Xie. “Shape memory polymer network with thermally distinct elasticity and plasticity.” *Sci. Adv.*,**2016**, *2*, e1501297.

[2] W. Zou, B. Jin, Y. Wu, H. Song, Y. Luo, F. Huang, J. Qian, Q. Zhao, T. Xie. “Light-triggered topological programmability in a dynamic covalent polymer network.” *Sci. Adv.*, **2020**, *6*, eaaz2362.

[3] B. Yang, W. Miao, H. Feng, Q. Zhao, T. Xie, N. Zheng. “On-demand catalyst-regulated distinctive topological transformations in a dynamic covalent network.” *J. Mater. Chem. A*, **2022**, *10*, 20242.

OC 19

RECYCLABLE SHORT ARAMID FIBER REINFORCED EPOXY COMPOSITES

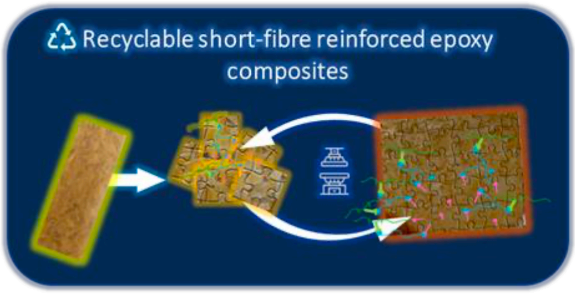
KARLA GARFIAS [1,2], KARIN ODELIUS[1,2], MINNA HAKKARAINEN[1,2]

[1]Department of Fiber and Polymer Technology, KTH Royal Institute of Technology, Teknikringen 56-58, 100 44 Stockholm, Sweden. – Email: kigg@kth.se
[2]Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, the Netherlands.

Abstract

The unique properties of fiber reinforced thermosets make them the ideal choice for high demanding applications and key players in the development of new technologies. However, the lack of reprocessability leaves them far behind from the current sustainability goals. In recent years, the development of covalent adaptable networks has emerged as a promising way to solve this problem. Current research has proved the feasibility of recycling this type of composites by chemical recycling of the thermosetting polymer with subsequent recovery of high performance fibers such as glass fibers[1,2] and carbon fibers[3-7]. Despite the indisputable success of previous studies, the possibility to recycle thermoset composites by thermal trigger still remains an open question. In addition, recycling thermoset composites reinforced with more sensitive fibers such as aramid fibers, and specifically short cut fibers, has not been addressed so far. Our study evaluates the possibility of recycling short aramid fiber reinforced epoxy composites by thermomechanical methods. In our approach, we developed a reprocessable thermosetting material based on a tri-epoxy resin cured with citric acid. We hypothesize that internal catalysis based on neighbouring group participation enable the transesterification exchange reactions required to reprocess the material and achieve a 90% recovery of the tensile stress at break after several recycling cycles. In a next step, we introduced aramid fibers with four different surface chemistries. Our results showed that it is possible to reprocess short aramid fiber composites by hot- pressing; resembling the reprocessing techniques of fiber reinforced thermoplastics. Additionally, our study suggests that the difference in the surface chemistry of the fibers led to distinct reprocessing outcomes.

Acknowledgement
This research forms part of the research programme of DPI, Project #843; Recyclable high-performance composites with reversible bonding.



1. M. Lejeail and H. R. Fischer, J. Appl. Polym. Sci., 2021, 138, 1–15.
2. W. Denissen, I. De Baere, W. Van Paepegem, L. Leibler, J. Winne and F. E. Du Prez, Macromolecules, 2018, 51, 2054–2064.
3. X. Kuang, Y. Zhou, Q. Shi, T. Wang and H. J. Qi, ACS Sustain. Chem. Eng., 2018, 6, 9189–9197.
4. R. L. Pérez, C. E. Ayala, M. M. Opiri, A. Ezzir, G. Li and I. M. Warner, ACS Appl. Polym. Mater., 2021, 3, 5588–5595.
5. K. Yu, Q. Shi, M. L. Dunn, T. Wang and H. J. Qi, Adv. Funct. Mater., 2016, 26, 6098–6106.
6. H. Si, L. Zhou, Y. Wu, L. Song, M. Kang, X. Zhao and M. Chen, Compos. Part B Eng., 2020, 199, 108278.
7. L. Yu, C. Zhu, X. H. Sun, J. Salter, H. A. Wu, Y. Jin, W. Zhang and R. Long, ACS Appl. Polym. Mater., 2019, 1, 2535–2542.

OC 20

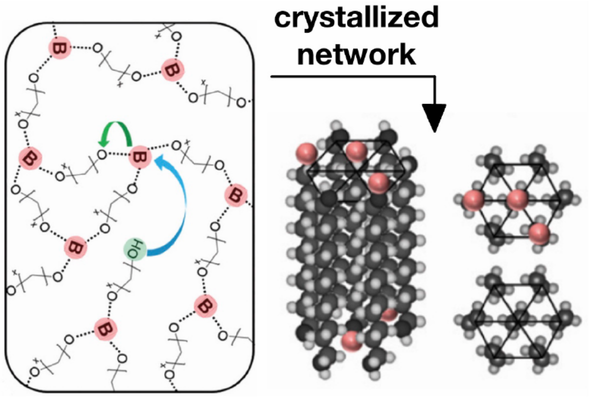
CRYSTALLINITY IN ETHYLENE VITRIMERS PROBED BY TIME-DOMAIN NMR, CALORIMETRY AND X-RAY SCATTERING

KAY SAALWÄCHTER,[1] BHASKAR SOMAN,[2] CHRISTOPHER M. EVANS[2]

[1]Institut für Physik – NMR, Martin-Luther-Universität Halle-Wittenberg, 06099 Halle (Germany) – Email: kay.saalwaechter@physik.uni-halle.de
[2]University of Illinois, Urbana-Champaign, IL (United States)

Abstract

Vitrimers, a new class of reconfigurable polymer networks based upon dynamic bonds, are considered a sustainable alternative to conventional thermosets. A potential partial crystallization can aid in further improving the mechanical properties, yet a balance with the degree of crosslinking (that normally impedes crystallization) has to be considered.[1,2,3] Here, we focus on a recently developed class of "ethylene vitrimers" made from (α,ω)-diamino alkanes and boric acid.[2] The samples were known to exhibit polymorphic crystal structures, which we now show to be distinguishable by proton NMR via their dipolar line width, enabling simple time-domain experiments based upon the related differences in transverse (T_2) relaxation.[4],[5] We can thus obtain absolute degrees of crystallinity in excess of 90%, which thus has to include the boric acid crosslinks. We can follow the kinetics of crystallization and crystal-crystal transformations in real time and elucidate the conditions under which the polymorphs form and interconvert, with a focus on recrystallization after full and partial melting. A notable increase of the melting point as well as the DSC-detected heat of melting upon long-time annealing is found to be not accompanied by an increase in crystallinity; rather, it takes place at nearly constant crystallinity (of order 90%). Therefore, T_m as well as the melting enthalpy are largely governed by the crystal perfection, which can also be followed in our NMR experiments.



DSC experiments are used to clarify an unexpected superheating effect, which challenges the determination of actual melting points. We further identify a strong memory effect in isothermal (re)crystallization. Implications of the dynamic nature of the vitrimers in relation to the kinetics of crystallization are discussed.

---

[1] Golitsyn, Y.; Pulst, M.; Samiullah, M.H.; Busse, K.; Kressler, J.; Reichert, D. *Polymer* **165,** 72 (2019)
[2] Soman, B.; Evans, C.M. *Soft Matter* **17,** 3569 (2022).
[3] Kuenstler, A.S.; Bowman, C.N. *ACS Macro Lett.* **12**, 133 (2023)
[4] Maus, A.; Hertlein, C.; Saalwächter, K. *Macromol. Chem.Phys*. **207**, 1150 (2006);
[5] Schäler, K.; Roos, M.; Micke, P.; Golitsyn, Y.; Seidlitz, A.; Thurn-Albrecht, T.; Schneider, H.; Hempel, G.; Saalwächter, K. *Solid State Nucl. Magn. Reson*. **72**, 50 (2015)

OC 21

REGIOSELECTIVE PHOTOCYCLOADDITION FOR LIGHT-STABILISED DYNAMIC MATERIALS DESIGN

ALYSSA J. GHIELMETTI[1], CHRISTOPHER BARNER-KOWOLLIK[2], FILIP E. DU PREZ[1*] AND HANNES A. HOUCK[1*]

[1]Polymer Chemistry Research group, Centre of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Faculty of Sciences, Ghent University, Krijgslaan 281 S4-bis, Ghent 9000, Belgium.

[2]School of Chemistry and Physics, Centre for Materials Science, Queensland University of Technology (QUT), 2 George St, Brisbane, 4000, QLD, Australia

Abstract

Triazolinedione-naphthalene chemistry was recently implemented into the concept of light-stabilized dynamic materials.[1] This class of photo-responsive polymers possess the unique property to form covalent bonds under light irradiation, which are thermally labile in the dark. The implementation of such a bond into polymer crosslinks yields materials that can reversibly form gels using light and darkness. Often material properties and reprocessing conditions of dynamic polymer networks are greatly impacted by the exact molecular network connectivity. A prominent example is the influence of endo/exo isomers of thermoreversible cycloaddition reactions (e.g. furan/maleimide) on the overall decrosslinking kinetics. On the contrary, the influence of regioisomerism is often overlooked and has not been studied thoroughly yet.

In this contribution, we will present the impact of regioisomers in light stabilized dynamic materials. The dynamic bond is based on the photo-driven [4+2] cycloaddition of substituted naphthalenes with triazolinediones, which yields two regioisomers. Herein, it is demonstrated that continuous equilibration of the two regioisomers under green light results in an enrichment of one of the regioisomers. When embedded into a macromolecular gel, this chemically inhomogeneous nature of the dynamic crosslinks can effectively change dissociation dynamics in a material. To bypass this limited control, a library of substituted naphthalene derivatives was screened to develop a completely regioselective TAD/naphthalene system. Moreover, it was found that guided naphthalene substitution allows for a fine control over the cycloreversion kinetics. In particular, 2,3-naphthalimides were identified to yield complete regioselectivity and fast dissociation kinetics.

Consequently, 2,3-naphthalimide-based monomers were synthesized and copolymerised with methyl methacrylate, methyl acrylate and N-isopropyl acrylamide. The obtained different copolymers were successfully photo-crosslinked with green light to obtain organogels that spontaneously collapsed in the dark. These findings offer new opportunities to further advance the development and applications of light-stabilised dynamic materials.

References

[1] H. A. Houck, E. Blasco, F. E. Du Prez, C. Barner-Kowollik, “Light-Stabilized Dynamic Materials.” *J. Am. Chem. Soc.,* **2019**, *141*, 12329–12337.

OC 22

DYNAMIC POLYURETHANES IN BIOINSPIRED NANOCOMPOSITES

SJOERD ENGELS, ANDREAS WALTHER

VITRIMAT, Johannes Gutenberg University
e-mail: sjoerd.engels@uni-mainz.de

Abstract

Polyurethanes (PUs) are a class of polymers that are characterized by the urethane group that is formed during the production process [1]. PUs are widely used in a variety of industrial and consumer applications, ranging from coating and care to low density elastomers (e.g. sneakers), to foam materials (e.g. mattresses, insulation), to adhesives, to high performance materials (e.g. automotive industry). PUs are further characterized by a high degree of tunability, both linear and crosslinked networks, solvent-free synthesis methods, and availability of polar groups. Conventional preparation of PUs involves reaction between isocyanate, polyol, and chain extender. In an earlier publication it was demonstrated that PUs can have great compatibility with cellulose nanofibrils (CNF) for preparation of bioinspired nanocomposites (NCs) with toughness and strength exceeding that of pure CNF films [2]. To further investigate PU-based CNF NCs, a selection of PUs with varying properties was prepared from the ground up [3]. Since it is important that these PUs are waterborne to be used in the preparation of CNF NCs, the preparation method chosen is specific for yielding aqueous PU dispersions in the end. Among these PUs, some are involving dynamic covalent bonds such as siloxane bonds and disulfide bonds.

These dynamic PUs were reprocessable via hot-pressing, displayed stress relaxation with a linear Arrhenius fit, and displayed thermoresponsive properties. These polymers were then used together CNF to prepare various NCs. These NCs were then subjected to tensile testing along with the pure PU polymers. Samples were prepared using both 50wt% and 90wt% CNF with all PUs. Particularly the NCs based on dynamic PUs displayed superior properties compared to pure CNF films. In addition, these NCs maintained a degree of thermoresponsive behavior that can be attributed to the dynamic PU components.

References

[1] J. O. Akindoyo, M. D. H. Beg, S. Ghazali, M. R. Islam, N. Jeyaratnam, A. R. Yuvaraj "Polyurethane types, synthesis and applications – a review" *RSC Adv.* **2016**, *6*, 114453.
[2] F. Lossada, D. Jiao, J. Guo, D. Hoenders, A. Eckert, A. Walther, ''Outstanding Synergies in Mechanical Properties of Bioinspired Cellulose Nanofibril Nanocomposites using Self-Cross-Linking Polyurethanes'' *ACS Appl. Polym. Mater.* **2019**, *1*, 3334-3342.
[3] H. Sardon, L. Irusta, M. J. Fernandez-Berridi, M. Lansalot, E. Bourgeat-Lami ''Synthesis of room temperature self-curable waterborne hybrid polyurethanes functionalized with (3-aminopropyl)triethoxysilane (APTES)'' *Polymer 51* **2010**, 5051-5057.

OC 23

VITRIMER-INSPIRED DNA HYDROGELS WITH TUNALE DYNAMICS

PIERRE LE BOURDONNEC, LUCA CIPELLETTI, RÉMI MERINDOL

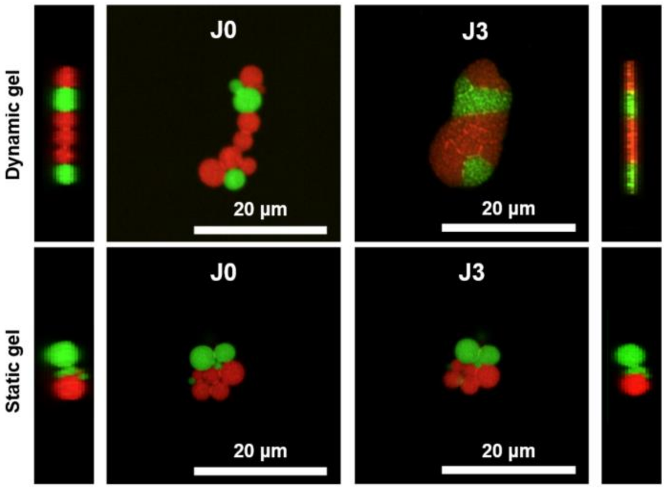
Laboratoire Charles Coulomns (L2C) – UMR5221 CNRS (France)
e-mail: p.l.bourdonnec@gmail.com

Abstract

Self-healing materials can be used in various fields of research (drug delivery, implants, packaging, ...). One main challenge with these materials is combining mechanical resistance and a quick rate of reorganisation. Indeed, fast reorganisation implies weak bonds in regards to the thermal energy which weakens the material. We try to overcome this trade- off by importing the associative exchange seen in vitrimers into supramolecular hydrogel design. These exchanges allow tuneable reorganisation at low temperatures while keeping a constant bond strength and node density.

We program this associative exchange mechanism into hydrogels using DNA. DNA offers the highest level of control in supramolecular structures as seen with DNA origamis but also with chemical reactions such as strand displacement reactions. The objective of this project is to use strand displacement to program an associative exchange in order to create dynamic hydrogels with a separate control on the elastic modulus of the material and its reorganisation speed.

In practice, we synthesize macroscopic DNA hydrogel by self-assembly of DNA single strands obtained from rolling circle amplification. We combine multiple approaches to describe the complex behaviour of these gels. We use rheology to characterize the viscoelastic properties of the gels between 15 °C and 95 °C in order to quantify the activation energy driving the associative and dissociative exchanges in the gel. We monitor the reorganisation kinetics by fluorimetry on model reactions. Finally, we use confocal laser scanning microscopy experiments to show the self-healing properties by incorporating fluorescent nucleosides into our DNA hydrogels. Thereby we demonstrate that DNA is a powerful tool to assemble macroscopic self-healing hydrogels with tuneable mechanics.



CLSM capture of a) a mix of 2 population of dynamic DNA microgel particles and b) a mix of 2 population of static DNA microgel particles in PEG during 2 days.

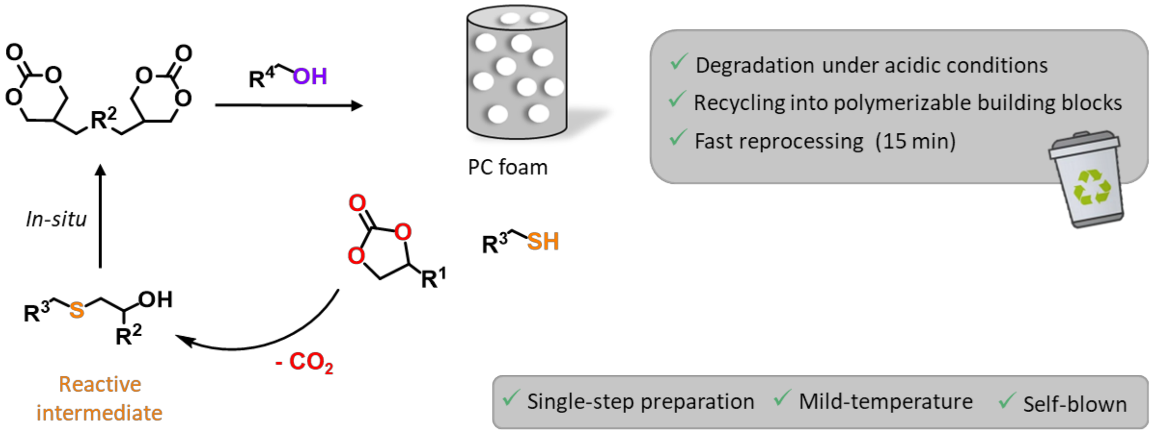
OC 24

CASCADE RING-OPENING POLYMERIZATION OF CYCLIC CARBONATES FOR THE PREPARATION OF RECYCLABLE SELF-BLOWING POLYCARBONATE FOAMS

TANSU ABBASOGLU, HARITZ SARDON

POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Center, Avda Tolosa 72, 20018 Donostia-San Sebastian (Spain)
e-mail: tansuabbasoglu@gmail.com, haritz.sardon@ehu.eus

Abstract



Polymeric foams play indispensable roles in industrial applications because of their superior thermal, mechanical, and optical properties. Today, increasing research efforts are directed toward the development of greener foam formulations that circumvent the use of isocyanates/blowing agents. Here, we present a straightforward, one-pot method to prepare self-blown polycarbonate (PC) foams by exploiting the Pearson reaction for the in-situ generation of the blowing agent (CO_2)—delivering a reactive hydroxythioether intermediate—promoting cascade ring-opening of the cyclic carbonate that yields a cross-linked polymer network. Moreover, we showcase the potential of recycle/reuse of the foams. Such hydroxyl-functionalized polycarbonate-based foams can be easily recycled into films through thermal compression molding. Furthermore, we demonstrate complete degradation of the foams in aqueous acid to approach for zero waste disposal. With abundant diversity and availability in nature of the main building blocks of the formulation, this new mild and facile process broadens the scope of direct and isocyanate-free synthesis strategy for self-foaming (pre)polymers that open up pathways to next-generation environmental-friendly foams.

Acknowledgments

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 860911 (https://www.vitrimat.eu/).

OC 25

REPROCESSABLE POLYURETHANE FOAMS VIA DYNAMIC COVALENT CHEMISTRIES

HIBA KASSEM[1,2], LUCIE IMBERNON[1], LAURA JONCKHEERE[1], FILIP DU PREZ[2]

[1]Recticel NV, Damstraat2, Industriezone 7, 9230 Wetteren, Belgium
Email: Kassem.hiba@recticel.com
[2]Polymer Chemistry Research Group, Center of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Faculty of Sciences, Ghent University, Krijgslaan 281 S4-bis, Ghent B-9000, Belgium
Hiba.kassem@ugent.be

Abstract

Due to their outstanding physical and chemical properties, polyurethanes are versatile materials used in many day-to-day applications such as coatings and foams (automotives, seatings, bedding, insulation…)[1]. Unlike thermoplastic polyurethanes, PU foams are thermosetting materials containing permanent crosslinks and therefore cannot be reprocessed or recycled. Therefore, producing a large amount of waste that mostly end up either being landfilled or incinerated[2–5].

Recently the new concept of covalent adaptable networks (CANs) was introduced. It consists in the addition of covalent adaptable bonds that allow three dimensional crosslinked networks to be reshaped. Under certain conditions, the covalent adaptable crosslinks are reversibly broken and reformed or exchanged which allows the malleability and reprocessability of these materials. Several studies have been reported describing a photo- or temperature-triggered rearrangement[6,7]. The aim of this project is to introduce thermally triggered dynamic chemical bonds in the backbone of PU foams via different chemical platforms. Additionally, this study will show how PU foams can be transformed from materials generating large volumes of waste, into sustainable materials that can be recycled and transformed into valuable products at their "end-life".

1. Simón D, Borreguero AM, de Lucas A, Rodríguez JF. Recycling of polyurethanes from laboratory to industry, a journey towards the sustainability. *Waste Manag*. 2018;76:147-171. doi:10.1016/J.WASMAN.2018.03.041
2. Gama N V, Ferreira A, Barros-Timmons A. materials Polyurethane Foams: Past, Present, and Future. doi:10.3390/ma11101841
3. Houbben M, Thomassin J-M, Jé Rô Me C. Supercritical CO 2 blown poly(e-caprolactone) covalent adaptable networks towards unprecedented low density shape memory foams †. *Cite this Mater Adv*. 2022;3:2918. doi:10.1039/d2ma00040g
4. Liu W, Chang Y-C, Hao C, et al. Improving Thermal Reprocessability of Commercial Flexible Polyurethane Foam by Vitrimer Modification of the Hard Segments. doi:10.1021/acsapm.2c00595
5. T. Sheppard D, Jin K, S. Hamachi L, et al. Reprocessing Postconsumer Polyurethane Foam Using Carbamate Exchange Catalysis and Twin-Screw Extrusion. *ACS Cent Sci*. 2020;6(6):921-927. doi:10.1021/acscentsci.0c00083
6. Denissen W, Winne JM, Du Prez FE. Vitrimers: Permanent organic networks with glass-like fluidity. *Chem Sci*. 2016. doi:10.1039/c5sc02223a
7. Winne JM, Leibler L, Du Prez FE. Dynamic covalent chemistry in polymer networks: A mechanistic perspective. *Polym Chem*. 2019. doi:10.1039/c9py01260e

Acknowledgements

This project received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska–Curie grant agreement No 860911

OC 26

CATALYST-FREE REPROCESSABLE POLYURETHANE ELASTOMERS *VIA* DISILOXANE EXCHANGE

J. DANNEELS[1,2*], E. DROCKENMULLER[2], D. MONTARNAL[3], D. J. DIJKSTRA[1]
[1]Covestro Deutschland AG, Kaiser-Wilhelm-Allee 60, 51365 Leverkusen, Germany
[2]Univ Lyon, Université Lyon 1, CNRS, Ingénierie des Matériaux Polymères, UMR 5223, F-69003, Lyon, France [3]Univ Lyon, CPE Lyon, CNRS, Catalyse, Polymérisation, Procédés et Matériaux, UMR 5128, F-69003, Lyon, France
*jens.danneels@covestro.com

Abstract

Since their discovery in 1937 by Otto Bayer, polyurethanes (PUs) have become ubiquitous in our everyday life.[1] From the soles of our shoes to the sponges we clean our dishes with, we come into contact with PU on a daily basis. The main part of the PU market consists of cross-linked materials such as rigid and flexible foams, elastomers, adhesives and coatings. These thermosetting materials have desirable mechanical properties for various applications but at the same time have the drawback of being unable to be reprocessed or recycled after production.[2] In the current climate, sustainability has become a main priority for industry, with the aim of becoming fully circular being the new guiding principle for companies such as Covestro. In this framework, the emergence of covalent adaptable networks (CANs), thermoset-like materials that flow upon heating, could be interesting to help achieve this goal in the scope of PU materials.[3] CANs own this ability to flow, and thus to be recycled or reprocessed, to the presence of exchangeable dynamic bonds in the network that are activated at elevated temperature. Some dynamic chemistries have already been explored for PUs, including hindered urea bonds, triazolinedione chemistry and disulfide bonds.[4] Here we will present disiloxane bonds as a new dynamic chemistry for PU materials, one which is already active without the addition of an external catalyst. We will show how these disiloxanes can easily be introduced in PU elastomers and devote particular attention to the viscoelastic behaviour of these elastomers compared to conventional PU elastomers.

Acknowledgments

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 860911 (https://www.vitrimat.eu/).

References

[1] O. Bayer "Das Di-Isocyanat-Polyadditionsverfahren (Polyurethane)." *Angew. Chem.*, **1947**, *59*, 257–288.
[2] H.-W. Engels, H.-G. Pirkl, R. Albers, R. W. Albach, J. Krause, A. Hoffmann, H. Casselmann, J. Dormish "Polyurethanes: Versatile Materials and Sustainable Problem Solvers for Today's Challenges" *Angew. Chem. Int. Ed.* **2013**, 52, 9422-9441.
[3] C. J. Kloxin, C. N. Bowman "Covalent adaptable networks: smart, reconfigurable and responsive network systems" *Chem. Soc. Rev.* **2013**, 42, 7161-7173.
[4] R. H. Aguirresarobe, S. Nevejans, B. Reck, L. Irusta, H. Sardon, J. M. Asua, N. Ballard "Healable and self-healing polyurethanes using dynamic chemistry" *Prog. Polym. Sci.*, **2021**, 114, 101362

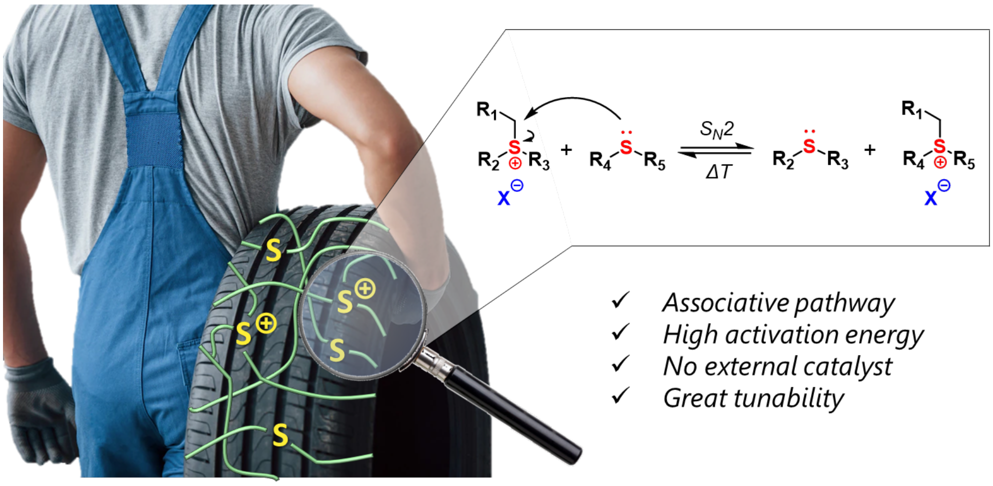
OC 27

UNLOCKING THE POTENTIAL OF TRANSALKYLATION: A SCARCELY DOCUMENTED EXCHANGE-PATHWAY FOR TRIALKYLSULFONIUM SALTS.

V. SCHOLIERS*, B. HENDRIKS, J. M. WINNE AND F. E. DU PREZ
Polymer Chemistry Research Group and Laboratory of Organic Synthesis, Department of Organic and Macromolecular Chemistry, Faculty of Science, Ghent University, Krijgslaan 281 S4-bis, Ghent B-9000, Belgium
Vincent.Scholiers@UGent.be

Abstract

The present work focuses on the synthesis of dynamic polymer networks through the introduction of thioether bonds in a polymer matrix. These thioether bonds can then be partially alkylated to create trialkyl sulfonium salts, which can be reshaped or "healed" after being damaged through the application of heat [1]. Similar to the exchange reaction of triazolium alkyl bonds [2], this chemical platform confers a very tuneable flow behaviour on the resulting materials, making them highly attractive for a wide range of applications, including flexible electronics, smart coatings, and optical applications. However, despite showing promising opportunities in re/upcycling polyolefin rubber waste, this chemical platform has only been very limited explored in a material perspective [3].



- ✓ *Associative pathway*
- ✓ *High activation energy*
- ✓ *No external catalyst*
- ✓ *Great tunability*

References

[1] B. Hendriks, J. Waelkens, J. M. Winne and F. E. Du Prez, Poly(Thioether) Vitrimers via Transalkylation of Trialkylsulfonium Salts, ACS Macro Lett. 6 (2017) 930–934.
[2] M. M. Obadia, B. P. Mudraboyina, A. Serghei, D. Montarnal and E. Drockenmuller, J. Am. Chem. Soc., 2015, 137, 6078–6083.
[3] Z. Tang, Y. Liu, Q. Huang, J. Zhao, B. Guo and L. Zhang, A Real Recycling Loop of Sulfur-Cured Rubber through Transalkylation Exchange of C-S Bonds, Green Chem. 20, (2018) 5454–5458.

OC 28

TAILOR-MADE VINYLOGOUS URETHANE VITRIMERS WITH SELF-ASSEMBLING BINARY AND TERNARY BLOCK AND RANDOM COPOLYMERS

SIRAPHAT WEERATHAWORN[1] AND VOLKER ABETZ[1,2]
[1]*Institute of Physical Chemistry, Universität Hamburg, Grindelallee 117, 20146 Hamburg, Germany.*
[2]*Institute of Membrane Research, Helmholtz-Zentrum Hereon, Max-Planck-Straße 1, 21502 Geesthacht, Germany.*
E-mail: siraphat.weerathaworn@uni-hamburg.de

Abstract

The combination of self-assembling block copolymers with the concept of vitrimers is a powerful tool for the design of reprocessable and recyclable materials with adjustable properties across a broad spectrum. There is no doubt that microphase separation plays an essential role in the thermal and mechanical properties of the resulting nanostructured networks. In this study, various narrow-disperse di- and triblock copolymers containing a hydroxyethyl methacrylate (HEMA) block and, for comparison, random copolymers of the same comonomers were synthesized in a controlled manner by photoiniferter reversible addition-fragmentation chain transfer (photoRAFT) polymerization using an ultraviolet source. Afterward, the HEMA units of the copolymers were modified by acetoacetate groups and cross-linked by various diamines *via* a condensation reaction forming vinylogous urethane bonds. The cross-linked and cured di- and triblock copolymer-based vitrimers possess superior thermal and mechanical properties compared to the vitrimers based on the corresponding random copolymers. Also, their characteristic properties can be adjusted by several types and amounts of diamines that are incorporated into the networks. In particular, they display tensile strength of 2.8(±0.1)–16.1(±0.6) MPa, strain at break of 1.3(±0.1)– 128.8(±1.2)%, and stress relaxation at 150 °C of 0.2–70.0 s. As the transamination reaction in these materials follows a thermoreversible associative dynamic exchange mechanism, it is also noteworthy that the resulting vitrimers are reprocessable and recyclable materials.

Overall, by the combination of these two classes of soft materials, namely vitrimers and block copolymers, materials with a wide range of adjustable mechanical properties and improved end-of-life management compared to permanently cross-linked thermosets can be synthesized. This may also open the door for the design of new toolboxes for more sustainable materials with tailored properties.

References

[1] W. Denissen, G. Rivero, R. Nicolaÿ, L. Leibler "Vinylogous Urethane Vitrimers." *Adv. Func. Mater.* **2015**, *25*, 2451–2457.
[2] J. Xu, V. Abetz "Nonionic UCST–LCST Diblock Copolymers with Tunable Thermoresponsiveness Synthesized via PhotoRAFT Polymerization." *Macromol. Rapid Commun.* **2021**, *42*, 2000648.
[3] S. Weerathaworn, V. Abetz "Tailor-Made Vinylogous Urethane Vitrimers Based on Binary and Ternary Block and Random Copolymers: An Approach toward Reprocessable Materials." *Macromol. Chem. Phys.* **2023**, *224*, 2200248.

OC 29

PHOSPHATE ESTER CHEMISTRY IN DYNAMIC COVALENT NETWORKS

SOUMABRATA MAJUMDAR[1], DIEDERIK VAN LUIJK[1], ROY WINK[1], HUIYI ZHANG[1], BRAHIM MEZARI[1], IVO BEEREN[2], MATT BAKER[2], ROLF A.T.M. VAN BENTHEM[1], HANS HEUTS[1], RINT SIJBESMA[1].
[1]*Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, The Netherlands.*
[2]*Complex Tissue Regeneration (CTR) Department, MERLN institute, Maastricht University, The Netherlands.*
email: s.majumdar@tue.nl

Abstract

Dynamic covalent networks (DCNs) are covalently crosslinked polymeric materials possessing chemical functionalities that can undergo bond exchange reactions upon activation by a stimulus such as heat or light.[1] This allows network topology alterations and imparts flow properties to an otherwise crosslinked material. Several dynamic covalent chemistries have been implemented in designing DCNs, of which the reactions, which do not require the use of external catalyst, have attained focus as they show persistent dynamic properties over multiple cycles of reprocessing. Here we focus on phosphate ester based reversible chemistries that have been implemented in the design of DCNs. Within the network, phosphate triesters can either be incorporated as a dynamic crosslink or can also be embedded as a dynamic chain extension link where the third ester substituent/acid might be used to alter the reactivity of the phosphorous center. The former has been demonstrated in a polytetrahydrofuran (PTHF) based network with phosphate triester crosslinks. The material showed appreciable topology rearrangement at high temperatures via phosphate triester transesterification without the aid of external catalysts.[2] Subsequently, a polycaprolactone (PCL) based network with β-hydroxyl containing phosphate triester links was studied aiming towards neighboring group assisted transesterification reaction. The material showed highly enhanced flow at much lower temperatures allowing reprocessing via extrusion.[3] β-hydroxyl containing phosphate triester links, however, are prone towards hydrolysis which limits the use to very specific applications. The hydrolytic stability was observed to increase significantly on switching from phosphate triester to phosphate diester salt with β-hydroxyl groups. Other recent observations on polymeric networks with β-hydroxyl containing phosphate triesters hint towards mechanical deactivation towards neighboring group assisted transesterification thus hint towards β-hydroxyl containing phosphate triester being a covalent catch-bond. Along with the above versatility in dynamic properties, phosphate esters also impart properties like biodegradability, flame retardancy and antifouling. The above results have been obtained with rheology, NMR spectroscopy and swollen state experiments. Considering the versatility that we have observed, we envision that phosphate esters and other organo-phosphorous moieties can be used to a variety of DCNs with systematic variations in material properties.

References

[1] Kloxin, C. J.; Scott, T. F.; Adzima, B. J.; Bowman, C. N. “Covalent Adaptable Networks (CANs): A Unique Paradigm in Cross-Linked Polymers.” *Macromolecules* **2010**, *43*, 2643−2653.
[2] Soumabrata Majumdar, Huiyi Zhang, Mohammad Soleimani, Rolf A. T. M. van Benthem, Johan P. A. Heuts, and Rint P. Sijbesma, “Phosphate Triester Dynamic Covalent Networks.” *ACS Macro Lett.* **2020**, *12*,1753–1758.
[3] Soumabrata Majumdar, Brahim Mezari, Huiyi Zhang, Jeroen van Aart, Rolf A. T. M. van Benthem, Johan P. A. Heuts, and Rint P. Sijbesm, “Efficient Exchange in a Bioinspired Dynamic Covalent Polymer Network via a Cyclic Phosphate Triester Intermediate.” *Macromolecules* **2021**, *54*, 7955−7962.

OC 30

INCREASING THE FLOW RESISTANCE OF ABA TRIBLOCK COPOLYMER-BASED NETWORKS BY CONTROLLING PHASE SEPARATION

CLÈMENT COUTOULY,[1] EVELYNE VAN RUMYBEKE,[1] CHARLES-ANDRÉ FUSTIN[1]

[1]*Bio and Soft Matter Division (BSMA), Institute of Condensed Matter and Nanosciences (IMCN),*
Université catholique de Louvain, Place Pasteur 1 & Place Croix du Sud 1,
1348 Louvain-la-Neuve (Belgium) – Email: charles-andre.fustin@uclouvain.be

Abstract

Block copolymers can form microphase separated structures in bulk or self-assemble into various structures in a selective solvent of one of the blocks. ABA triblock copolymers, in particular, can form structures similar to their simpler AB diblock counterparts but are especially interesting because of the ability of the B blocks to form bridges between A domains, leading to the formation of reversible networks. Due to this property, triblock copolymers have been considered for a variety of applications, especially in the bulk state, such as pressure sensitive adhesives or thermoplastic elastomers. However, a major drawback of these systems is their rapid loss of mechanical properties at high temperatures, limiting their range of applications. A potential way to circumvent this limitation would be to design ABA triblock copolymers that keep, or even reinforce, their microphase separation at high temperatures, therefore increasing their resistance to flow.

We report here on two such systems based on ABA triblock copolymers having a low Tg Poly(*n*-butyl acrylate) (P*n*BA) central block and either rigid or soft A blocks. These materials have been characterized by linear shear rheology, dynamical mechanical analysis (DMA) and Small Angle X-ray Scattering (SAXS) to establish structure-properties relationships. The first system uses Polystyrene (PS) as rigid outer blocks and exhibits, if the copolymer composition is properly adjusted, a lower disorder-to-order temperature (LDOT) behavior increasing the microphase separation upon a temperature increase. Contrary to triblock copolymers with a classical upper order-to-disorder temperature (UODT) behavior, the flow regime is not reached, even at temperatures well above the glass transition of the PS. Instead, a low frequency plateau is observed in rheology, showing the increased lifetime of the microphase separated PS domains. [1]

The second system is based on the low Tg poly(heptafluorobutyl acrylate) (PHFBA) as soft outer blocks. These triblocks show strong microphase separation, even for very short PHFBA blocks, from room to high temperature (200 °C), conferring high structural and thermal stability to the material. As for the PS-based triblocks, rheology revealed the appearance of a second plateau in the low-frequency region, observable up to different temperatures that depend on the PHFBA block length.

---

[1] C. Coutouly, E. van Ruymbeke, L. Ramos, P. Dieudonné-George, C.A. Fustin, *J. Rheol.* **2022**, *66*, 1305.

OC 31

FRONTAL POLYMERIZATION OF COVALENT ADPTABLE NETWORKS

STEFAN HIMER, DAVID REISINGER, SANDRA SCHLÖGL, ELISABETH ROSSEGGER
Polymer Competence Center Leoben GmbH, Roseggerstrasse 12, 8700 Leoben (Austria)
Email: elisabeth.rossegger@pccl.at

Abstract

Frontal polymerization (FP) enables the conversion of monomers into polymers in a localized reaction zone (front) which self-propagates through the bulk, similar to the domino effect (see Figure 1a). The front is driven by the released heat from exothermic reactions, with no external energy input required except during initiation. Owing to fast curing and energy efficiency, this method has been investigated for numerous monomer types and various applications. Epoxy resins are one of the most technically relevant monomers and are commonly cured by photopolymerization or thermal curing. Conventional thermal curing suffers from high energy consumption and long curing times, while photopolymerization proceeds faster, but is limited to thin films, since the penetration depth of light is restricted. To overcome these drawbacks, radical induced cationic frontal polymerization (RICFP) has been established (see Figure 1b).[1] Like classic thermal/photo-cured epoxy networks, the networks formed are characterized by high chemical and thermomechanical resistance.

Nowadays, in addition to energy efficiency, recyclability, reusability and reprocessability are also important factors that can be achieved by introducing dynamic covalent bonds into thermosets (see Figure 1c). In our recent work, we introduced dynamic bonds into a frontally polymerizable resin by using monomers with free hydroxyl- and ester groups. As catalysts, we investigated various commercially available Zn(II) salts to enable frontal polymerization on the one hand and rapid exchange reactions at elevated temperatures on the other. The networks were thermally stable up to 250 °C and were able to release 63% of the initial stress at 200 °C within 13 minutes, despite having glass transition temperatures above 100 °C. The rate of exchange reactions could be adjusted by adapting temperature and catalyst loading.

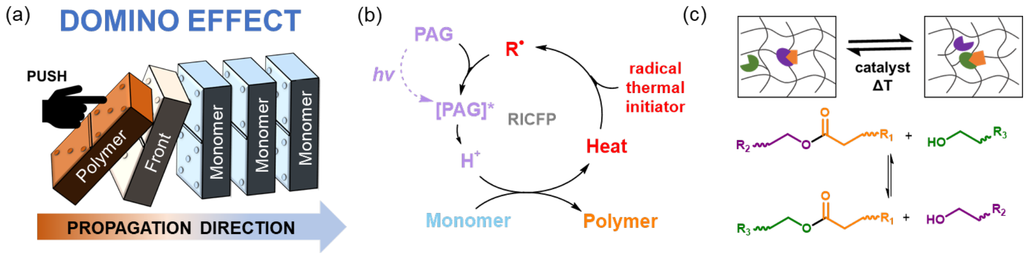


Figure 1 (a) General scheme of the domino-effect in FP, (b) radical induced cationic frontal polymerization mechanism and (c) transesterification scheme

References

[1] M.S. Malik, S. Schlögl, M.Wolfahrt, M. Sangermano "Review on UV-Induced Cationic Frontal Polymerization of Epoxy Monomers." *Polymers* **2020**, *12*, 2146

OC 32

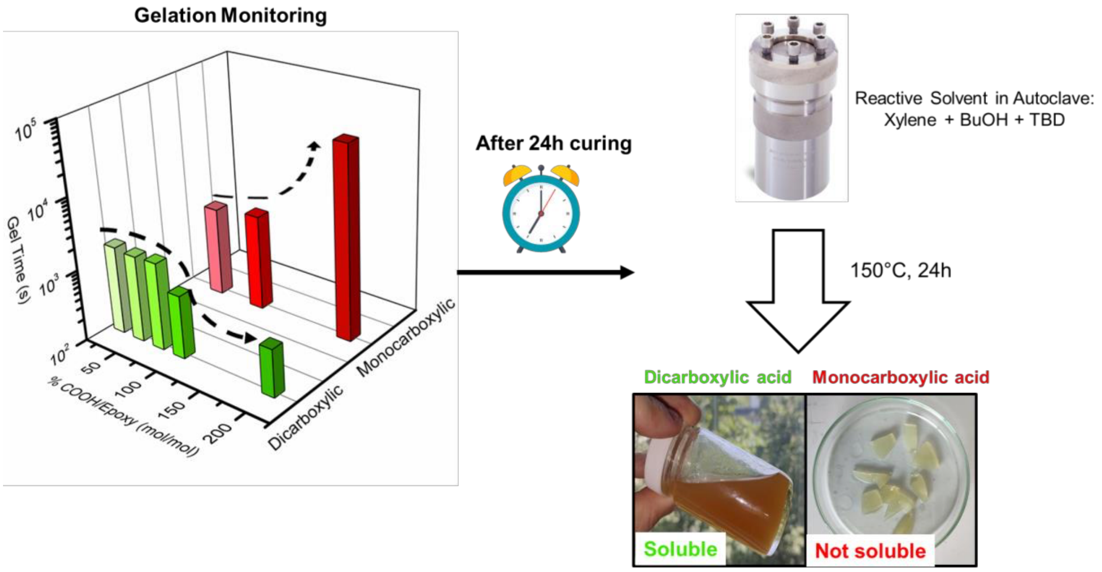
CROSS-LINKED POLYETHYLENE COPOLYMERS BY RACTIVE EXTRUSION USING VITRIMERS CHEMISTRY

DIEGO CIARDI, MICHEL CLOITRE, FRANCOIS TOURNILHAC

Molecular, Macromolecular Chemistry and Materials, ESPCI, Paris (France)
Email: diego.ciardi@espci.fr

Abstract

This study describes the fabrication based on vitrimer chemistry[1] of a dynamic network with exchangeable bonds starting from a linear polymer with lateral pendant reactive groups. Cross-linking is achieved at 150°C on a random copolymer of ethylene comprising 50 glycidyl methacrylate units per chain, in the presence of a commercial dicarboxylic acid and a metal catalyst. The gel time determined from viscoelastic measurements shows a decreasing trend as the quantity of dicarboxylic acid increases. The final material is soluble in a reactive solvent which is known to cleave ester-bonds, demonstrating the presence of ester bonds which can undergo exchange reaction. Control experiments using a monocarboxylic acid leads to chemical gelation at a time which is significantly longer than with the dicarboxylic acid and increases with the acid content. Most importantly, the final product is insoluble in the reactive solvent, indicating that permanent bonds due to irreversible side reactions have been formed. We will analyze the chemical reactions leading to crosslink formation using IR spectroscopy in both cases and present how they control the nature of the bonds and the kinetics of gelation. Finally, bulk network dynamics are also evaluated in relation to different polymer functionalization and catalysts to investigate how dynamic bonds can rearrange when an external stimulus is applied.



References

(1) Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-Like Malleable Materials from Permanent Organic Networks. Science 2011, 334 (6058), 965–968.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 691102.

OC 33

SYNTHESIS OF BIOBASED BENZOXAZINES FOR ANTICORROSION APPLICATION ON MAGNESIUM

LOUIS VAN RENTERGHEM, ROMAIN TAVERNIER, LEÏLA BONNAUD, ROYA MALEKKHOUYAN, MARJORIE OLIVIER, JEAN-MARIE RAQUEZ

Materia Nova Research Center, Avenue N. Copernic 3, 7000 Mons, Belgium. University of Mons (UMons), Place du Parc 23, 7000 Mons (Belgium)
e-mail: louis.vanrenterghem@umons.ac.be

Abstract

The growing demand for lightweight materials in the automotive, aeronautic, electronics and construction industries has lead to a renewed interest for magnesium alloys due to their low density, high strength-to-weight ratio and easy recyclability. However, the weak resistance of magnesium alloys to salt water, moisture and acids limits their use in many applications[1]. Various protections have been considered to prevent the degradation of magnesium but most of them include toxic hexavalent chromium compounds[2]. A more environment friendly alternative consists in the use of protective organic coating. Interestingly, thermosetting benzoxazine resins exhibit good thermal, anti-corrosion and alkaline resistance and thus appear as promising candidates[3]. In addition, such resin precursors can be readily obtained via a solvent free process from renewable phenolic and amine compounds[4]. Recently, we also demonstrated that the incorporation of additional dynamic exchangeable covalent groups, such as carbamate, within the resin network leads to healable and recyclable materials[5].

In this frame, this research focus on the use of ester and hydroxyl functions also known to undergo dynamic exchangeable bonds to develop innovative benzoxazine structures for coatings exhibiting self-healing and enhanced adhesion on magnesium substrates. Finally, the reduction of VOC emissions upon coating application is also considered thanks to the use of a dry process.

Keywords : benzoxazines ; anti-corrosion ; magnesium

References

1. *Prince, P. L. Protection de l ' alliage de magnésium AZ31 : Mécanismes de corrosion , couches inhibitrices et anodiques. 4-22 (2021).*
2. *Pommiers, S., Frayret, J., Castetbon, A. & Potin-gautier, M. Alternative conversion coatings to chromate for the protection of magnesium alloys. Corrosion Science* ***2014****, 84, 135–146.*
3. *Renaud, A. et al. A new corrosion protection approach for aeronautical applications combining a Phenol-paraPhenyleneDiAmine benzoxazine resin applied on sulfo-tartaric anodized aluminum. Prog. Org. Coatings* ***2017****, 112, 278–287.*
4. *Bonnaud, L. et al. High-Performance Bio-Based Benzoxazines from Enzymatic Synthesis of Diphenols. Macromolecular Chemistry and Physics* ***2018****, 1800312, 1–11.*
5. Wen, ZB, Bonnaud, L., Dubois, Ph. & Raquez, JM. Catalyst-free reprocessable crosslinked biobased polybenzoxazine-polyurethane based on dynamic carbamate chemistry, *J Appl Polym Sci*. **2022**.

OC 34

TOWARDS SUSTAINABLE POLYMER NETWORKS BY COMBINING ASSOCIATIVE AND DISSOCIATIVE DYNAMIC COVALENT BONDS

ALEIX COSTA CORNELLÀ[1], FRANCESCA FURIA[1], GUY VAN ASSCHE[1], JOOST BRANCART[1]
[1]Physical Chemistry and Polymer Science, Department of Materials and Chemistry, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium. – Email: aleix.costa.cornella@vub.be

Abstact

Fossil-based carbon use is leading the planet to a climate change, and polymers play a big role in it. A class of polymers that is specially concerning are network polymers which are crosslinked by means of permanent covalent bonds.

Introducing dynamic bonds into polymer networks can produce materials that can be more easily processed, applied, and recycled than their permanent counterparts. Moreover, they show improved toughness, stretchability, and the ability of healing physical damage. Nevertheless, despite these intrinsic benefits, there are still several sustainability issues that remain neglected. For example, the use of renewable feedstock, the use of hazardous chemicals, or to deal with the material at the end of its useful life.

The behaviour of these polymer networks heavily depends on the kinetics and thermodynamics of the dynamic bonds, which are entirely different for each mechanism. The viscosity of vitrimers shows a linear behaviour (Arrhenius behaviour) as a function of the inverse of temperature through the associative exchange of bonds, while dissociative networks can exhibit an abrupt change in viscosity above a critical temperature. Both systems have their strengths and weaknesses, but both suffer from the same compromise. For elastomeric networks, a choice or compromise has to be made between healing/reprocessing under mild conditions or to avoid creep behaviour under operational conditions.

Here we tackled both problems in one system. On the one hand, we tackled the reprocessing/self-healing problem by developing a strategy to engineer the relaxation time regime in dynamic polymer materials. We achieve this control by combining, in a single network, Diels-Alder and β-hydroxy ester bonds. Diels-Alder bonds based on furan and maleimide are dissociative dynamic covalent bonds and show an abrupt change in viscosity above a critical temperature. β-hydroxy ester bonds are associative dynamic covalent bonds and show an Arrhenius behaviour. By tuning the ratio between Diels-Alder bonds and β-hydroxy ester bonds it is possible to access the complete range of relaxation times between the two mechanisms. On the other hand, The materials are also designed guided by the 12 principles of green chemistry. They are synthesized using 100% bio-based raw materials, based on fatty acids, without using any solvent, and are potentially (bio)degradable.

With this strategy the design of the mechanical properties is decoupled from the relaxation dynamics. Combining two types of dynamic bonds with very dissimilar relaxation dynamics empowers a range of applications where the materials can be tailored according to its application, its processing, as well as the timescale of its use. Additionally, this approach is not exclusive to our system but can be generalized to any compatible pair of dissociative and associative dynamic covalent bonds.

OC 35

A STUDY OF EUGENOL-BASED DUAL-CURING SYSTEMS WITH DYNAMIC EXCHANGEABLE BONDS

Adrià Roig[a], Xavier Ramis[b], Silvia De la Flor[c]*, Àngels Serra[a]*

[a] *Universitat Rovira i Virgili, Dept. Analytical Chemistry and Organic Chemistry, C/ Marcel·lí Domingo 1, 43007 Tarragona, Spain.*
[b] *Universitat Politècnica de Catalunya, Thermodynamics Laboratory ETSEIB, Av. Diagonal 647, 08028 Barcelona, Spain.*
[c] *Universitat Rovira i Virgili, Dept. of Mechanical Engineering, Av. Països Catalans 26, 43007 Tarragona, Spain*

Abstract

Thermosets are widely used in daily life applications due to their exceptional mechanical properties. Dual-curing is an excellent methodology for preparing these materials and involves two polymerization processes, simultaneous or sequential, that can be triggered by an external stimulus such as heat or UV-light [1]. Nevertheless, the highly cross-linked structure of thermosets hampers the recyclability or reprocessability, causing serious environmental issues. For this reason, covalent adaptable networks (CANs) have been centering the interest of both the academic and industrial worlds. These materials can be reprocessed thanks to dynamic bonds in their cross-linked structure that can undergo reversible chemical reactions in certain conditions [2]. CANs behave as permanently cross-linked thermosets below at a specific temperature, but they can flow, altering their behavior from a viscoelastic solid to a fluid-like plastic. In recent years, the depletion of fossil resources has concerned the scientific world. For this reason, the use of renewable resources and finding greener synthetic routes to prepare vitrimeric materials, have attracted researchers. A potential bio-based compound is eugenol, an aromatic compound that contains phenol and allyl groups that can be modified to get a suitable functionality and, therefore, to prepare a wide range of different vitrimers [3].

In this work, we report the preparation of a series of vitrimeric materials using a synthesized acrylate-epoxy-eugenol monomer cured with different amines. The di-functional compound enables the dual-curing being the first step an aza-Michael reaction and a second epoxy-amine condensation at higher temperatures. The sequentiality of the curing can be achieved by properly selecting the catalyst and was studied by DSC. The completion of the reaction was confirmed by FTIR. The final materials were characterized by DMTA, showing that the materials had $T_{\tan\delta}$s higher than room temperature and high homogeneity. The presence of β-amino esters and disulfide groups enables the fast relaxation of the network at low temperatures (110 °C in 15 min) *via* reversible aza-Michael reaction and disulfide metathesis and reveals an Arrhenius-type dependence between viscosity and temperature. The use of different amines allows tailoring the properties of the final materials.

References

[1] X. Ramis, X. Fernández-Francos, S. De la Flor, F. Ferrando, À. Serra. Click-based dual-curing thermosets and their application, in Q. Guo (Ed.), Structure, Properties and Application, Thermosets, second. ed. Chap. 16, Elsevier, 2018 pp 511-541.

[2] W. Denissen, J. M. Winne, F. E. Du Prez. Vitrimers: permanent organic networks with glass-like fluidity. *Chem. Sci.* **2016**, *7*, 30-38.

[3] T. Liu, C. Hao L. Wang, Y. Li, W. Liu, J. Xin, J. Zhang. Eugenol-derived biobased epoxy: shape memory, repairing, and recyclability. *Macromolecules*, **2017**, *50*, 8588-8597.

OC 36

Catalyst-Free Covalent Adaptable Networks activated by fluorinated groups

DIMITRI BERNE[1], FLORIAN CUMINET[1], BAPTISTE QUIENNE[1], RINALDO POLI[2], SYLVAIN CAILLOL[1], ERIC LECLERC[1], VINCENT LADMIRAL[1]

[1] ICGM, Univ. Montpellier, CNRS, ENSCM, 34293 Montpellier (France)
[2]CNRS, LCC, UPS, INP, Université de Toulouse, 31077 Toulouse, (France)
Email: dimitri.berne@enscm.fr

Abstract

The tremendous interest that have generated fluorinated molecules in the last decades finds its origin in the peculiar properties bestowed by F atoms. Fluorine is the second smallest atom (van der Waals radius = 1.47 Å) of the periodic table and exhibits the strongest electronegativity (4.0 on the Pauling scale). The C–F bond is consequently short (1.35 Å) and has a very high dissociation energy of 105.4 kcal.mol^{-1}. These electronic features often have major consequences on the lipophilicity, the pKa, the metabolic stability and, of course, the reactivity of fluorinated molecules.[1] As a consequence, the attack of fluorinated esters or amides by alcohols or amines should be considerably enhanced. In addition, fluorinated acrylates are prone to Michael additions. These reactivities allow broadening the range of accessible fluorinated Covalent Adaptable Networks (CANs).

Here we report our work on the use of various fluorinated groups as neighbouring activating groups in Covalent Adaptable Networks. For transesterification[2,3], transamidation, and aza-Michael exchange[4], the fluorine electron-withdrawing effect was demonstrated by DFT to considerably decrease the activation barrier of the exchange and by kinetics experiments to strongly increase the exchange reaction rate. These effects are also at work in material synthesis and properties, as exemplified by the characterization (rheology, reprocessing) of a broad range of fluorinated CANs using transesterification[2,3], transamidation and aza-Michael exchange. These studies demonstrate the potential and versatility of fluorinated groups as activating neighbouring groups in CANs.

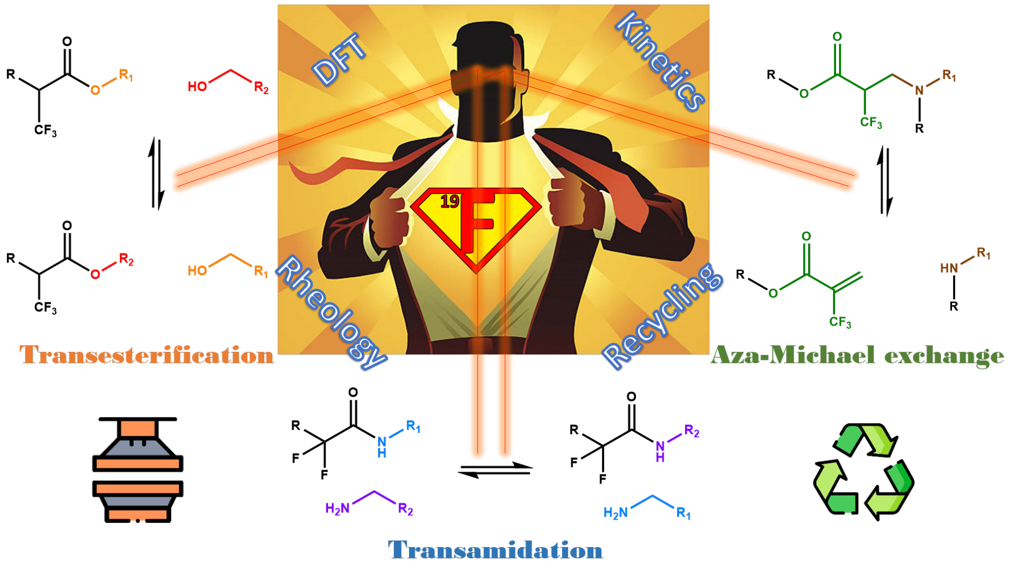


Figure 1. Representative illustration of the fluorine neighbouring activation effect on transesterfication, transamidation and aza-Michael exchange.

---

[1] J. P. Bégué, D. Bonnet-Delpon, *Bioorganic and Medicinal Chemistry of Fluorine*, John Wiley & Sons, **2007**.

[2] D. Berne, F. Cuminet, S. Lemouzy, C. Joly-Duhamel, R. Poli, S. Caillol, E. Leclerc, V. Ladmiral, *Macromolecules* **2022**, *55*, 1669.

[3] F. Cuminet, D. Berne, S. Lemouzy, E. Dantras, C. Joly-Duhamel, S. Caillol, E. Leclerc, V. Ladmiral, *Polym. Chem.* **2022**, *8*, 5255.

[4] D. Berne, B. Quienne, S. Caillol, E. Leclerc, V. Ladmiral, *J. Mater. Chem. A* **2022**, *10*, 25085.

OC 37

SELF-HEALING BEHAVIOR AND DYNAMIC NETWORK FORMATION OF IONICALLY MODIFIED POLY(ISOBUTYLENE-CO-ISOPRENE) RUBBER

BRIGITTE VOIT,[1,2] FRANK BÖHME,[1] MARCUS SUCKOW,[1,2] ALLADIN SALLAT[1,2]

[1]Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, 01069 Dresden (Germany) – Email: voit@ipfdd.de
[2]Organic Chemistry of Polymers, Technische Universität Dresden, 01062 Dresden (Germany)

Abstract

The conversion of commercially available brominated poly(isobutylene-co-isoprene) rubber (BIIR) with alkyl imidazoles results in the formation of ionomers which are able to form dynamic networks by ionic association. The allylic bromine functionalities available in BIIR were utilized as good leaving groups in a nucleophilic substitution reaction with alkylimidazole derivatives to form imidazolium bromide moieties, which leads to the formation of reversible ionic clusters that can act as physical cross-links. We have shown that the properties of ionically modified BIIR are comparable with those of sulfur cross-linked samples, but also show pronounced self-healing behavior. Compared to other self-healing rubbers described in the literature, the overall performance of the ionically modified BIIR described here is outstanding.[1]

The focus of this presentation is on the nature of self-healing of ionically modified rubbers obtained by reaction of BIIR with various alkyl imidazoles such as 1-methylimidazole, 1-butylimidazole, 1-hexylimidazole, 1-nonylimidazol and 1-(6-chlorohexyl)-1H-imidazole.[2] Based on stress-strain and temperature dependent DMA measurements, a structural influence of the introduced ionic imidazolium moieties on the formation of ionic clusters and, as a consequence on the mechanical strength and self-healing behavior of the samples could be evidenced. In particular, it could be shown that samples with increased chain dynamics exhibit pronounced self-healing behavior. By adjusting the chain mobility, materials with excellent mechanical behavior and simultaneous self-healing could be obtained.

For further improvement of the already good mechanical and dynamic mechanical properties of the self-healing BIIR for potential use in technical applications, the reinforcement of the material by fillers, e.g. silica particles, is indispensable. Rubber composites were prepared by mixing bromobutyl rubber (BIIR) with silica particles in the presence of 1-butylimidazole. In addition to pristine (precipitated) silica, silanized particles with aliphatic or imidazolium functional groups, respectively, were used as filler. During compounding, the bromine groups of BIIR were converted with 1-butylimidazole to ionic imidazolium groups which formed a dynamic network by ionic association. Based on DMA temperature and strain sweep measurements, cyclic tensile tests, and stress–strain measurements it could be concluded that interactions between the ionic groups and interactions with the functional groups of the silica particles strongly influence the mechanical and viscoelastic behavior of the composites. A particularly pronounced reinforcing effect was observed for the composite with pristine silica, which was attributed to acid–base interactions between the silanol and imidazolium groups. Thus, the overall performance of the ionically modified rubbers could be further increased by compounding with surface modified silica without losing self-healing.[3]

---

[1] Das, A.; Sallat, A.; Böhme, F.; Suckow, M.; Basu, D.; Wießner, S.; Stöckelhuber, K. W.; Voit, B.; Heinrich, G. ACS Appl. Mater. Interfaces 2015, 7, (37), 20623-20630

[2] Suckow, M.; Mordvinkin, A.; Roy, M.; Singha, N. K.; Heinrich, G.; Voit, B.; Saalwächter, K.; Böhme, F. Macromolecules, 2018, 51, 468-479.

[3] Sallat, A.; Das, A., Schaber, J.; Scheler, U.; Bhagavatheswaran, E. S.; Stöckelhuber, K. W.; Heinrich, G.; Voit, B.; Böhme F. RSC Adv. 2018, 8, 26793.

OC 38

PROCESSING AND CHEMICALMODIFICATION OF POLYOLEFIN VITRIMERS BY REACTIVE EXTRUSION

B. RIGATELLI,[1,2] E. DROCKENMULLER,[1] D. MONTARNAL[2]

[1]Université de Lyon, Université Lyon 1, CNRS, Ingénierie des Matériaux Polymères, UMR 5223, F-69003 Lyon (France) – E-mail: benedetta.rigatelli@univ-lyon1.fr
[2]Univ. Lyon, CPE Lyon , CNRS, Catalyse, Polymérisation, Procédés et Matériaux, UMR 5128, F-69003, Lyon (France)

Abstract

Cross-linked polyolefins are characterized by remarkable performances such as dimensional stability at high temperatures, excellent solvent and creep resistance; such materials are employed in a variety of applications in which lifespan is critical (pipes, cables). Nevertheless, due to the abovementioned stability, the recyclability of those compounds remains nowadays an unsolved issue. The necessity of moving towards a more sustainable circular economy by re-designing the chemistry of cross-linked materials appears to be one of the main challenges of the coming decades. Within this context, the outstanding potentiality of covalent adaptable networks (CANs) in the field of recyclable thermoset was recognized for the first time in 2010 [1]. CANs can retain their cross-linked structure displaying high performances at service temperatures, while the activation of dynamic exchange reactions at processing temperatures allows these materials to flow, be re-shaped or be recycled. Among all the different dynamic chemistries available, only a few have been implemented in cross- linked polyolefins. The typical strategy implies the use of a polyolefin (either neat or functionalized) as a starting material and a bifunctional cross-linker carrying the exchangeable bonds [2]. While reactive extrusion is the ideal processing technology to achieve proper cross- linking and envision upscalability to high throughputs, the control of the exchange dynamics and the viscosity increase is crucial [3]. We will present and compare dynamically cross- linked PEs obtained by reactive extrusion from a commercially available maleic anhydride- grafted PE and diamines comprising highly exchangeable dynamic bonds. We will address in particular the curing reactions – or eventual side-reactions – at stake in these systems by combining a mechanistic analysis on model compounds and a thorough mechanical and viscoelastic characterization of the PE networks. The (re)processability of such materials will be discussed based on capillary rheometry experiments.

Acknowledgments

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 860911 (https://www.vitrimat.eu/).

References

[1] C. J. Kloxin, T. F. Scott, B. J. Adzima, C. N. Bowman "Covalent Adaptable Networks (CANs): A Unique Paradigm in Cross-Linked Polymers." *Macromolecules* **2010**, *43*, 2643–2653.
[2] M. Röttger, T. Domenech, R. van der Weegen, A. Breuillac, R. Nicolaÿ, L. Leibler, "High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis." *Science* **2017**, *356*, 62–65.
[3] C. Taplan, M. Guerre, J. M. Winne, F. E. Du Prez, "Fast processing of highly crosslinked, low-viscosity vitrimers." *Mater. Horiz.* **2020**, *7*, 104-110.

OC 39

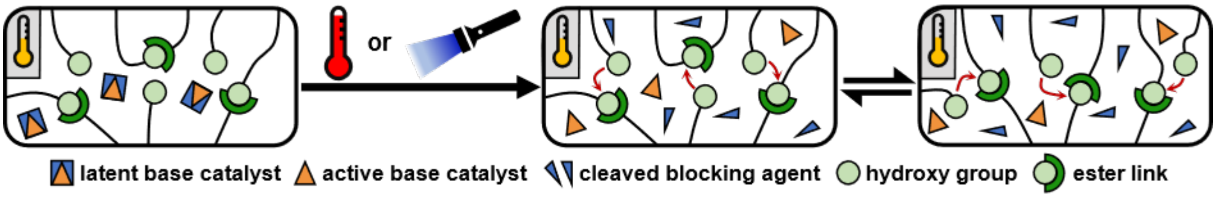
LATENT BASE CATALYSTS FOR AN ON-DEMAND ACTIVATION OF DYNAMIC EXCHANGE REACTIONS IN COVALENT POLYMER NETWORKS

David Reisinger[1], Matthias Udo Kriehuber[1], Simon Kaiser[1], Elisabeth Rossegger[1],
Kurt Dietliker[2], Marco Sangermano[3], Bernhard Rieger[4], Sandra Schlögl[1]

[1]*Polymer Competence Center Leoben GmbH, Roseggerstrasse 12, 8700 Leoben (Austria)*
– Email: david.reisinger@pccl.at
[2]*SCD Dr. Sommerlade Chemistry Design GmbH, Rheinfeldener Straße 27, 79395 Neuenburg am Rhein (Germany)*
[3]*Politecnico di Torino, DISAT, Corso Duca degli Abruzzi 24, 10124 Torino (Italy)*
[4]*WACKER-Chair of Macromolecular Chemistry, Technical University of Munich, Lichtenbergstraße 4, 85748 Garching (Germany)*

Abstract

In covalent adaptable networks, a defined onset of dynamic bond exchange reactions, and the associated suppression of undesired creep at operating temperatures is difficult to realize. For numerous systems, including the widely used transesterification-based ones, latent catalysts pose a versatile and straightforward approach to overcome this challenge.[1] In response to an external trigger, such as light or temperature, a highly active catalyst is released, enabling an on-demand reorganization of the network topology (see figure below).



We synthesized a library of latent base catalysts to selectively release the catalyzing species for thermoactivated transesterification in dynamic polymer networks. As a first step, a photolatent base was incorporated in an optically transparent thiol-epoxy polymer, and the spatiotemporal activation of dynamic transesterification was enabled by the light-mediated release of a strong guanidine base from a quaternary ammonium salt.[2] Adverse effects of this class of photolatent catalysts (low solubility, narrow absorption window) were overcome by using photoactive *N*-substituted derivatives of amidine bases. Owing to their commercial availability, an important step toward the technical application of spatially resolved activatable dynamic polymers has been made.[3] Apart from photolatent bases, recently introduced thermolatent bases allow the production of composites and objects in any spatial geometry without restrictions regarding their optical transparency. The manufactured 3D-printed objects and composite structures exhibit an outstanding creep resistance prior to catalyst activation. However, once a defined temperature threshold is exceeded, they can be efficiently reshaped and mended.[4]

---

[1] F. van Lijsebetten, T. Debsharma, J. M. Winne, F. E. Du Prez, *Angew. Chem. Int. Ed.* **2022**, *61*, e202210405.

[2] D. Reisinger, K. Dietliker, M. Sangermano, S. Schlögl, *Polym. Chem.* **2022**, *13*, 1169.

[3] D. Reisinger, S. Kaiser, E. Rossegger, W. Alabiso, B. Rieger, S. Schlögl, *Angew. Chem. Int. Ed.* **2021**, *60*, 14302.

[4] D. Reisinger, M. U. Kriehuber, M. Bender, D. Bautista-Anguís, B. Rieger, S. Schlögl *Submitted manuscript*

OC 40

LATENT CATALYSTS TO TUNE THE VISCOSITY PROFILE IN PU VITRIMERS

G. VOZZOLO[1]; M. XIMENIS[1]; M. FERNANDEZ[1] AND H. SARDON[1]

[1]Faculty of Chemistry, Basque Country University UPV/EHU, 20018 San Sebastián (Spain).
Email: giulia.vozzolo@ehu.eus

Abstract

Vitrimers are dynamic polymer networks containing exchangeable covalent bonds that can be activated by internal/external stimuli. These materials represent an appealing compromise between thermosets and thermoplastics, by combining the superior mechanical properties and solvent resistance of the formers and the reprocessability/recyclability of the latter.

Although vitrimers are considered very promising in substituting their thermosets counterparts in the plastic market, several challenges must still be overcome.[1]

In the field of low T_g vitrimers, one of the current challenges is to find strategies to suppress irreversible deformation (i.e. creep) at service temperature, without losing the reprocessability/recyclability of the material at higher temperatures.[2] [3] In fact, creep is a relevant drawback that could prevent vitrimers from being used for a variety of applications in which elastomers are currently employed.[4]

In light of these considerations, latent catalysts can represent an attractive strategy to trigger the dynamicity of the systems upon limited conditions.

Among the already described latent catalysts, tetraphenylborate salts caging strong bases were found to be the most interesting ones since they combine high versatility with the easiness and cheapness of their synthesis and adequate thermostability. These salts can be activated either thermally or by UV or even visible light irradiation (if an appropriate photosensitizer is added to the system).[5]

In the present study, we describe a versatile approach to suppress creep in PU-containing disulfide vitrimers. Such dynamic bonds are activated under basic conditions allowing the network reprocessing. Here we found that the incorporation of a thermal latent base as an additive to the network triggers the dynamic exchange only at the service temperature, avoiding creep and deformation when compared to the free base addition.

In addition, this latent base shows reversibility up to 150 ºC.

Acknowledgments

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 860911 (https://www.vitrimat.eu/).

References

[1] V. Schenk, K. Labastie "Vitrimer composites: current status and future challenges" Mater. Adv., **2022**, *3*, 8012–8029

[2] F. V. Lijsebetten, K. De Bruycker "Suppressing Creep and Promoting Fast Reprocessing of Vitrimers with Reversibly Trapped Amines" Angew.Chem. Int. Ed., **2022**, *61.9:* e202113872

[3] L. Li, X. Chen "Vitrimers Designed Both To Strongly Suppress Creep and To Recover Original Cross-Link Density after Reprocessing: Quantitative Theory and Experiments" Macromolecules, **2018**, *51*, 5537−5546

[4] W. Denissen, J. M. Winne "Vitrimers: permanent organic networks with glass-like fluidity" Chem. Sci. **2016**, *7*, 30−38

[5] F. Gamardella, S. Muñoz "Recyclable Organocatalyzed Poly(Thiourethane) Covalent Adaptable Networks" Polymers **2020**, *12*, 2913

OC 41

DIELECTRIC POLYMER WITH DESIGNABLE LARGE MOTION UNDER LOW ELECTRIC FIELD

Chengcheng Zhang, Binjie Jin, Tao Xie*

State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

Abstract

Dielectric elastomers (DEs) can demonstrate fast and large in-plane expansion/contraction due to electric field (e-field)-induced Maxwell stress. For robotic applications, it is often necessary that the in-plane actuation is converted into out-of-plane motions with mechanical frames. Despite their performance appeal, their high driving e-field (20–100 V μm^{-1}) demands bulky power accessories and severely compromises their durability. Here, a dielectric polymer that can be programmed into diverse motions actuated under a low e-field (2–10 V μm^{-1}) is reported. The material is a crystalline dynamic covalent network that can be reconfigured into arbitrary 3D geometries. This gives rise to a geometric effect that markedly amplifies the actuation, leading to designable large motions when the dielectric polymer is heated above its melting temperature to become a DE. Additionally, the crystallization transition enables dynamic multimodal motions and active deployability. These attributes result in unique design versatility for soft robots.

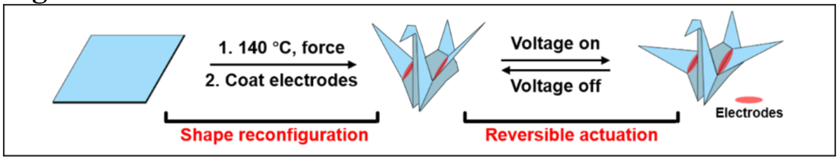
References

[1] Y. Qiu, E. Zhang, R. Plamthottam, Q. Pei. “Dielectric elastomer artificial muscle: materials innovations and device explorations.” *Acc. Chem. Res.* **2019**, 52, 316-325.

[2] Q. Zhao, W. Zou, Y. Luo, T. Xie. “Shape memory polymer network with thermally distinct elasticity and plasticity.” *Sci. Adv.* **2016**, 2, e1501297.

[3] M. Watanabe, N. Wakimoto, H. Shirai, T. Hirai. “Bending electrostriction and space-charge distribution in polyurethane films.” *J. Appl. Phys.* **2003**, 94, 2494.

Figure



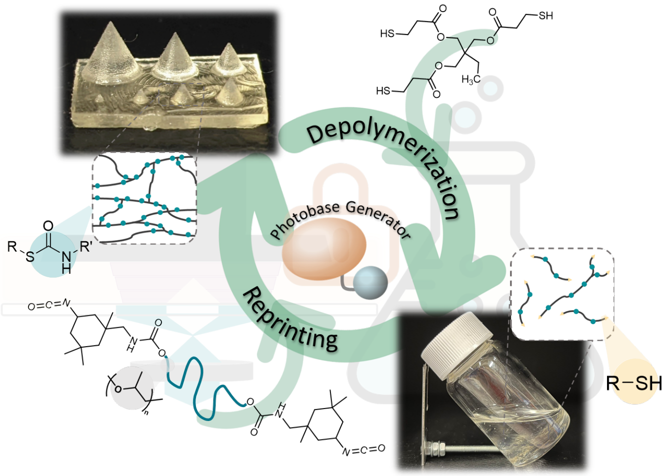
OC 42

LOOP 3D PRINTING: RECYCLABLE PHOTORESINS FOR LIGHT-MEDIATED ADDITIVE MANUFACTURING

Xabier Lopez de Pariza[1], Oihane Varela[1], Samantha Catt[2], Timothy E. Long[3], Eva Blasco[2], and Haritz Sardon[1]
[1]POLYMAT and Departamento de Química Aplicada, Facultad de Ciencias Químicas, University of the Basque Country UPV/EHU, Joxe Mari Korta zentroa, Tolosa Hiribidea 72, Donostia-San Sebastián 20018, Spain.
[2]Ruprecht-Karls-Universität Heidelberg, Organic Chemistry Institute (OCI), 69120 Heidelberg, Germany; Ruprecht-Karls-Universität Heidelberg, Institute for Molecular Systems Engineering and Advanced Materials (IMSEAM), Germany, 69120 Heidelberg
[3]Arizona State University, School of Molecular Science and Biodesign Center for Sustainable Macromolecular Materials and Manufacturing, Tempe, Arizona 85281, United States.
Email: xabier.lopezdepariza@ehu.eus

Abstract

Additive manufacturing (AM), also known as 3D printing, emerged as a rapidly developing manufacturing method with a high impact in industrial processing.[1] A myriad of complex 3D structures from microscopic to macroscopic scale have been reported, with applications ranging from general purpose objects to engineering materials.[2,3] Advances in this field rely on chemistries which enable the process to be feasible, and more recently aim at unattainable properties such as recyclability. Here, we develop an approach that enables the printing of a resin that could be re-printed with retained properties and appearance. To that end, we take advantage of the potential of polythiourethane chemistry, which not only permits the "click" efficient photobase catalyzed reaction between polythiols and polyisocyanates in the presence of light, allowing a fast-printing process, but also chemical recycling, reshaping and reparation of the printed structures allowed by the high dynamicity of the thiourethane bonds generated over the printing process. We investigated the effect of the formulation and the photocatalyst on the formed polythiourethane networks, optimized printing conditions both in the macroscale and microscale via DLP or DLW respectively and studied the reparation and recycling conditions to yield circular photoprintable resins.



References

(1) Thakar, C. M.; Parkhe, S. S.; Jain, A.; Phasinam, K.; Murugesan, G.; Ventayen, R. J. M. 3d Printing: Basic Principles and Applications. *Mater. Today Proc.* **2022**, *51*, 842–849.
(2) Ligon, S. C.; Liska, R.; Stampfl, J.; Gurr, M.; Mülhaupt, R. Polymers for 3D Printing and Customized Additive Manufacturing. *Chem. Rev.* **2017**, *117* (15), 10212–10290.
(3) Narupai, B.; Nelson, A. 100th Anniversary of Macromolecular Science Viewpoint: Macromolecular Materials for Additive Manufacturing. *ACS Macro Lett.* **2020**, *9* (5), 627–638.

OC 43

BIO-BASED, RECYCLABLE, DIGITAL LIGHT PROCESSING 3D PRINTABLE DYNAMIC COVALENT NETWORKS

ANNA LIGUORI[1], KARLA ITZEL GARFIAS GONZALEZ[1], MINNA HAKKARAINEN[1]
[1]KTH Royal Institute of Technology, Department of Fibre and Polymer Technology, Teknikringen 58, 100 44 Stockholm, Sweden – Email: liguori@kth.se

Abstract

With the increasing concerns on the environmental issues and with the depletion of fossil-based resources, the design of 3D recyclable thermosets from bio-based molecules is strongly demanded. In the present work, two different bio-based thermosets were obtained by means of digital light processing (DLP) 3D printing and carefully characterized also in terms of mechanical and chemical recyclability. The first cured thermoset (XSB) was based on a vanillin-derived photocurable Schiff-base resin (SB) synthesized through a triple step process, including (i) the incorporation of a –OH terminated short aliphatic chain to extend the vanillin molecule, (ii) a methacrylation reaction, (iii) a Schiff-base reaction with ethylene diamine[1]. The second typology consisted of a composite thermoset (XSB+OCNPs) obtained by DLP of SB resin after the modification of the resin by oxidized carbon nanoparticles (OCNPs), properly synthesized starting from hydrothermal carbonization of α-cellulose through a microwave assisted procedure followed by an oxidation step[2]. The presence of OCNPs improved the printability of the resins, enabling obtainment of 3D objects characterized by a greater resolution. The printed thermosets showed high thermal stability, with a 5% degradation temperature around 300°C; glass transition temperatures in the range 81-93 °C and excellent solvent resistance properties against common solvents. XSB turned out to be more rigid than XSB+OCNPs, showing higher elastic modulus and stress at break. The thermomechanical analysis documented a typical vitrimer-like behavior in both the thermosets, mainly demonstrated by the presence of a constant storage modulus plateau at a temperature around 100°C above the glass transition. Moreover, the stress relaxation analysis documented the capability of both networks to release the stress, showing a decrease of the stress relaxation time with the temperature increase. The mechanical recyclability was demonstrated by reprocessing with hot-press, by exploiting the imine bonds metathesis pathway. The chemical recyclability was obtained by placing the specimens in ethylene diamine to utilize the transimination mechanism[1]. The presence of OCNPs turned out to be beneficial on both the mechanical and the chemical recyclability of the networks. The work was carried out in the frame of the project "Sustainable". The project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 101021859.

References

[1] A. Liguori, S. Subramaniyan, J. G. Yao, M. Hakkarainen, "Photocurable extended vanillin-based resin for mechanically and chemically recyclable, self-healable and digital light processing 3D printable thermosets" Eur. Polym. J. 178 (2022) 111489
[2] N. B. Erdal, K. H. Adolfsson, T. Pettersson, M. Hakkarainen, "Green Strategy to Reduced Nanographene Oxide through Microwave Assisted Transformation of Cellulose" ACS Sustainable Chem. Eng. 2018, 6, 1, 1246–1255.

OC 44

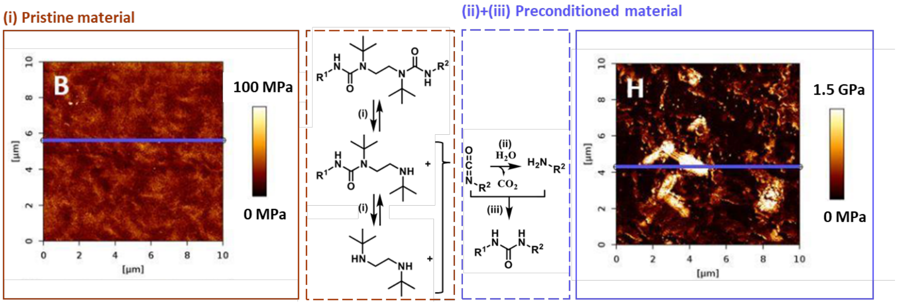
SELF-STRENGTHENING THERMOPLASTIC POLYURETHANES FOR HIGHLY POROUS BIODEGRADABLE SMALL-DIAMETER VASCULAR GRAFTS

KATHARINA EHRMANN[1], MARKUS FITZKA[1], KLAUS ABLEIDINGER[1], HELGA BERGMEISTER[2,3], STEFAN BAUDIS[1,4], ROBERT LISKA[1]
[1] Institute for Applied Synthetic Chemistry, Technische Universität Wien, Getreidemarkt 9/163, 1060 Vienna
[2] Ludwig Boltzmann Institute for Cardiovascular Research, Währinger Gürtel 18-20, 1090 Vienna
[3] Institute of Biomedical Research, Medical University of Vienna, Währinger Gürtel 18-20, 1090 Vienna
[4] Christian Doppler Laboratory for Advanced Polymers for Biomaterials and 3D Printing, Vienna

Abstract

Recently, dynamic urethane and urea bonds have been investigated intensively for reprocessable and recyclable materials in the context of vitrimers. However, they remain largely underexplored for thermoplastic poly(urethane urea)s (TPUUs), a generally highly researched class of polymers due to their versatile use in industry, e.g. as medical grade engineering materials. Upon implementation of dynamic hindered urea bonds into polyurethanes we found that they exhibit significantly superior mechanical performance through simple incubation of the material in water. Most notably, strains at break could be increased up to 10x compared to the pristine material, which led us to term the effect "self-reinforcement". We have elucidated the mechanism of self-reinforcement in small molecule studies and investigated its matrix-dependent effects on material properties (Figure 1).

Figure 1: Self-strengthening mechanism and phase-separation of the material found in AFM-nanoindentation experiments before and after



The hindered urea bonds reversibly open at room temperature. In the presence of water, partial hydrolysis of emerging isocyanates occurs and in situ generated amines can react with intact isocyanates to form urea bonds. Kinetic studies of these reactions proof that the rates of hydrolysis and non-hindered urea formation match well enough for this cross-reaction to occur. At the same time, cross reaction efficiency is strongly dependent on matrix rigidity. Self-strengthening TPUUs reconcile the contradicting properties of mechanical performance and processability in solution-based techniques. This is particularly important for highly porous biomedical scaffolds such as vascular grafts. We have shown that self-reinforcement is beneficial in electrospun biodegradable small-diameter vascular grafts. Notably, biodegradability of such scaffolds is enhanced compared to reference grafts despite their superior mechanical performance.

OC 45

MODELING MULTIPLE STRESS RELAXATIONS BEHAVIORS OF DYNAMIC POLYMER NETWORK NEAR ITS GLASS TRANSITION TEMPERATURE

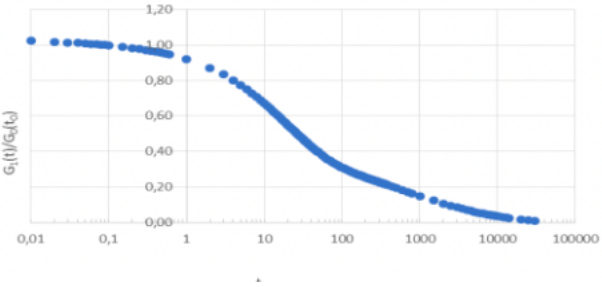
ISIS CASTRO-CABRERA, ARMAND FAHS, SOPHIE BELIOZ, PASCAL CARRIERE
Laboratoire MAPIEM (MAtériaux, Polymères, Interfaces et Environement Marin) –
Université de Toulon (France)
e-mail: pascal.carriere@univ-tln.fr

Abstract

Long fiber reinforced thermosets are particularly sought after for structural applications in the wind energy, aerospace and marine industries due to their low density, good mechanical strength and good stability in operation. This good stability is conferred by permanent covalent bonds which characterize thermoset materials, which makes them very difficult to recycle. Indeed, they end up being incinerated or buried [1]. However, the introduction of reversible covalent bonds in the networks is an opportunity to develop the recycling of these materials. It is now necessary to understand in detail the structure-property relationships between the dynamics of the network, the structure of the network and, the consequences of the reactivity of these reversible covalent bonds [2].

The proposed study focuses on the relaxation behavior of epoxy-amine vitrimer systems with a high glass transition temperature (Tg) and a hardener possessing disulfide dynamic covalent bonds. Usually, the studies of these systems do not take into account the full relaxation nor its complexity [3]. All the networks studied in stress relaxation show that the most relevant rheological model must integrate two distinct relaxation times. It appears that the first relaxation time seems to be correlated to the direct effect of reversible covalent bonds on the evolution of viscosity with temperature especially to its concentration, while the second relaxation time can be mainly attributed to the segmental movements that classically characterize the relaxation of a three-dimensional network.

The presented results show, how some vitrimers behave just above Tg, allowing to complete the relaxation spectrum and the associated activation energies, usually studied an hundred degrees above Tg. Thus, it is possible to model the pseudo-permanent behavior of these networks at low temperatures until their flow at high temperatures, data necessary for the establishment of a complete time-temperature superposition diagram.



Master curve of DGEBA- 4,4’- diaminodiphényl disulfide network stress relaxation at $T_{ref} = T_g + 10$ K

References

[1] S. R. Naqvi ; H. M. Prabhakara.; E. A. Bramer ; W. Dierkes ; R. Akkerman ; G. Brem,Resour., Conserv. Recycl., 2018, 136, 118−129
[2] J. M. Winne, L. Leibler and F. E. Du Prez, Polym. Chem., 2019, 10, 6091–6108
[3] A. Ruiz de LuzuriagA ; G. Solera ; I. Azcarate-Ascasua . V. Boucher ; H.J. Grande ; A. Rekondo, Polymer, 2022, 239, 124457

OC 46

THERMO-REVERSIBLE CROSSLINKED RUBBER AND ITS rGO/SILICA NANOCOMPOSITES VIA MELT REACTIVE BLENDING

FRANCESCO CANTAMESSA[1], FABIO CARNIATO[2], GIACOMO DAMONTE[3], ORIETTA MONTICELLI [3], ROSSELLA ARRIGO[1], ALBERTO FINA[1]

[1]*Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, 15121 Alessandria, Italy*
Email: alberto.fina@polito.it
[2]*Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale, 15121, Alessandria, Italy*
[3]*Dipartimento di Chimica e Chimica Industriale, Università di Genova, 16146 Genova, Italy*

Abstract

A covalent adaptable network based on the thermo-reversible crosslinking of an ethylene-propylene rubber through Diels-Alder (DA) reaction was prepared through melt blending, as an environmental-friendly alternative to traditional synthesis in organic solvents. Functionalization of the rubber with furan groups was carried out in a melt blender and subsequently mixed with different amounts of bismaleimide (BM) in a microextruder. Reaction was observed by FT-IR spectroscopy and crosslinking quantified via solvent extraction up to approx. 85%. Crosslinking degree is reflected in the mechanical properties, exhibiting higher stiffness and tensile strength with increasing BM content, still yielding soft and highly deformable rubbers. The thermally-activated cleavage of the network was first proven by solubilization test at 110°C, whereas reprocessing as a melt required higher temperatures, in the range of 150°C. Experimental evidence provided insights on the dissociative mechanism during melt mixing. Indeed, because the retro DA reaction defines an equilibrium state, the full dissociation of the network is not possible in the molten state, but the equilibrium can be sufficiently shifted towards the dissociated form to allow melt reprocessing. The full recyclability of DA-crosslinked rubbers was demonstrated via multiple reprocessing via compression moulding and tensile test, showing stiffness and strength are slightly increased upon multiple recycling, while elongation at break is maintained.[1]

Nanocomposites based on the thermo-reversible rubber were prepared with two different nanoparticles, namely reduced graphene oxide (rGO) and silica. These were selected not only based on their wide use into rubbers, but also to exploit bonding between nanoparticles and the polymer network. Indeed, DA reaction onto graphene and related materials were previously proposed in literature, thanks to the presence of both diene and dienophile, without the need of pre-functionalize these fillers. On the other hand, silica may be easily functionalized covalently to bring diene o dienophile sites. In both cases, the nanoparticles take an active role as crosslinking points in the dynamic polymer network. rGO was added at 5 or 10wt% loading, aiming at the preparation of reinforced and thermally conductive elastomers. Results evidenced for homogeneous dispersion of rGO and remarkable increase in stiffness (up to 8 MPa) and tensile strength (up to 2 MPa) compared to the unfilled rubber, along with a thermal conductivity up to 0.47 W/mK, while retaining melt reprocessability.[1] A maleimide-functionalized silica (Sil-M) was added at 10 or 20wt% as a reinforcement filler, demonstrating both tensile strength and elongation at break were found significantly higher than for pristine Sil. While the crosslinking obtained with Sil-M was not quantitative, the combination of a moderate content of BM (2.7 wt%) and 10 wt% of Sil-M turned out that provide highly crosslinked materials up of 86%, with 1.97 MPa elastic modulus, 1.3 MPa strength and 188% strain at break.[2]

Overall, results reported in this paper demonstrate the possibility to develop a new class of recyclable composite rubbers for the substitution of conventional rubbers.

[1] F. Cantamessa, G. Damonte, O. Monticelli, R. Arrigo, A. Fina ACS Appl. Polym. Mater. 2022, 4, 4796−4807
[2] F. Cantamessa, F. Carniato , A. Fina. Under review

POSTER CONTRIBUTIONS

P1

NHC DIMERS AS DYNAMIC CROSS-LINKING POINTS FOR REPROCESSABLE FUNTIONAL MATERIALS

KARINE ABOU EZZE, AUDREY LLEVOT, DANIEL TATON

University of Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, Pessac (France)
Email: karine98@live.com, audrey.llevot@enscbp.fr, taton@enscbp.fr

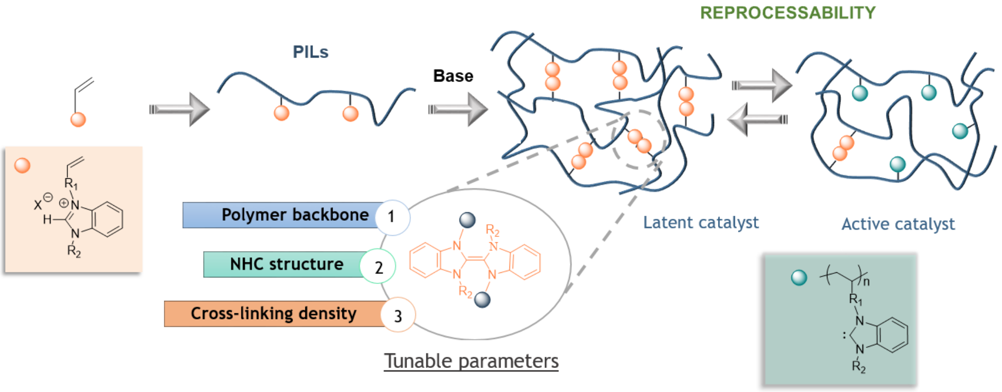
Abstract

Polymer networks find widespread applications in a variety of areas, ranging from engineering polymers, to task-specific functional materials, such as biomaterials, sensors or heterogeneous catalysts. To solve their recyclability issue, the introduction of reversible chemical cross-links, which are dynamic by stimulation, attracted increasing attention over the past decade. Under specific stimuli, these cross-links can exchange each other, enabling the material to be reprocessed. The introduction of novel chemistries as dynamic cross-linking points is of high interest to broaden the scope of functional recyclable materials.

N-Heterocyclic carbenes (NHCs) enable to achieve breakthrough in molecular synthesis, being used both as organocatalysts and powerful ligands. Their versatility has also been proven in polymer science. For instance, in 2006, Bielawski dimerized bis-NHC to form thermoreversible polymers. This thermoreversibility was provided by the carbene/dimer equilibrium, which can be modulated by temperature.[1] [2]

The aim of this project is to introduce NHC dimers as dynamic cross-linking point for the production of reprocessable functional materials.

For this purpose, the optimal conditions to prepare NHC dimers by deprotonation of benzimidazolium salts have been investigated on small molecular analogues. To study their dynamic exchange, a cross-over reaction between two dimers featuring different substituents was performed. The successful results proven by NMR spectroscopy and mass spectrometry, granted us the ability to shift to the macromolecular scale. Following the same methodology, poly(ionic liquids) (PILs) bearing benzimidazolium pendant functions were deprotonated in the presence of a base to generate poly(NHC)s. Upon this reaction, the NHCs dimerized to yield a cross-linked polymer. Their thermo-mechanical propertie of the networks, as well as their self-healing ability, provided by the dimer metathesis reaction, were investigated. Additionally, the catalytic activity of the polymer networks was studied. Indeed, upon thermal stimulus, the NHC dimers dissociated to form NHCs, which are interesting organocatalysts, for instance in the benzoin condensation reactions.[3] Thus, the synthesized polymer networks meet requirements of modern applications, such as self-healing capacity and catalytic activity.



[1] J. W. Kamplain, C. W. Bielawski, *Chem. Commun. Camb. Engl.* **2006**, 1727–1729.
[2] B. C. Norris, C. W. Bielawski, *Macromolecules* **2010**, *43*, 3591–3593.
[3] M. Fèvre, J. Pinaud, Y. Gnanou, J. Vignolle, D. Taton, *Chem. Soc. Rev.* **2013**, *42*, 2142.

P2

LIGNIN-BASED BENZOXAZINES: A SUSTAINABLE PLATFORM FOR THE DESIGN OF CATALYST-FREE VITRIMERS

A. ADJAOUD[1,2], L. PUCHOT[1], C. FEDERICO[1], R. DAS[1], P. VERGE[1]

[1]Luxembourg Institute of Science and Tehnology, Hautcharage (Luxembourg)
[2]University of Luxembourg, Esch-sur-Alzette (Luxembourg)
Email: pierre.verge@list.lu, antoine.adjaoud@list.lu

Abstract

Lignin, an earthbound polymer, epitomized the main source of phenolic compounds for the conception of bio-derived materials. Strategies toward lignin valorization flourished as lignin can be incorporated as fillers for composites, depolymerized into high-valued added chemicals, or modified to produce lignin-based materials. Polybenzoxazines (PBZs) emerged as a promising alternative to phenolic and epoxy resins thanks to their competitive features such as superior mechanical properties and thermal stability. As unmodified lignin macromonomer meets few reactivity toward benzoxazine chemistry, we have reported a promising green and eco-friendly approach to enhance the reactivity of lignin1. A technical soda lignin was esterified in solvent-free condition with phloretic acid, a naturally occurring compound extracted from the leaves of apple trees. This sustainable synthetic route grants technical lignin with ester bonds and an increased number of phenolic reactive sites. Therefore, this enriched platform of ortho-free phenolic rings was employed for the design of a series of lignin-based benzoxazines (LBZs)2. The properties of the monocomponent bio-based resins can be easily tuned depending on the amine used to close the benzoxazine ring. Bio-based amines synthons such as long-alkyl chain stearylamine confers hydrophobicity to LBZs coatings (□= 96 °), while furfurylamine, derived from furfural, furfurylamine provide LBZs resin with high-Tg (Tg= 197 °C) and high thermal stability (CR800= 45.8 %) well adapted for fire-retardancy applications. Finally, amino-alcohol derivatives grant recyclability to the cross-linked lignin-vitrimers thanks to the internally catalyzed transesterification dynamic exchanges3,4 (Figure 1).

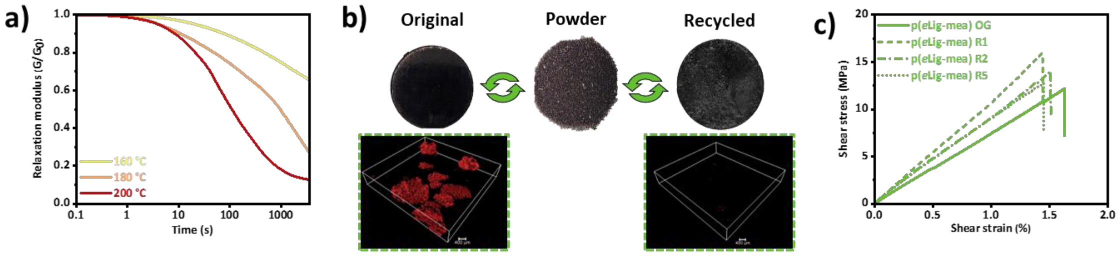


Figure 1 *a) Stress relaxation, b) Mechanical recycling, and c) Shear stress curves of recycled lignin-based vitrimer*

References

[1] Adjaoud, A.; Dieden, R.; Verge, P., *Polymers*, **13**, *4*, 2021.
[2] Adjaoud, A.; Puchot, L.; Federico, C.; Das, R.; Verge, P., *Chem. Eng. J.*, **453**, *139895*, 2023.
[3] Adjaoud, A.; Trejo-Machin, A.; Puchot, L.; Verge, P., *Polym. Chem.*, **12**, *3276-3289,* 2021.
[4] Adjaoud, A.; Puchot, L..; Verge, P., *ACS Sustain. Chem.* Eng., **10**, *594−602*, 2022.

Acknowledgements The authors would like to thank the FNR for the funding of the project LIGNOBENZ (C18/MS/12538602).

P3

IRON-COORDINATED DYNAMIC HYDROGEL NETWORKS: FROM FABRICATION TO APPLICATIONS

ROBERTO BARETTA, MARCO FRASCONI

Department of Chemical Sciences, University of Padova, via Marzolo 1, 35131 Padova (Italy)
Email: Roberto.baretta@phd.unipd.it

Abstract

Transition metal-coordination complexes are attracting increasing interest as supramolecular cross-linkers to engineer hydrogels with tunable and dynamic mechanical properties. Nonetheless, there is still a limited understanding of how metal-ligand interactions influence the structure and properties of these networks. In this context, we present novel strategies to understand the formation and explore applications of cellulose-based hydrogels by coordination with Fe^{3+} ions[1].

We have developed a method for the fabrication of redox-responsive hydrogel thin films by the coordination of electrogenerated Fe3+ ions with carboxymethyl cellulose (CMC). By applying different electrochemical deposition pulses, we can tune the crosslinker density that, in turn, modulates the thickness, the morphology, and the mechanical properties of the surface-confined metal-coordinated hydrogel films. In addition, the dynamic nature of the metal-ligand coordination network is reflected into a swelling-dependent evolution of mechanical and electrochemical properties of the hydrogel film in water and different salty solutions. When the hydrogel is swelled in salty solutions, in fact, it tends to expand its volume without breaking; on the other hand, when the hydrogel is swelled in water, it collapses and reduces its thickness because of the extended conformation of the polyelectrolyte chains in the hydrogel. The reorganization process of the network is reversible by switching the ionic strength of the solutions and therefore it can be employed for the development of smart membranes, in which the permeability toward a range of molecules is tuned by the swelling conditions of the hydrogel films.

The dynamic nature of our metal-coordinated hydrogel network has been further implemented in the development of biosensors. Indeed, the biocompatible gelation reaction between CMC and Fe^{3+} can be employed to entrap enzymes and simultaneously, by the addition of $Fe(CN)^{64-}$, to induce a template synthesis of metal-organic frameworks nanozymes in the polymer network. Depending on the crosslinking density of the network, the hydrogel composite can be employed for the colorimetric sensing of glucose[2] or drop-casted on electrode surfaces for the development of stable electrochemical (bio)sensing platforms[3].

Therefore, we have not only demonstrated the versatility of the dynamic metal-coordinated hydrogel both as thin film and bulk network for membranes and sensing applications, but we have also investigated how the reorganization process induced by metal complexes influences the polymer structure, which can lead to novel knowledge for the development of smart materials.

1 Gabrielli, V.; Baretta R.; Pilot, R.; Ferrarini, A.; Frasconi, M.; *Macromolecules* **2022**, *55*, 450-461
2 Baretta, R.; Gabrielli, V.; Frasconi, M.; *ACS Appl. Nano Mater.* **2022**, *5*, 13845-13853
3 Baretta, R.; Raucci, A.; Cinti, S.; Frasconi, M. *Sens. Actuators B Chem.* **2023**, *376*, 132985

P4

MIXED COVALENT CROSSLINKS FOR DYNAMIC COVALENT HYDROGELS WITH TUNABLE TIME-DEPENDENT MECHANICAL PROPERTIES

TAHA BEHROOXI KOHLAN, TOVE KIVIJARVI, ANNA FINNE WISTRAND

Department of Fibre and Polymer Technology, School of Engineering Sciences in Chemistry, Biotechnology and Health, KTH Royal Institute of Technology, Teknikringen, 56-58, SE 10044 Stockholm, Sweden
E-mail: tahabk@kth.se

Abstract

Mechanical properties of the extracellular matrix (ECM) have been shown to be influential in determining the cellular response during tissue regeneration. Even though hydrogels are considered to be a potential candidate to recapitulate the properties of ECM, static hydrogels fail to mimic the spatiotemporal changes and dynamic properties of native tissues. To overcome the drawbacks of static hydrogels, dynamic covalent hydrogels have been proposed by providing time-dependent mechanical properties and tunable processability. Moreover, to have a higher precision in designing hydrogels and for better control over their micro-environment, stimuli-responsive moieties can be introduced to the hydrogel. In this regard, internal stimuli such as hydrolysis and external stimuli such as light can be combined to obtain tailorable hydrogels with spatiotemporal control over the micro-environment and macro-mechanical properties. In this study, combinations of kinetically distinct reversible Schiff base linkages are evaluated to prepare dynamic hyaluronic acid (HA) based hydrogel with time-dependent mechanical properties. Rheology is used to study the mechanical properties of the hydrogels with respect to hydrolytic stability and the composition of the utilized linkers. Furthermore, the possibility of manipulating the properties of the hydrogel through external stimulus (i.e., light) is explored through the incorporation of light-responsive moieties in the hydrogel for spatiotemporal control on the introduction of the desired materials.

P5

SUSTAINABLE BIOBASED UV-CURABLE EPOXY VITRIMER FROM CASTOR OIL

MATTEO BERGOGLIO[1], DAVID REISINGER[2], SANDRA SCHLÖGL[2], THOMAS GRIESSER[3], MARCO SANGERMANO[1]

[1] Politecnico di Torino, Department of Applied Science and Technology,
Corso Duca degli Abruzzi 24, 10129 Torino (Italy) - Email: matteo.bergoglio@polito.it
[2] Polymer Competence Center Leoben GmbH, Roseggerstrasse 12, A-8700 Leoben (Austria)
[3] Department of Chemistry of Polymerc Materials, University of Leoben, Otto Glöckel-Strasse 2, Leoben 8700 (Austria)

Abstract

Vitrimers brought new properties in thermosets polymers allowing reshaping, self-healing, re-processing and network rearrangement without changing structural integrity. In this study, epoxidized castor oil (ECO) was successfully used as the only precursor of a bio-based sol-vent-free vitrimer. To increase material sustainability, the synthesis was made with a UV-curing process, without using solvents or high temperatures, and decreasing the synthesis time. Real time Fourier transformed infrared spectroscopy and photo-DSC were used to monitor the cationic photopolymerization process settling the optimal amount of photo-initiator. Finally, mechanical properties, thermal resistance, glass transition temperature and vitrimeric properties have been investigated by variating the amount of transesterification catalyst after having set-tled the optimal amount of photo-initiator used for curing reaction. Mechanical properties were determined by both DMTA and tensile tests. Glass transition temperature (T_g) was evaluated by DMTA. Thermogravimetric analysis and vitrimeric properties by stress relaxation experiments evaluated thermal resistance. Overall, the ECO-based vitrimer showed optimum thermal resistance (up to 200°C) and good mechanical properties (elastic modulus of about 10 MPa) and can therefore be considered a starting point for obtaining more sustainable vitrimers.

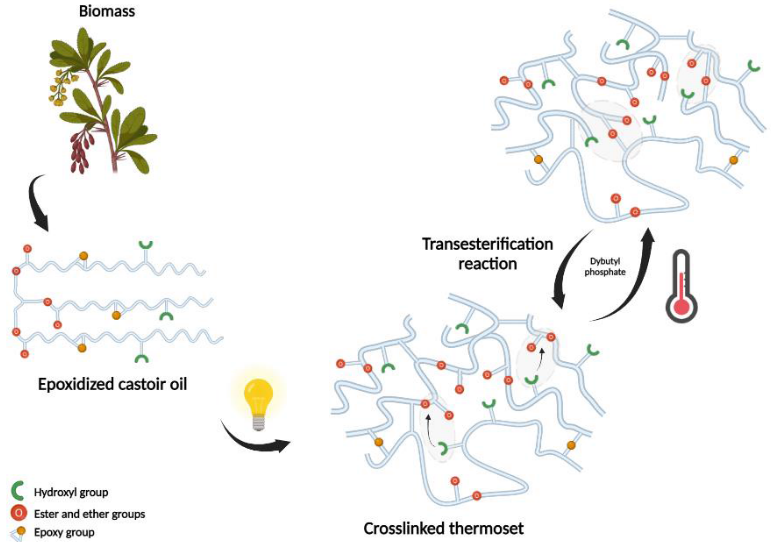


Figure 1. *Schematic representation of synthesis and transesterification reaction of bio-based epoxy derived vitrimer.*

P6

AMINO-YNE CLICK CHEMISTRY FOR THE PREPARATION OF STIMULI-RESPONSIVE HYDROGELS

SARA BESCÓS, JESÚS DEL BARRIO, MILAGROS PIÑOL, LUIS ORIOL

[1] *Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza,*
Zaragoza 50009, Spain; Email: sbescos@unizar.es

Hydrogels are three-dimensional polymeric networks capable of holding large amounts of water, which are of high interest for biomedical applications such as drug delivery. In order to be synthetized under physiological conditions, efficient, fast and selective reactions are desirable. Among the different possibilities, the outstanding *amino-yne* click reaction, which was first report in materials science in 2017 and for hydrogels in 2018,[1,2] can take place spontaneously, at room temperature and in aqueous media by simply mixing amines (*amino-*) and propiolates (*-yne*). Interestingly, the formed β-aminoacrylate bond has turn out to be cleavable in acidic conditions or in contact with singlet oxygen, and its dynamic transamination has been studied for both small molecules and vitrimers.[3]

The objective of this work is to study the application of *amino-yne* chemistry for the preparation of drug delivery platforms based on stimuli-sensitive hydrogels. To this end, a model reaction was first optimized between different amines, among which there is an amino-based drug (benzocaine), and a triethylene-glycol chain functionalized with a propiolate group, along with the study of drug release under acidic conditions (Fig. 1a). Then, PEG tetra-alkynoate was synthesized so di and multifunctional amines can be used for hydrogel formation in PBS (pH 7.4) (Fig. 1b). The viscoelastic properties are currently under study, as well as the influence of different stimuli on the material's final performance and degradation.

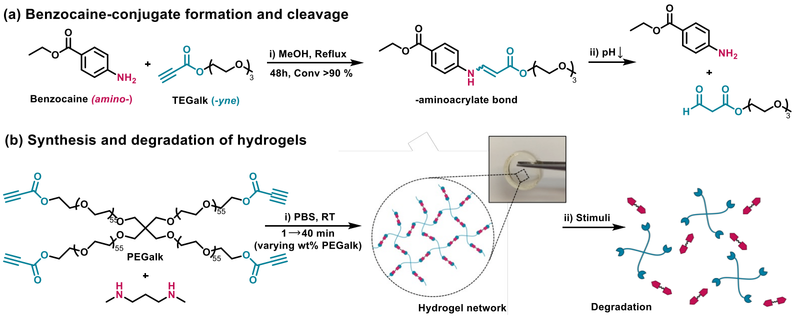


Figure 1. Scheme of a) drug-conjugate formation and cleavage and b) synthesis and degradation of hydrogels.

Acknowledgments

Financial support from Ministerio de Ciencia e Innovación (PID2021-126132NB-I00) and Gobierno de Aragón (project LMP93_21) is gratefully acknowledged. S. Bescós acknowledges Gobierno de Aragón for her PhD grant.

References

[1] He, B.; Su, H. "Spontaneous Amino-Yne Click Polymerization: A Powerful Tool toward Regio- and Stereospecific Poly(β-Aminoacrylate)s" *J. Am. Chem. Soc.* **2017**, *139*, 5437–5443.
[2] Fenton, O. S.; Andresen, J. L. "β-Aminoacrylate Synthetic Hydrogels: Easily Accessible and Operationally Simple Biomaterials Networks" *Angewandte Chemie International Edition* **2018**, *57*, 16026–16029.
[3] Guo, X.; Gao, F. "Dynamic Enamine-One Bond Based Vitrimer via Amino-Yne Click Reaction" *ACS Macro Lett.* **2021**, *10*, 1186–1190.

P7

MECHANICAL RECYCLING OF VITRIMERS: STRUCTURAL REARRANGEMENTS AT THE WELDING INTERFACE AS A FUNCTION OF REPROCESSING CONDITIONS

VINCENT BOULIC, MARIAPAOLA STAROPOLI, STEPHAN WESTERMANN,
FRÉDÉRIC ADDIEGO

Luxembourg Institute of Science and Technology - Email: Vincent.boulic@list.lu

Abstract

Mechanical recycling, also known as physical or thermal recycling, is a method using conventional manufacturing processes. In the case of vitrimers, this recycling is mainly based on hot pressing but also injection molding or extrusion for special cases.[1] Vitrimers are first cut into fine particles that are subsequently heated above their Tv (topology freezing temperature) and Tg (glass transition temperature) for enabling malleabilty and reshaping [2]. In particular, the particles are pressed, injected or extruded to reform the solid shape of interest.

As reported by Zhang and al., the efficiency of hot press recycling relies on temperature, heating time, pressure and particles size [3]. In fact, these parameters strongly affect the contact surface between the particles [4], determining the ability of the dynamic bonds to create links between each other and the consequent re-processing efficiency. [2,5,6]

To our best knowledge, the structural rearrangments occuring at the welding interface have never been investigated by a comprehensive study, which is the purpose of the present research. The used methodology relies on studying simplified samples shape, with a unique welding interface reflecting mechanical recycling. Structural rearrangements are studied by a multiscale approach combining micro-computed x-ray tomography (µCT), scanning electron microscopy (SEM), atomic force microscope (AFM) with nanomechanical measurements, and conventional mechanical testing. The influence of reprocessing conditions (number of reprocessing steps, temperature and time) is also studied on these structural rearrangements.

References

[1] H. Zhang, J. Cui, G. Hu, and B. Zhang, “Recycling strategies for vitrimers,” *Int. J. Smart Nano Mater.*, vol. 13, no. 3, pp. 367–390, 2022.

[2] D. Montarnal, M. Capelot, F. Tournilhac, and L. Leibler, “Silica-like malleable materials from permanent organic networks,” *Science (80-.).*, vol. 334, no. 6058, pp. 965–968, 2011.

[3] B. Zhang *et al.*, “Influences of processing conditions on mechanical properties of recycled epoxy-anhydride vitrimers,” *J. Appl. Polym. Sci.*, vol. 137, no. 41, pp. 1–12, 2020.

[4] L. Yu, X. Sun, Y. Jin, W. Zhang, and R. Long, “Mechanics of vitrimer particle compression and fusion under heat press,” *Int. J. Mech. Sci.*, vol. 201, no. March, p. 106466, 2021.

[5] Z. Zhou *et al.*, “Unraveling a path for multi-cycle recycling of tailored fiber-reinforced vitrimer composites,” *Cell Reports Phys. Sci.*, vol. 3, no. 9, p. 101036, 2022.

[6] C. Li, B. Ju, and S. Zhang, “Construction of a new green vitrimer material: introducing dynamic covalent bond into carboxymethyl cellulose,” *Cellulose*, vol. 28, no. 5, pp. 2879–2888, 2021.

P8

AN ANALYSIS OF THE PROCESSING PROPERTIES OF A BENZOXAZINE VITRIMER FOR THE USE AS A MATRIX FOR COMPOSITES

K. BOURDON[1,2], T. HUBER[1], D. F. SCHMIDT[1]
[1] *Department of Materials Research and Technology (MRT), Luxembourg Institute of Science and Technology (LIST), Hautcharage, Luxembourg,*
[2] *University of Luxembourg, Esch-sur-Alzette,* killian.bourdon@list.lu

Vitrimers are cross-linked networks with chemical and mechanical properties comparable to thermosets but which can be recycled, reshaped, repaired and welded like thermoplastics thanks to the presence of exchangeable dynamic covalent bonds [1].

Vitrimers are not only useful on their own but also as matrix phase for composites [2][3]. This work focuses on the processing properties of the benzoxazine vitrimer poly(PEG_{400}-DPA-mea_{75}/fa_{25}) with dynamic transesterification bonds developed by Verge et al. [4]. Being biobased and showing an interesting property profile, this vitrimer is of particular interest for the use in sustainable composites. We aim to determine the viscosity profile of the vitrimer precursor in order to define the ideal processing temperature. The benzoxazine precursor as received contains between 2 % and 5 % of moisture and due to its high viscosity typically traps a large amount of air. Comparing the viscosity of the as-received benzoxazine precursor and a sample degassed at 55 °C overnight will help to understand the plasticizing effect of water.

Both viscosity and gelation time of the degassed and as-received benzoxazine precursors are measured at different temperatures (50 °C, 80 °C, 100 °C & 120 °C and 100 °C, 120 °C and 140 °C, respectively). For both the as-received and degassed precursors, the viscosity and the gelation time decrease with increasing temperature. The viscosity of the degassed material is higher, and its gelation time is shorter at all measured temperatures.

The decrease of viscosity of the degassed material allows us to process uncured benzoxazine films of different thicknesses (0.45-2 mm), which is not possible with the as-received benzoxazine which flows at room temperature. It also allows us to make prepregs without using any solvent.

We will present the porosity level observed by μ-CT for composites produced from these precursors via 3 different processes, using twill 2/2 (200 tex) weaves of carbon and flax fabric as well as unidirectional flax fabric (200 tex): vacuum assisted compression moulding using degassed benzoxazine, compression moulding using prepregs and vacuum assisted compression moulding using a stack of fabrics and uncured benzoxazine films.

References

[1] D. Montarnal, M. Capelot, F. Tournilhac, and L. Leibler, "Silica-Like Malleable Materials from Permanent Organic Networks," *Science (80-.).*, vol. 334, no. 6058, pp. 965–968, Nov. 2011

[2] M. Ahmadi, A. Hanifpour, S. Ghiassinejad, and E. van Ruymbeke, "Polyolefins Vitrimers: Design Principles and Applications," *Chem. Mater.*, vol. 34, no. 23, pp. 10249–10271, Dec. 2022,

[3] Y. Xu, S. Dai, L. Bi, J. Jiang, H. Zhang, and Y. Chen, "Catalyst-free self-healing bio-based vitrimer for a recyclable, reprocessable, and self-adhered carbon fiber reinforced composite," *Chem. Eng. J.*, vol. 429, 2022,

[4] A. Adjaoud, A. Trejo-Machin, L. Puchot, and P. Verge, "Polybenzoxazines: a sustainable platform for the design of fast responsive and catalyst-free vitrimers based on trans-esterification exchanges," *Polym. Chem.*, vol. 12, no. 22, pp. 3276–3289, 2021

P9

NANOSTRUCTURED AND TUNABLE PRESSURE SENSITIVE ADHESIVES FROM MIXTURES OF VITRIMER LATEXES

JULIE BRATASANU[1], ELODIE BOURGEAT-LAMI[1], ERIC DROCKENMULLER[2], DAMIEN MONTARNAL[1]

[1] *Catalyse, Polymérisation, Procédeés et Matériaux (CP2M), CNRS, Université Lyon 1, ESCPE, Lyon (France)*
[2] *Ingénierie des Matériaux Polyméres (IMP), CNRS; Université Lyon 1, Polytech, Lyon (France)*
e-mail: julie.bratasanu@univ-lyon1.fr

Abstract

Pressure sensitive adhesives (PSAs) are non-reactive networks of soft, viscoelastic polymers which adhesion mechanism is mainly based on efficient energy dissipation during the debonding step. These adhesives are widely used in our everyday life, ranging from repositionable (e.g. Post it ©) to high-strength binders (e.g. the automotive field) and are arousing growing interest among industrial companies due to their ease of use, and their environmental, health and safety benefits.

We aim at developing new nanostructured waterborne PSAs and proposing an advanced understanding of adhesion through the enhanced control on the viscoelastic properties of different nanophases.

Our strategy builds thus on the synthesis by miniemulsion polymerization of a library of latexes incorporating dynamic siloxane crosslinks[1]. The use of different acrylic monomers allows to obtain latexes with a wide range of viscoelastic properties (*T*g, entanglement molar mass), that are subsequently mixed together and sintered into a single polymer network through dynamic covalent bonds.

We will present how the formulation of these PSAs affects their nanostructuration, their rheological behavior and their adhesive performances.

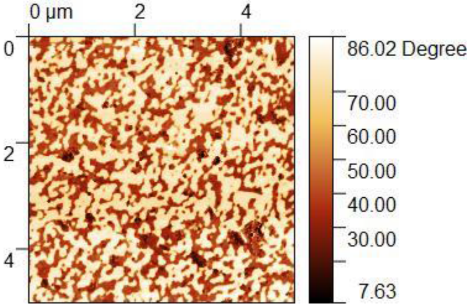


Figure 1: AFM imaging (Tapping mode, phase contrast) of a mixture of latexes with different Tg

References

[1] D. Khedaioui, C. Tribout, J. Bratasanu, F. D'Agosto, C. Boisson, D. Montarnal, *Angewandte Chemie* **2023**
[2] E. Degrandi-Contraires, R. Udagama, E. Bourgeat-Lami, T. McKenna, K. Ouzineb, C. Creton, *Macromolecules* **2011**, *44*, 2643–2652.
[3] J. Chopin, R. Villey, D. Yarusso, E. Barthel, C. Creton, M. Ciccotti, *Macromolecules* **2018**, *51*, 8605–8610.
[4] . A. Lopez, E. Degrandi-Contraires, E. Canetta, C. Creton, J. L. Keddie, J. M. Asua, *Langmuir* **2011**, 27, 3878–3888.
[5] A. Jourdain, R. Asbai, O. Anaya, M. M. Chehimi, E. Drockenmuller, D. Montarnal, *Macromolecules* **2020**, *53*, 1884–1900.

P10

TWO-PHOTON MICROSCOPY AS VISUAL TOOL FOR POLYMER COMPATIBILIZATION MONITORING: PE-EVOH case

SILVIA D'AURIA[1], ILARIA FERRABOSCHI[1], ALESSANDRO PEDRINI[1], JEROME VACHON[2], CRISTINA SISSA[1], ROBERTA PINALLI[1], ENRICO DALCANALE[1]

[1]Department of Chemistry, Life Sciences and Environmental Sustainability and INSTM UdR Parma, University of Parma, Parco Area delle Scienze 17/A, 43124 Parma (Italy)
– Email: silvia.dauria@unipr.it
[2] SABIC Europe B.V., Urmonderbaan 22, 6160 AH Geleen (The Netherland)

ODIN, a multiple hydrogen bonding motif, is a promising tool for polymer functionalization with the goal of obtaining adaptable networks. X-ray crystallography revealed that ODIN dimer is made up of two conventional and two bifurcated hydrogen bonds (Figure 1, top left). Fluorescence measurements resulted in a K_a of $4 \cdot 10^4$ M^{-1}.[1] Several prior investigations show that ODIN can be used to construct a supramolecular polymer via the dimerization cross-linking.[1] In this study, we investigate the capability of ODIN to act as compatibilizer for the creation of homogenous blends between two immiscible polymers, PE-HEMA and EVOH. We introduce two-photon microscopy (2PM) as a novel technique for investigating the compatibilization at the sub-micrometer level, both on the surface and in the bulk, detecting the presence of ODIN used also as fluorescent probe. 2PM is a nonlinear fluorescence imaging technique often used for analyzing thick biological tissues. [2] In this case, we use 2PM to show polymer mixing using 3D images of the resulting films. After functionalizing PE-HEMA with 1.4% molar ODIN its ability to form multiple hydrogen bonding to interact with EVOH, was observed. Different blends were made, and the resulting films were evaluated using 2PM (Figure 1, top). It was shown that ODIN is uniformly distributed throughout the films, both on the surface and in the bulk. According to 2PM analysis of the thermally reprocessed specimen, repeated processing enables the reformation of ODIN dimers as the most stable H-bonding array in the solid state, partially reversing the compatibilization (Figure 1, bottom).

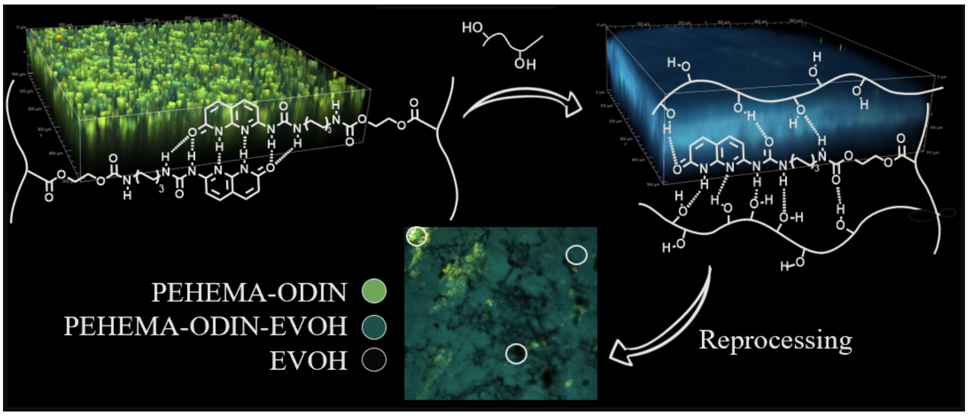


Figure 1. Schematic figure of the work presented, formation of the blend between PE-HEMA-ODIN and EVOH, and relative fluorescent 3D-image are presented (on the top); image of the reprocessed sample (below).

---

[1] J. Tellers, S. Canossa, R. Pinalli, M. Soliman, J. Vachon, E. Dalcanale, *Macromolecules* **2018**, *51*, 7680-7691.

[2] F.Helmchen, W. Denk, *Nat Methods* **2005**, *2*, 932–940.

P11

POLYESTER NETWORKS BASED ON TULIPALINE A

Islam ISMAEL, Martin DANKO

Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia;
email: martin.danko@savba.sk

Abstract

Motivated by advantages of polyester and the thiol-ene Michael reaction, in the current work, linear and star-shaped copolyesters with a pendant functional double bonds obtained via the coordination-insertion or the cationic ring-opening copolymerization of ε-caprolactone (CL) with α-methylene-γ-butyrolactone (MBL) [P(CL-co-MBL)] were synthetized [1]. Followed crosslinking using 1,5-pentanedithiol and pentaerythritol tetrakis *via* light initiated thiol-ene Michael reaction was carried out. The effect of the content of MBL, molar mass of copolyester and ratio of thiol/MBL in the network were studied. The reaction was followed by decreasing of FTIR band at 1650 cm-1 related to bouble bond. Formed organo-gels exhibited gel content in range 66-99 %. (Figure 1). The thermal and mechanical properties of the obtained materials were determined. In addition, the self-healing properties and malleability of these materials were examined and compared based on the crosslinking density of the used polyester network, temperature and the time of self-healing.

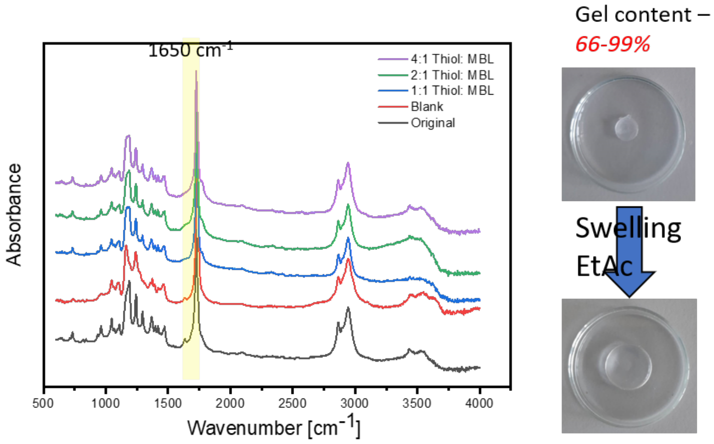


Figure 1: *FTIR spectra of linear copolyester P(MBL-co-CL), mixture with thiol before the reaction and gels obtained with various SH/MBL ratio. Picture of the gel with its swelling ability.*

Acknowledgements: *The authors thank the grant Agency VEGA for financial support through grant VEGA 2/0168/21 and project APVV-19-0338. This work was also performed during the implementation of the project Building-up Centre for advanced materials application of the Slovak Academy of Sciences, ITMS project code 313021T081 supported by the Integrated Infrastructure Operational Programme funded by the ERDF.*

Key words: Polyester, Tulipalin A, ε-Caprolactone, Thiol-ene reaction, Gels, Covalent adaptable networks (CANs)

References

[1] 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, 3582-3596.

[2] Hong M.; Chen E. Coordination ring-opening copolymerization of naturally renewable α-methylene γ-butyrolactone into unsaturated polyesters. *Macromolecules* 2014, 47, 3614−3624.

P12

UNVEILING THE CAPABILITIES OF DISULFIDE VITRIMERS: RAPID RELAXATION AND CONTROLLED CREEP

ADRIÀ ROIG[1], VALERIA D'AGOSTINO[2], ÀNGELS SERRA[1], SILVIA DE LA FLOR[2]

[1] *Univ. Rovira i Virgili, Dpt. Analytical & Organic Chemistry, C/ Marcel·lí Domingo, 43007, Tarragona, Spain*
[2] *Univ. Rovira i Virgili, Dept. of Mechanical Engineering. Av. Països Catalans 26, 43007 Tarragona, Spain*
E-mail: silvia.delaflor@urv.cat

Abstract

Vitrimers, a subclass of covalently adaptable networks (CANs), is a new promising class of polymeric materials that are gaining attention thanks to their thermosetting characteristics but with the capability of being reshaped, reprocessed, and recycled. These distinguishing properties, so unusual in classical thermosets because of covalent cross-links, make them more environmentally friendly than conventional thermosets [1,2]. Many uses of vitrimers, like traditional thermosets, require high levels of creep resistance to ensure their long-term performance and reliability in various applications during the service life while maintaining higher relaxation rates at low temperatures. That is the reason for the increasing efforts in the research on designing CANs systems with these requirements [3,4]. However, most of the proposed solutions in the literature have adverse effects on chemical activity and, thus, on reprocessability.

This work presents the vitrimeric behavior of a series of disulfide materials cured through an epoxy-amine reaction with different proportions of two commercially available epoxy resins, one aromatic and the other aliphatic, and cystamine as a crosslinker. The thermomechanical and viscoelastic properties can be tailored by varying the proportions of the epoxy monomers. The completion of the curing reaction was verified using FTIR spectrometry, and the thermal and mechanical properties of the final materials were investigated using DMTA analysis. All the materials presented glass transition temperatures above 60 °C and high rigidity in the glassy state depending on the proportion of the aromatic resin. The viscoelastic properties and the vitrimeric behavior were studied by stress relaxation tests revealing that all the materials could relax the stress in less than 1 minute at 160 °C. The topology freezing temperature of all the materials was calculated through creep experiments showing a clear trend depending on the proportion of the epoxy resins. Creep tests at service temperatures (0ºC and 25ºC) showed that creep could be reduced depending on the proportion of the aromatic epoxy resin, even maintaining extremely fast relaxation rates. The strain behavior with temperature was also characterized by dilatometry tests. Finally, to test the mechanical behavior and their functional properties, the self-heling and self-welding ability of the sample with the highest content of aromatic resin was tested with excellent results, highlighting the great potential of these materials.

References

[1] D. Montarnal et al., "Silica-like malleable materials from permanent organic networks" *Science*, **2011**, 334, 965.
[2] W. Denissen et al." Permanent organic networks with glass-like fluidity". *Chem. Sci.*, **2016**, 7, 30–38.
[3] F. Van Lijsebetten et al "Suppressing Creep and Promoting Fast Reprocessing of Vitrimers with Reversibly Trapped Amines" *Angew. Chem. Int. Ed.* **2022**, 61, e202113872.
[4] A. Hubbard, et al." Creep Mechanics of Epoxy Vitrimer Materials", *ACS Appl. Polym. Mater.* **2022**, 4254.

P13

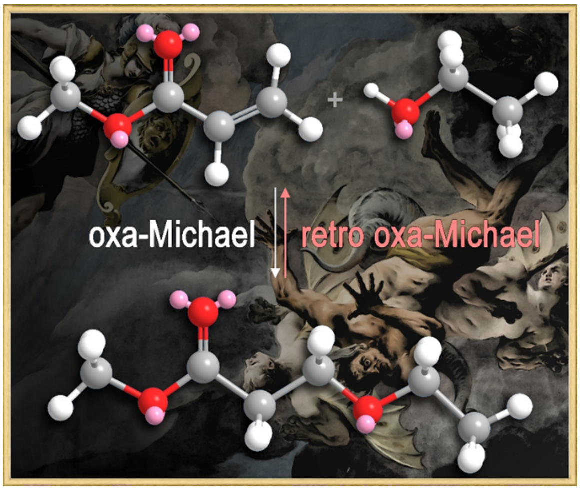
EXPLOITING RETRO OXA-MICHAEL CHEMISTRY IN POLYMERS

KARIN RATZENBÖCK,[A,B] JOHANNA M. UHER,[A,B] SUSANNE M. FISCHER,[A,B] DAVID EDINGER,[A,B]
VIKTOR SCHALLERT,[A,B] EMA ŽAGAR,[C] DAVID PAHOVNIK[C] AND CHRISTIAN SLUGOVC*[A,B]

[a] *Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria. E-mail: david.edinger@tugraz.at*
[b] *Christian Doppler Laboratory for Organocatalysis in Polymerization, Stremayrgasse 9, 8010 Graz, Austria*
[c] *National Institute of Chemistry, Department of Polymer Chemistry and Technology, Hajdrihova 19, 1000 Ljubljana, Slovenia*

Abstract

One way to obtain recyclable polymeric materials is to include reversible bonds in polymers. Herein, we study the reversibility of the oxa-Michael reaction and explore its scope and limitations in simple model systems and further in linear polymers as well as in polymer networks. The results show that the retro oxa-Michael reaction of sulfone, acrylate or acrylonitrile based adducts is considerably fast at elevated temperatures (>100 °C) if Brønsted bases (e.g. KOH) are used as catalysts. Under these conditions, alcohols can easily be exchanged in oxa-Michael adducts within minutes. Furthermore, poly(ether)s derived from oxa-Michael reactions can be depolymerized into small fragments in the presence of alcohols and show self-healing characteristics in networks.[1]



References

[1] K. Ratzenböck, J. M. Uher, S. M. Fischer, D. Edinger, V. Schallert, E. Žagar, D. Pahovnik, C. Slugovc, "Exploiting Retro Oxa-Michael Chemistry in Polymers." *Polym. Chem.* **2023**, Advance Article

P14

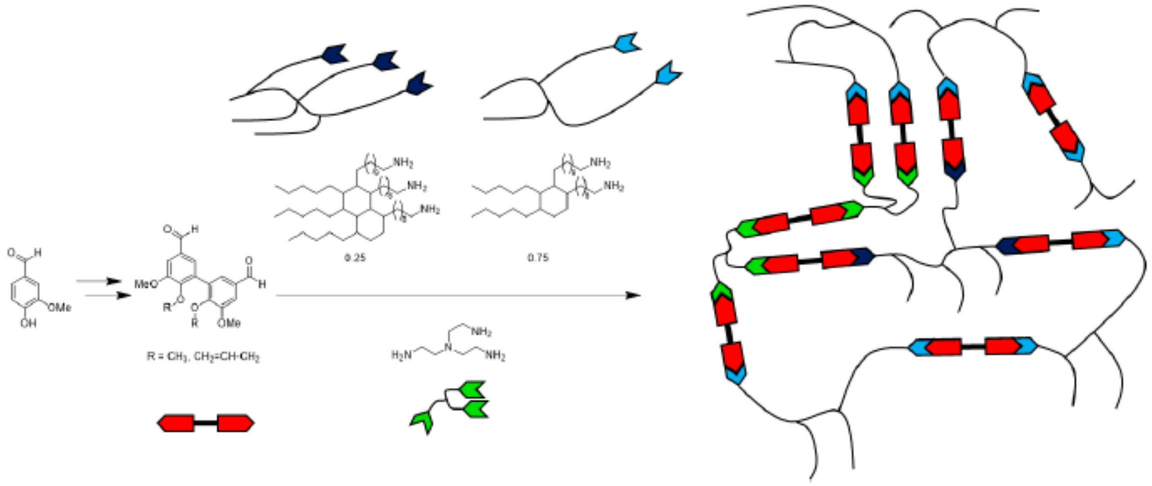
FAST STRESS-RELAXING RENEWABLE DIVANILLIN-BASED POLYIMINES COVALENT ADAPTABLE NETWORKS (CANS)

NOÉ FANJUL MOSTEIRÍN[1], KARIN ODELIUS[1]

[1] *Wallenberg Wood Science Center, WWSC, Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-100 44, Stockholm, (Sweden) – Email: noefm@kth.se.*

Abstract

Thermosets are permanently crosslinked networks that exhibit both high mechanical strength and chemical resistance as compared to our everyday thermoplastics. Despite their good property performance, due to their permanent crosslinked structure, they cannot be reshaped or remolded after cure and use, which prevents them from being recycled.[1] To tackle the aforementioned issues covalent adaptable networks (CANs), represent an opportunity to fill the gap between thermosets and thermoplastics.[2,3] Vanillin, represents an interesting aromatic renewable building block that bears an aldehyde moiety, making it a suitable candidate for the preparation of polyimine CANs by condensation with polyamines. In addition, the presence of an aromatic moiety could confer stiffness and thermo-chemical stability. In the present work, reversible renewable crosslinked polyimines were synthesized by reaction between functionalized divanillin-based aldehydes bearing methyl and allyl substituents on the phenol moiety along with a long chain fatty acid-based bis/tris amine and a short chain tris-amine. Variation of the ratios of long and short amines lead to the formation of a battery of renewable novel vitrimers with both different thermal and mechanical properties. Furthermore, the so obtained CANs were successfully reprocessed up to three times without losing mechanical performance and the starting bis-aldehyde monomers were efficiently retained by chemically recycling under acidic conditions as a consequence of the presence of reversible imine functionality.



Scheme 1. Synthesis of crosslinked polyimine divanillin-based CANs.

Acknowledgements

The authors would like to acknowledge funding from the Knut and Alice Wallenberg foundation through Wallenberg Wood Science Center.

[1] A. Rahimi, J. M. García, *Nat. Rev. Chem.* 2017, **1**, 46.
[2] M. A. Lucherelli, A. Duval and L. Avérous, *Prog. Polym. Sci.*, 2022, **127**, 101515.
[3] T. Vidil and A. Llevot, *Macromol. Chem. Phys.*, 2022, **223**, 2100494.

P15

ADDITIVE MANUFACTURING OF UNCONVENTIONAL POLYMER NETWORKS BASED ON REVERSIBLE DYNAMIC COVALENT BONDS

FRANCESCA FURIA[1], ALEIX COSTA CORNELLÀ[1], GUY VAN ASSHE[1], JOOST BRANCART[1]

[1]Physical Chemistry and Polymer Science, Department of Materials and Chemistry, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium. – Email: Francesca.furia@vub.be

Abstract

Additive manufacturing (AM) techniques allow rapid prototyping of complex 3D shapes and custom-made products. They quickly attracted a lot of interest from many researches and the range of materials that can be used is rapidly expanding. Recently, polymers networks based on dynamic covalent bonds have been introduced into this world, based either on associative or dissociative chemistries.

In this study, dissociative and associative dynamic bonds were combined in the same network. The associative network provides the thermal and mechanical support needed during the AM processing at high temperatures, while the dissociative network (partially) decrosslinks to achieve the desired flow behavior. Combining DA bonds and exchangeable esters in the same network, it is possible to print objects with sharps edges and smooth finish using material extrusion AM. Different fractions of the two dynamic bonds have been tested to evaluate the effect on the printability and to find the optimum composition. The viscoelastic behavior of these double dynamic networks was studied using rheometry to elucidate the effect of the composition on the gelation and shear thinning behavior. The healing property is preserved after printing. Healing is possible at temperatures far below the Tgel and the printing temperature.

Dissociative covalent polymer networks, e.g. based on the thermoreversible Diels-Alder (DA) reaction, typically undergo a reversible gel transition at a certain temperature (Tgel). When heated above Tgel, the dynamic equilibrium shifts towards the dissociation of the DA adducts to the extent that the polymer network is broken down and the polymer melt can flow through a nozzle as a viscous melt. Once in contact with the printing bed at a temperature below Tgel, the dynamic equilibrium shifts back to the formation of the adducts, reforming the polymer network structure. This reactive printing process is slower compared to the melting and recrystallization of thermoplastics in extrusion-based AM. The main drawback for additive manufacturing of dissociative networks is the sharp and drastic change from a rubbery network to a low viscosity liquid at temperatures above Tgel, rendering it difficult to be extruded.

Associative covalent networks rely on exchange reactions where the crosslink density of the network stays constant with temperature, but the speed at which these dynamic covalent bonds exchange increases. Recent studies showed that in presence of the transesterification reaction it proved possible to extrude at high temperatures and pressures, though with a rough surface finish. There is no net change in the crosslink density, but the exchange speed is fast enough for the material to flow and they also present thermal stability.

P16

SYNTHESIS AND CHARACTERIZATION OF BORINIC VITRIMERS

I. GÖDE,[1] M. BONNARD,[2] L. CHABAUD,[2] A. GUÉRINOT,[1*] M. PUCHEAULT,[2] R. NICOLAŸ.[1*]

[1] *Molecular, Macromolecular Chemistry and Materials, ESPCI Paris, CNRS, PSL University, Paris, France*
[2] *Institut des Sciences Moléculaires, Université de Bordeaux, Bordeaux, France*
* *amandine.guerinot@espci.psl.eu and renaud.nicolay@espci.psl.eu*

Vitrimers are cross-linked networks containing dynamic covalent bonds [1]. Within these networks, exchange reactions take place through an associative mechanism [2], which provides unique characteristics to these materials [1,2].

Borinic acid chemistry could offer new opportunities to design vitrimers with novel properties. Borinic acid derivatives [3], combine the strength of boron-oxygen dynamic bonds, already illustrated with dioxaborolane vitrimers [4], with specific attributes, such as their charged or neutral character, and the labile N-B coordination bond in the case of borinato derivatives. To obtain borinic vitrimers, the possibility for borinic acid derivatives to undergo exchange reactions was first investigated., It was found that the exchange kinetics are globally fast, with $t_{1/2}$ <20 min in the case of borinato exchange for example.

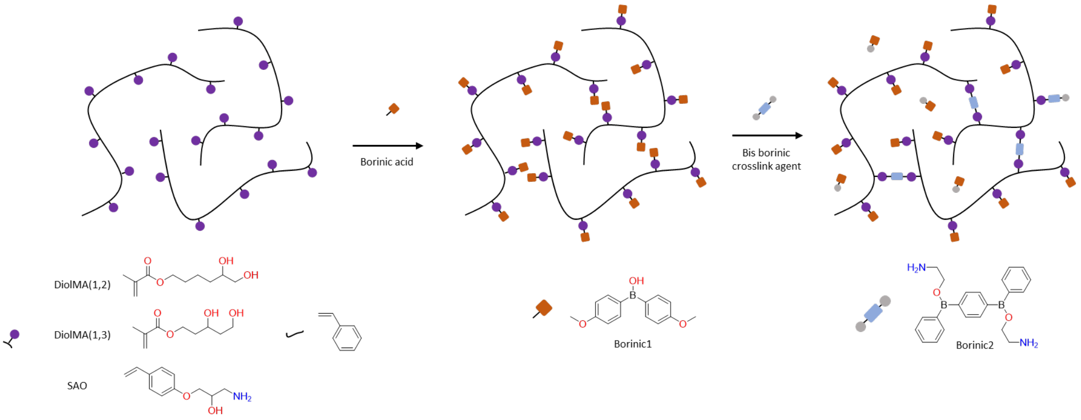


Figure 1. General synthetic scheme for the synthesis of borinic vitrimers.

Functional polymers bearing diol or aminoalcohol functions were subsequently synthesized by free radical copolymerizations of styrene with different functional monomers, namely 5,6-dihydroxyhexyl methacrylate (DiolMA(1.2)), 3,5-dihydroxypentyl methacrylate (DiolMA(1.3)), and amino-3-(*para*-vinylphenoxy)propan-2-ol (SAO) (Figure 1). The resulting copolymers were characterized by NMR, DSC, TGA, GPC, indicating that thermally stable (330°C) copolymers with glass transition temperatures around 90 °C had been prepared. In order to obtain vitrimers (Figure 1), diol or amino alcohol functions were transformed into borate or borinato functions, respectively, by condensation with dimethoxyphenylborinic acid (Borinic1). The resulting polymers were finally crosslinked with a bis-borinic compound (Borinic2). The characterization of these new polymers and networks is ongoing.

Keywords: Vitrimers, dynamic covalent chemistry, borinic esters, borinato derivatives

References

[1] N. van Zee, R. Nicolaÿ. Vitrimers. *Prog. Polym. Sci.*, **2020**, 104, pp.101233.
[2] J. M. Winne , L. Leibler and F. E. Du Prez , *Polym. Chem.*, **2019**, 10, 6091-6108
[3] L. Marciasini, B. Cacciuttolo, M. Vaultier, M. Pucheault. *Organic Letters* **2015** *17* (14), 3532-3535
[4] M. Röttger, T. Domenech, R. van der Weegen, A. Breuillac, R. Nicolaÿ, L. Leibler. *Science* **2017**, 356 (6333), 62-65

P17

NEW BIOMASS-DERIVED ANTIMICROBIAL POLYMER SURFACES

ELISABETTA GOVER[1], ALFREDO RONDINELLA[1], MARILISA ALONGI[2], MARILENA MARINO[2], LARA MANZOCCO[2], LORENZO FEDRIZZI[1], DANIELE GOI[1], PAOLO STRAZZOLINI[2], CLARA COMUZZI[2]

[1]*Department of Polytechnic of Engineering and Architecture (DPIA), University of Udine, Via delle Scienze 206, 33100 Udine (Italy) – Email: gover.elisabetta@spes.uniud.it*

[2]*Department of Agricultural, Food, Environmental and Animal Sciences (Di4A), University of Udine, Via delle Scienze 206, 33100 Udine (Italy)*

Abstract

More than 300 million tons of plastic materials are produced worldwide annually, generating a significant environmental impact and thus making it mandatory to find sustainable alternatives. Accordingly, the design of new cost-effective materials, environmentally friendly and arising from renewable resources is needed.[1] In addition, the UN 2030 Agenda for Sustainable Development has recognized the growing antibiotic resistance as one of the major threats to global health, food safety, and development.[2] In this context, the use of antimicrobial materials has been strongly encouraged as an effective strategy to limit and face the risks coming from the pathogens spread. Considering all these targets, we here present a new material synthesized using vanillin as a building block to generate the polymeric matrix, while properly activating it by adding a photoactive agent. Vanillin represents a convenient starting material derived from the depolymerization of lignin, a largely available discard product of the wood industry, previously employed to synthesize several biopolymers.[3] Usually, the described products were cross-linked by covalent bonds, whereas our purpose was to assemble the network through supramolecular interactions, given the need to regenerate the activity of the material periodically. Herein we report the synthesis and physical, chemical, and biological characterization of a new bio-based vanillin-derivate material, where the selected molecule acting as the cross-linker (meso-Tetra (4-methylphenyl)porphine, 4MeP) also possesses a photoactive feature, generating Reactive Oxygen Species (ROS) upon light irradiation. Thus, three strategies were tested to obtain the initial powder mixture suitable to form the polymeric films after heating. The so obtained materials proved to be variously active, demonstrating that the synthetic pathway significantly affected the antimicrobial activity of the surfaces. Careful physicochemical characterization of the polymers ruled out the presence of cross-linking covalent bonds, demonstrating the essential supramolecular nature of the interactions involved. The observed antimicrobial effect has been ascribed to the efficiency of ROS formation, making the material suitable for decontamination processes at low environmental impact.

P18

DYNAMIC COVALENT SYSTEMS BASED ON BENZODIAZABORINES

E. GUERREIRO, M.P. ROMERO, L. ORIOL, J. DEL BARRIO

Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Dpto.
de Química Orgánica 50009, Zaragoza Spain
e-mail: guerreiro@unizar.es

Abstract

Imines, oximes and hydrazones have been widely investigated in the context of dynamic covalent networks and reconfigurable materials. In this work, we have focused on the reaction between acyl hydrazides and 2-formylphenylboronic acid (FPBA) derivatives leading to the family of boron-containing heterocycles benzodiazaborines (DAB).1 These compounds undergo dynamic dimerization in solution (see Figure 1).

Our NMR experiments on model small molecule compounds show that the stability of the dimers is determined by the type of substituents at heterocycle ring. Additionally, the monomer-dimer equilibrium shifts in the presence of water or by changing the temperature.

The reversible DAB dimerization has been used for the crosslinking of multiarm polymers in solution. Such a crosslinking strategy allows for the formation of dynamic organogels with viscoelastic behavior whose rheological properties are currently being studied in our laboratories.

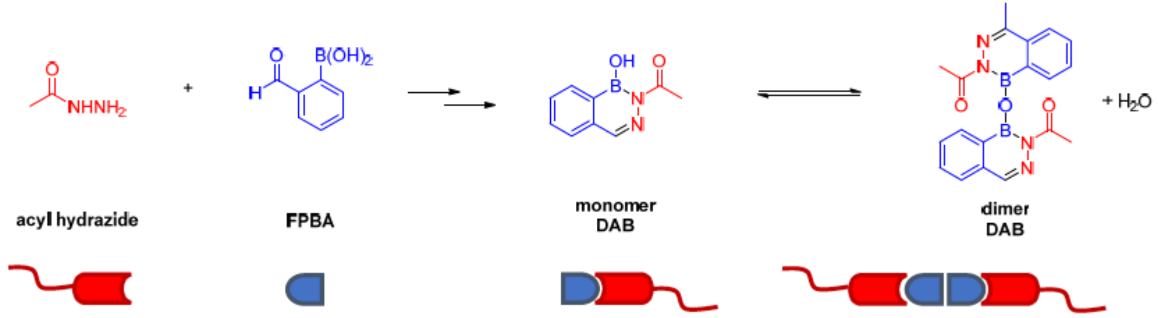


Figure 1. Reaction between acyl hydrazides and FPBA to form benzodiazaborines as strategy for polymer crosslinking.

Acknowledgements

J.D.B acknowledges grant RYC-2015-18471, funded by MCIN / AEI /10.13039/501100011033 and by “European Social Fund Investing in your future;” and grant CTQ2017-84087-R funded by MCIN / AEI / 10.13039/501100011033, and by “European Regional Development Fund a way of making Europe” by the European Union. E.G.G.

acknowledges Gobierno de Aragón for his PhD grant. The authors additionally would like to acknowledge the use of Servicio General de Apoyo a la Investigación-SAI, Universidad de Zaragoza.

References

[1] H. Gu, Bane, S. et al “Formation of hydrazones and stabilized boron–nitrogen heterocycles in aqueous solution from carbohydrazides and ortho-formylphenylboronic acids” Org. Biomol. Chem 2017, 15 (36), 7543–7548

P19

VANILLIN-BASED EPOXY VITRIMERS: LOOKING AT CYSTAMINE HARDENER FROM DIFFERENT PERSPECTIVE

SOLÈNE GUGGARI,[1,2], FIONA MAGLIOZZI,[2] SAMUEL MALBURET,[2] ALAIN GRAILLOT,[2]
MATHIAS DESTARAC,[2] MARC GUERRE[2*]

[1]Laboratoire des IMRCP, Université de Toulouse, CNRS UMR 5623, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 9 (France)
e-mail: marc.gurre@cnrs.fr, solene.guggari@specificpolymers.fr
[2]SPECIFIC POLYMERS, Zac Via Domita, 150 Avenue des Cocadières, 34160 Castries (France)

Abstract

Improving the efficiency, the sustainability and the end-of-life of polymer networks is a crucial challenge in materials science due to their important role in our society. Thus, the development of vitrimers represents a considerable interest to address the issue of recyclability while maintaining high thermomechanical performances. Epoxy vitrimers are one of the most versatile materials and candidates with potential outcome in industrial applications. This class of vitrimers encompasses many advantages compared to traditional epoxy materials such as recyclability and reprocessability.1 These properties are quite uniquely induced by the incorporation of dynamic reversible covalent bonds.

Recently, the incorporation of aromatic disulfide bridges has expanded the development of new eco-friendly epoxy materials.2,3 Herein, we present the bio-based aliphatic disulfide cystamine hardener with a vanillin-derived bio-sourced epoxy to prepare fully bio-based epoxy vitrimers. This work provides a comparative thermomechanical study between cystamine and an aromatic disulfide benchmark hardener (4-AFD) issued from petrol ressources. Thanks to DSC and rheological analyses, we demonstrated that the presence of this aliphatic hardener has a significant influence not only on the reactivity, but most importantly, on the resulting dynamic properties and on the recyclability of the epoxy networks. A unique and counterintuitive accelerating effect of the dynamic exchanges with the aliphatic disulfide hardener cystamine was evidenced by stress relaxation experiments. Thus, the exchange dynamics offered by cystamine could become considerably attractive as a viable alternative to the petrochemical-based counterparts. Beyond the bio-based character of cystamine, this discovery opens new perspectives as it could enable a fine tuning of the exchange dynamics by simply adjusting the ratio of cystamine in any epoxy formulation.

This project has received funding from the Bio Based Industries Joint Undertaking (JU) under grant agreement No 101023190. The JU receives support from the European Union's Horizon 2020 research and innovation program and the Bio Based Industries Consortium.

References

[1] F.-L. Jin, X. Li and S.-J. Park, *Journal of Industrial and Engineering Chemistry*, **2015**, 29, 1–11.
[2] A. Llevot, E. Grau, S. Carlotti, S. Grelier and H. Cramail, *Macromolecular Rapid Communications*, **2016**, 37, 9–28.
[3] A. Genua, S. Montes, I. Azcune, A. Rekondo, S. Malburet, B. Daydé-Cazals and A. Graillot, *Polymers*, **2020**, 12, 2645.

P20

FINE-TUNING LIGNIN-DERIVED EPOXY VITRIMER BY CHANGING ITS CROSSLINK DENSITY

HAFEEZULLAH MEMON

College of Textile Science and Engineering, International Institute of Silk, Zhejiang Sci-Tech University, Hangzhou 310018, China, hm@zstu.edu.cn

Abstract

There has been increasing interest in developing vitrimers materials due to their dual properties of thermosets and thermoplastics, including recyclability, self-healing, weldability, robustness, and chemical stability. The properties of thermosets are driven by their crosslinking density; thus, in this research, a series of lignin-derived epoxy vitrimers were formulated having different crosslinking densities by attenuating the blend ratio of two epoxy monomers, N,N-diglycidyl-4-glycidyloxyaniline and butanediol diglycidyl ether. However, the same stoichiometric ratios were kept with an imine-containing lignin-derived curing agent. The dynamic nature of these all epoxy vitrimers pertained to this dynamic imine bond. The glass transition temperature and reaction enthalpy were decreased by decreasing the crosslink density. The positive relation in mechanical, thermal, and dynamic properties, including relaxation times and activation energy for bond exchange, were also determined with the crosslink density. The resins with higher crosslink densities showed lower strength retention efficiency, which was obvious to the poor mobility of chemical bonds. This research would be useful in carefully designing the chemistry to obtain the required mechanical, thermal, and thermomechanical vitrimers and their composites.

Keywords
vitrimers, crosslink density, fine-tuning, dynamic properties, lignin-derived

P21

TAILORING VISCOELASTIC PROPERTIES OF DYNAMIC SUPRAMOLECULAR POLY(BUTADIENE)-BASED ELASTOMERS

MATTHEW HYDER[1], ADAM D. O'DONNELL[1], ANN M. CHIPPINDALE[1], IAN M. GERMAN[2], JOSEPHINE L.HARRIES[3], OLGA SHEBANOVA[4], IAN W. HAMLEY[1], WAYNE HAYES[1]

[1]Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6DX, UK
– Email: m.hyder@pgr.reading.ac.uk
[2]Kinectrics Inc., 17-18 Frederick Sanger Road, The Surrey Research Park, Guildford, Surrey, GU2 7YD, UK
[3]Domino UK Ltd, Trafalgar Way, Bar Hill, Cambridge, CB23 8TU, UK
[4]Diamond Light Source, Diamond Light Source Ltd, Harwell Science & Innovation Campus, Didcot, OX11 0DE, UK

Abstract

The discovery and development of new adhesive materials is critical for real-world applications of polymeric composite materials. We report the design and synthesis of a library of structurally related phase-separated supramolecular polyurethanes whose mechanical properties and adhesive characteristics can be enhanced through minor structural modifications of the polymer end-group. The interplay between phase separation of the hard domain polar end-groups and soft polybutadiene domains, coupled with tuneable self-assembly afforded by the polar end-groups, gives rise to a class of materials with tuneable mechanical properties. Exceptionally strong supramolecular adhesives and mechanically robust self-healing elastomers were identified. The mechanical properties were investigated through tensile testing. Finally, rheological analysis of the supramolecular materials was used to identify suitable healing and adhesive temperatures in addition to elucidate the supramolecular polyurethanes' thermal-responsive nature.[1]

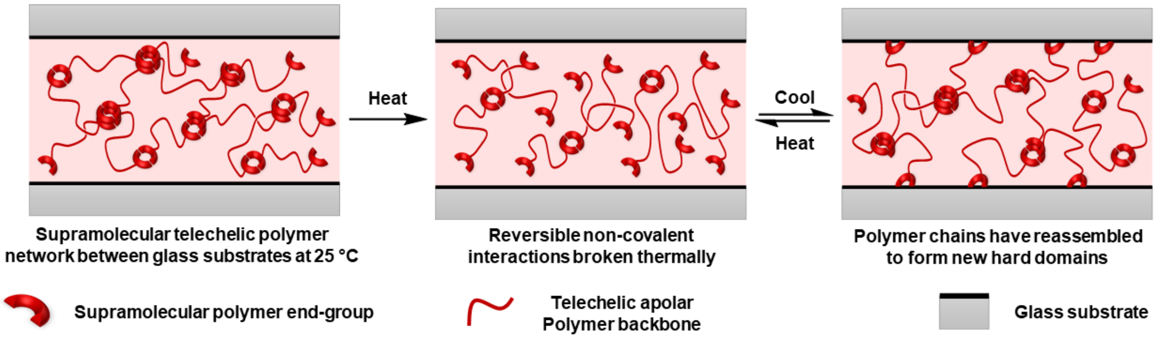


Figure 1: Schematic representation of the thermal adhesion of a supramolecular polyurethane (SPU) between glass substrates.

---

[1] M.Hyder, A.D. O'Donnell, A.M. Chippindale, I.M. German, J.L. Harries, O. Shebanova, I.W. Hamley and W. Hayes, *Mater. Today Chem.*, 2022, **26**, 101008.

P22

DIFFERENTIATING REVERSIBLY CROSSLINKED ELASTOMERS VIA HYBRID NETWORKS COMPRISING COVALENT AND NON-COVALENT INTERACTIONS

JENNIFER HUGHES, ANDREW SLARK

Department of Chemistry, University of Sheffield, UK,
e-mail: Jhughes9@sheffield.ac.uk, A.Slark@sheffield.ac.uk

Abstract

PUs are phase separated multi-block copolymers with high performance. However irreversible covalent crosslinking limits recyclability and reprocessing of traditional elastomers, requiring demanding conditons.

In order to overcome this problem we have synthesised novel reversibly crosslinked PU elastomers which can be recycled 3 times whilst maintaining the same mechanical properties. The dynamic networks combine reversible covalent bonds (Diels-Alder cycloadditions) and non-covalent bonds (hydrogen bonding) to achieve high performance and reprocessability. Structure-property relationships have been developed using different amorphous maleimide terminated prepolymers. These were copolymerised with multifunctional furan crosslinkers capable of different degrees of hydrogen bonding. This allowed for tunable thermal and mechanical properties *via* DMA and tensile testing. Phase separation and the synergy between reversible covalent and non-covalent interactions played a significant role in providing improved mechanical performance at higher temperatures.

This work shows it is possible to design recyclable PU elastomers with mild reprocessing conditions (e.g 100-120°C, 10 min at 30 bar) and robust mechanical performance. Furthermore, it shows that the thermal and mechanical properties can be tuned *via* structural design.

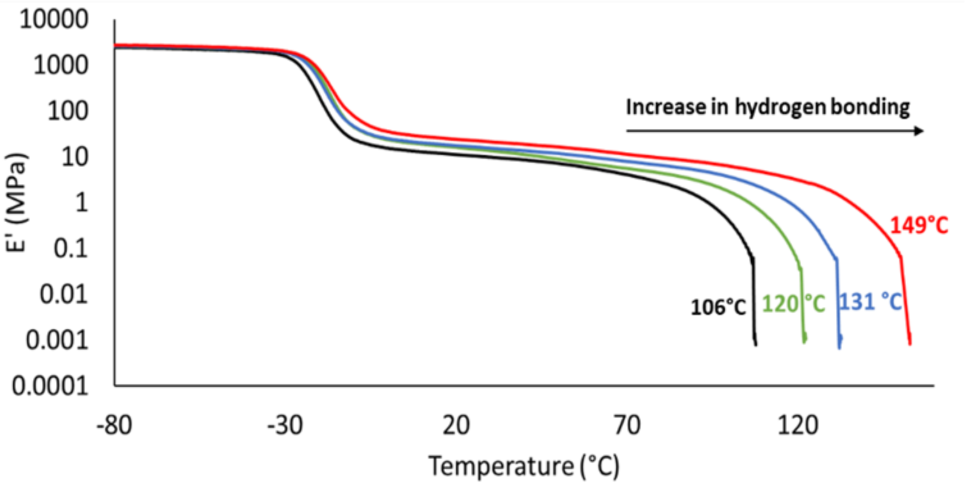


Figure 1- *DMA data showing the change in retro Diels-Alder temperature with different crosslinker structures.*

P23

PLA-IONIC LIQUID COMPOSITE - NOVEL "GREEN" FUNCTIONAL MATERIAL

TEODORO KLASER[1] NIKOLA BARAN[1], SANJA RENKA[1], ŽELJKO SKOKO[2], LUKA PAVIĆ[1] AND ANA ŠANTIĆ[1]

[1] Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia
[2] Department of Physics, Faculty of Science, University of Zagreb, Bijenička cesta 32, 10000 Zagreb, Croatia
Email: tklaser@irb.hr

Abstract

An effective solution to the negative environmental impact of synthetic polymers includes their replacement with biopolymers derived from renewable resources. Among various types of biopolymers, polylactic acid (PLA) is especially attractive since it shows good biocompatibility and biodegradability. Ionic liquids (IL) are considered to be the ‘‘green’’ alternatives to volatile organic compounds in many applications, ranging from organic synthesis to solid state electrochemistry. We have combined two green materials, PLA and IL, to prepare green functional polymers. PLA was modified with 1-butyl-1-methylpyrrolidinium bis(trifluoromethyl sulfonyl)imide (BMPy-TFSI) to prepare new material with hybrid properties, resulting in a rubber like material with high ionic conductivity. The thermal, structural, and electrical properties of prepared PLA-IL was thoroughly studied using differential scanning calorimetry, X-ray diffraction, Raman and impedance spectroscopies. Thus, IL modified PLA polymer is an advanced (multi)functional material with outstanding potential in applications of several area as an ionic active material with ductile mechanical properties.

P24

HIGH-PERFORMANCE, DEGRADABLE, AND UV-CURABLE POLYBENZOXAZINE VITRIMERS FOR 3D PRINTING APPLICATIONS

CHARLES JEHL, ANTOINE ADJAOUD, LAURA PUCHOT, JOAMIN GONZALEZ-GUTIERREZ,
ALEXANDER S. SHAPLOV AND PIERRE VERGE

*Luxembourg Institute of Science and Technology (LIST), 5 Avenue des Hauts-Fourneaux, 4362
Esch-sur-Alzette, Luxembourg, charles.jehl@list.lu and pierre.verge@list.lu*

Abstract

Among the various existing thermoset resins, polybenzoxazine (PBz) are of growing interest due their unique properties. Their precursors are obtained from the Mannich condensation of a phenol, a primary amine, and a methylene donor, e.g., paraformaldehyde. The polymerization of the precursors is activated by heat and proceeds through a cationic ring- opening polymerization process. PBz have elevated thermal stability, high T_g, excellent mechanical and dielectric properties, near-zero shrinkage upon polymerization, low water absorption and low flammability.[1] However, like in all thermosets, their cross-linked nature prevents their reprocessability and recyclability. To overcome this issue, dynamic covalent bonds, namely ester and aliphatic alcohol sites, were introduced into the PBz structure, allowing transesterification reactions to happen above a certain temperature. This vitrimeric behavior, in combination with the unique properties of PBz, creates high-performance materials with new end-of-life possibilities (reshaping and chemical recycling), suitable for a wide range of applications. One of the tested applications was the 3D-printing, which provides freedom of design and access to more complex structures. At first trials the decrease in viscosity of the resin during the curing step led to a collapse of the printed structure before its shape was fixed. To solve this problem the additional methacrylic functionality was introduced into the benzoxazine monomer allowing under UV-radiation to provide the rigidity to the preform before completing its thermal curing. The poster will present the synthesis and printing of the new monomers, as well as the illustration of the recycling strategy enabled by the dynamic bonds (Fig. 1).

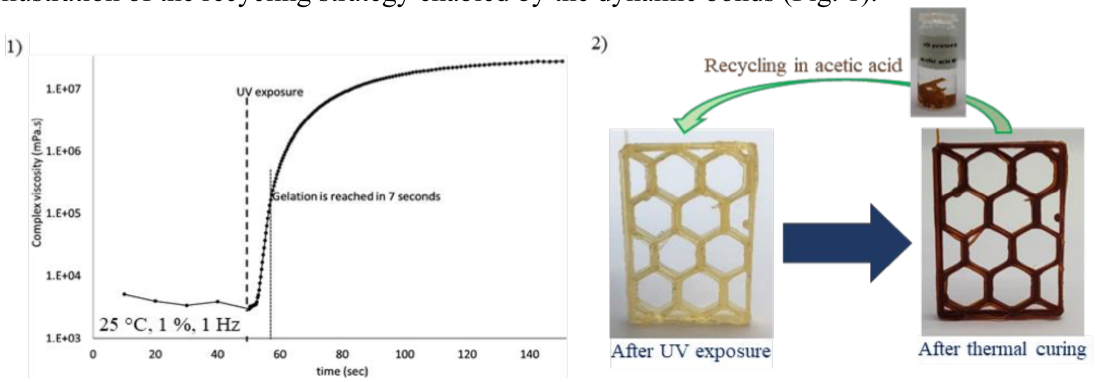


Figure 1: (1) Rheometer analysis of the UV-curable resin and (2) representative diagram of the printing and curing process of a part and its recycling

Acknowledgements

This work was supported by the Luxembourg National Research Fund (FNR) through project SusPoCo (Agreement number PRIDE21/16748260).

References

[1] A. Trejo-Machin, L. Puchot, P. Verge, “A cardanol-based polybenzoxazine vitrimer: recycling, reshaping and reversible adhesion”, RSC, 2020, 7026-7034.

P25

TOWARD VITRIMERS FROM POLY(AMIDO AMINE)S MADE OF TULIPALIN A

J. KOLLÁR, F. PIPPIG, M. DANKO, K. MOSNÁČKOVÁ, J. MOSNÁČEK

[1]*Polymer Institute of the Slovak Academy of Sciences; Dúbravská cesta 9, 84541 Bratislava, Slovak Republic – E-mail:*Jozef.Kollar@savba.sk

Abstract

Tulipalin A is considered as a renewable monomer. It can be derived from tuliposide found in tulips or can be synthesized from biomass sugar-based itaconic anhydride. Tulipalin A has been successfully polymerized via radical and ring opening co-polymerizations [1]. Furthermore, it can undergo Michael addition and amide formation [2]. The reaction is leading to polymers with a broad Đ and adhesive properties. It was found that the polymers made with this strategy have linear or branched structure. One opportunity to extend the scope of application of the material is crosslinking. If the crosslinking is made with bonds, which can be cleaved and reformed depending on temperature, pH or via irradiation then it is possible to create materials render properties depending on external conditions. Poly(amido amine)s were reacted for example with furandialdehyde (FDA) and with bis(maleimides) (BM). The reaction with FDA is leading to imine bonds [3] and the reaction with BMs forms diels-alder adducts [4]. The formation of the networks was analyzed with rheology. The chemical composition was determined with FTIR and NIR measurements. The thermal properties were studied using DSC and TG analysis. Finally, the mechanical properties were determined with the help of tensile tests. The presented polymer networks are aimed to be used as self-healing materials or materials showing shape memory properties. The chemistry is selected with a focused on an environmental friendly strategy.

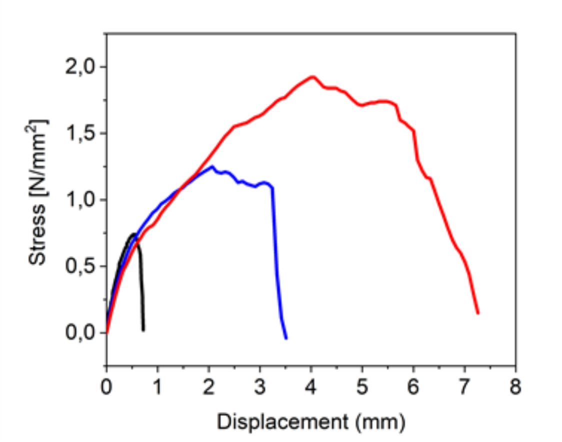


Figure 1: Tensile tests of poly(amido amine)s made of Tuliplain A with 64 mg (red), 128 mg (blue) and 144 mg (black) of FDA pro 1 g of polymer.

Acknowledgments

The authors thank the grant Agency VEGA for financial support through Grant VEGA 2/0168/21 and projects APVV-19-0338 and APVV-21-0297. This work was also performed during the implementation of the project Building-up Centre for advanced materials application of the Slovak Academy of Sciences, ITMS project code 313021T081 supported by the Integrated Infrastructure Operational Programme funded by the ERDF.

References

[1] Kollár, J., Danko, M., Pippig, F., Mosnáček, J., Frontiers in Chemistry 2019, 7, nr. 845
[2] Jean, M.; Le Roch, M.; Renault J.; Uriac P., Organic Letters 2005, 7, 2663-2665.
[3] Dhers, S.; Vantomme G.; Avérous L., Green Chemistry 2019, 21, 1596-1601.
[4] Wilson, J. F.; Chen, E. X.-Y., ACS - Sustainable Chemistry & Engineering 2019, 7, 7035-7046.

P26

REPROCESSABLE VANILLIN-BASED POLYSCHIFF VITRIMER NETWORKS: TUNING MECHANICAL AND THERMOMECHANICAL PROPERTIES BY NETWORK DESIGN

FLORIAN C. KLEIN[1], MALTE VOGT[1] AND VOLKER ABETZ[1,2]

[1]*Institute of Physical Chemistry, Universität Hamburg, Grindelallee 117, 20146 Hamburg, Germany.*
[2]*Institute of Membrane Research, Helmholtz-Zentrum Hereon, Max-Planck-Straße 1, 21502 Geesthacht, Germany.*
E-mail: florian.klein-1@uni-hamburg.de

Abstract

Bio-based polymer building blocks derived from abundant biomass represent a promising class of monomers for the synthesis of sustainable high-performance polymers. Vanillin derived from lignin can be used as a bio-based aromatic molecular platform for chemical modifications. The use of various vanillin aldehyde monomers with bio-based and non-toxic di- and triamines leads to covalent adaptable polyschiff networks and thus enables sustainable thermally reprocessable polymeric materials. These tailored covalent adaptable networks are reprocessable because of imine exchange reactions. A process for the preparation has been developed to obtain homogeneous films and crosslinked materials that are thermally reprocessable while maintaining their mechanical performance. The network structures, mechanical properties, and thermal stability of the obtained polymeric sheets were characterized in detail. By systematically adjusting the composition of the network building blocks, the mechanical and thermomechanical properties could be varied from materials with high elastic modulus to materials with high flexibility and elastomeric behavior. Furthermore, the stress-relaxation behaviors of the different network materials were investigated and the influence of the network segment morphology was elaborated.

By combining bio-based building blocks and the degradability of polyschiff networks under acidic conditions, sustainable vitrimer materials with chemical recyclability were produced under controlled conditions. These types of vitrimer materials have a potential to replace traditional polymeric ones in composites, electronic, biomedical, adhesive, and coating applications with enhanced reusability.

References

[1] K. Hong, Q. Sun, X. Zhang, L. Fan, T. Wu, J. Du, Y. Zhu, "Fully Bio-Based High-Performance Thermosets with Closed-Loop Recyclability" *ACS Sustain. Chem. Eng.* **2022**, *10*, 1036-1046.

[2] M. Liu, F. Gao, X. Guo, Q. Liang, J. He, J. Zhong, C. Lin, F. Lin, L. Shen, "Room temperature-curable, easily degradable, and highly malleable and recyclable vanillin-based vitrimers with catalyst-free bond exchange" *Polym. Test.* **2022**, *115*, 107740.

[3] H. Geng, Y. Wang, Q. Yu, S. Gu, Y. Zhou, W. Xu, X. Zhang, D. Ye, "Vanillin-Based Polyschiff Vitrimers: Reprocessability and Chemical Recyclability" *ACS Sustain. Chem. Eng.* **2018**, *6*, 15463-15470.

P27

RELAXING, FAST AND SLOW – UNRAVELING THE VISCOELASTIC BEHAVIOUR OF DUAL TRANSITION METAL -PAA HYDROGELS

ARTHUR LENOCH[1,2*], MONIKA SCHÖNHOFF[1,2], CORNELIA CRAMER[1,2]
[1]*Center for Soft Nanoscience, Busso-Peus-Str.10, 48149 Münster, Germany*
[2]*University of Münster, Institute of Physical Chemistry, Corrensstraße 28/30, 48149 Münster, Germany*
*[*a.lenoch@wwu](mailto:a.lenoch@wwu)*

Abstract

Viscoelastic relaxation of polymer networks with transition metal crosslinks is controlled by the underlying metal-ligand exchange kinetics. In the frequently studied model system Fe(III)-poly(acrylic acid) (PAA), the metal polymer association relaxes sufficiently fast to provide these hydrogels the ability to self-heal upon damage. A key factor for self-healing is the high mobility of the ferric ion in the swollen network [1].

With both Rouse-like chain and crosslink relaxation, differently activated processes dominate the dynamics at different timescales, making such materials inherently thermorheologically complex. In a recent work, we analyzed the interplay of these mechanisms and the crosslinking equilibrium, thus establishing a reliable time-temperature-scaling protocol to obtain activation energies [2].

Combining the crosslinking species with another metal can lead to the emergence of two relaxation modes in the viscoelastic spectrum [3]. Here, we study the dynamics of a dual type network in which slowly relaxing Cr(III) crosslinkers are included into the Fe-PAA hydrogel. Notably, rheological measurements of the relaxation time suggest a cooperativity of the metal species, indicating possible clustering of metal polymer bonds. Our rheological measurements are further substantiated by pulsed field gradient NMR studies of the polymer diffusion.

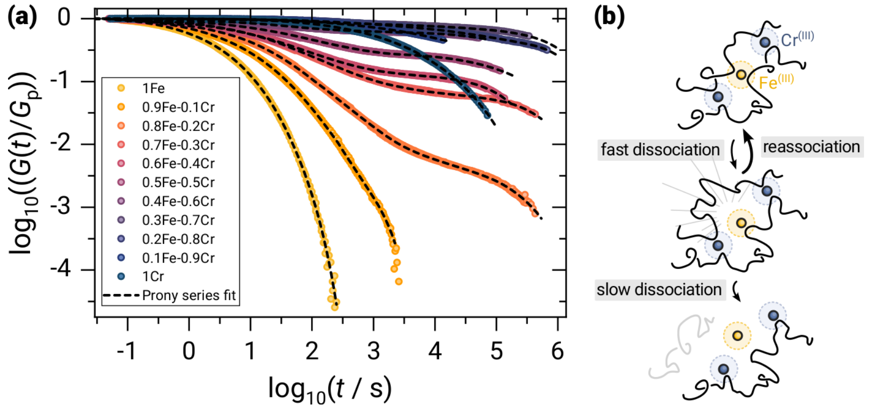


Figure 1: (a) Relaxation moduli mastercurves for different fractions of Fe/Cr-crosslinkers. **(b)** Sketch of Cr crosslinks prolonging the lifetime of a Fe crosslink.

References

[1] Z. Wei, J. He, T. Liang, H. Oh, J. Athas, Z. Tong, C. Wang, Z. Nie, "Autonomous self-healing of poly(acrylic acid) hydrogels induced by the migration of ferric ions." *Polym. Chem.* **2013**, *4*, 4601–4605.
[2] A. Lenoch, M. Schönhoff, C. Cramer, "Modelling viscoelastic relaxation mechanisms in thermorheologically complex Fe(III)–poly(acrylic acid) hydrogels." *Soft Matter.* **2022**, *18.44*, 8467–8475.
[3] S. C. Grindy, R. Learsch, D. Mozhdehi, J. Cheng, D. G. Barrett, Z. Guan, P. B. Messersmith, N. Holten-Andersen, "Control of hierarchical polymer mechanics with bioinspired metal-coordination dynamics." *Nat. Mater.*, **2015**, *14(12)*, 1210

P28

UCST-EXHIBITING POLYMERS: CONTROLLED RADICAL POLYMERIZATION AND THE EFFECT ON THE TRANSITION TEMPERATURE

NIKOLA KŘIVÁNKOVÁ[1,3], WOUTER VAN DER WIJNGAART[2,3], ULRICA EDLUND[1,3]

[1]Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Teknikringen 56-58, 100 44 Stockholm (Sweden) – Email: nikolakr@kth.se
[2]Department of Intelligent Systems, KTH Royal Institute of Technology, Malvinas väg 10, 100 44 Stockholm (Sweden)
[3]Digital Futures, KTH Royal Institute of Technology, Osquars Backe 5, 100 44 Stockholm (Sweden)

Abstract

Stimuli-responsive materials with reversible supramolecular networks controlled by a change in temperature have been of interest over the last decades[1]. Their ability to change properties at an external trigger has already been studied for example in drug delivery systems[2], tissue engineering[3], filtration[4], or to control the enzymatic activity[5]. These polymers exhibit temperature-dependent solubility properties. Herein, we study the synthesis of polymers undergoing an upper critical solution temperature (UCST) phase transition and its effect on the cloud point.

Poly(*N*-acryloyl glycinamide) (PNAGA) is a non-ionic polymer capable of undergoing a sharp UCST transition forming a reversible hydrogen bond network in aqueous solutions at temperatures below UCST. However, the ability to undergo a sharp UCST transition is quite sensitive and an improper choice of reaction conditions or the presence of impurities could result in the hindrance of the UCST properties[1]. Liu et al. (2013) showed PNAGA polymers having UCST phase transitions independent of the molar mass or polydispersity when synthesized by the atom transfer radical polymerization[6]. We investigate the possibility to polymerize the *N*-acryloyl glycinamide monomer by the single-electron transfer controlled radical polymerization and how it affects the cloud point of the resulting PNAGA polymers.

---

[1] Seuring, J., Bayer, F. M., Huber, K. & Agarwal, S. 2012. *Macromolecules*, 45, 374-384.
[2] WANG, D., XIA, Y. Z., ZHANG, D., SUN, X. M., CHEN, X. N., OLIVER, S., SHI, S. X. & LEI, L. 2020. *ACS Appl. Polym. Mat.*, 2, 1587-1596.
[3] Shi, X. H., Gao, H. J., Dai, F. Y., Feng, X. Q. & Liu, W. G. 2016. *Biomaterials Sci.*, 4, 1673-1681.
[4] WU, G. G., LI, Y. P., HAN, M. & LIU, X. X. 2006. *J. of Membr. Sci.*, 283, 13-20.
[5] SEMENYUK, P. I., KUROCHKINA, L. P., MAEKINEN, L., MURONETZ, V. I. & HIETALA, S. 2021. *Polymers*, 13.
[6] Liu, F., Seuring, J. & Agarwal, S. 2013. *Polym. Chem.*, 4, 3123-3131.

P29

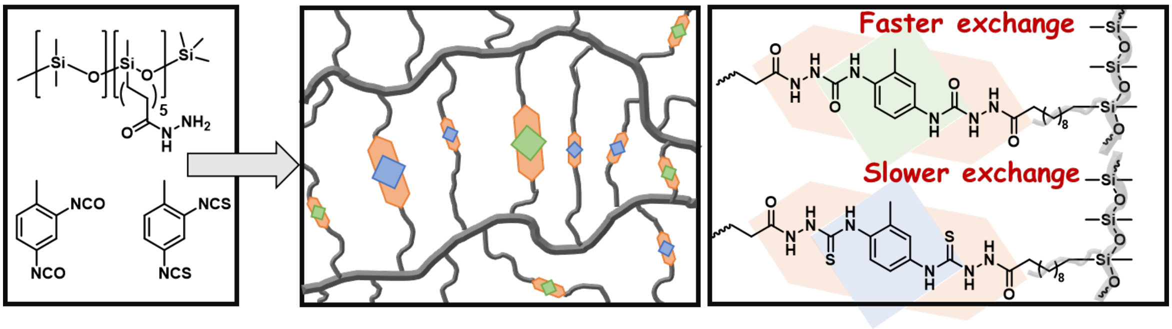
A COMBINED EXPERIMENTAL AND COMPUTATIONAL APPROACH TO DYNAMIC COVALENT AND NON-COVALENT CHEMISTRIES COOPERATES TOWARDS SUSTAINABLE MATERIALS

STEFAN MAESSEN, ANJA PALMANS
Eindhoven University of Technology, s.j.d.maessen@tue.nl

Abstract

The widespread use of polymeric materials has immensely improved our quality of life in recent decades and will continue to do so for the foreseeable future. It has however drastically affected the environment around us due to an excess of plastic waste and inefficient methods of dealing with it. This incentivized research towards sustainable plastics that can either be repaired or reused to improve their usage lifetime and decrease waste generation. One particular area of interest is that of coatings and thin films, where repairable materials are desired over the highly stable chemically crosslinked networks currently in use.

To achieve this, dynamic covalent networks (DCNs) can be used, in which crosslinked polymers harboring dynamic covalent bonds yield materials with good mechanical properties and reusability. This research focusses on two particular moieties, that of acylsemicarbazides (ASC) and thioacylsemicarbazides (TASC), which, in addition to their dynamic covalent nature also undergo supramolecular interactions via intermolecular hydrogen bonding. Together, these dynamic features with unique (de)formation mechanisms allow for wide tunability of the resulting polymer networks. Here, we combine computational and experimental chemistries to gain understanding on the underlying dynamic covalent and supramolecular mechanisms in various model systems containing ASC or TASC moieties. With these studies, we elucidate the difference in behavior between various chalcogens (O and S). Then, by preparing siloxane functionalized (T)ASC molecules, more insight and control will be gained over the properties of the functionalities in an apolar environment. Finally, siloxane-based, (T)ASC grafted polymers will be made to prepare DCNs which will be tested on their tunable healing and reusability properties for their use in coating materials and thin films.



P30

ACRYLIC BASED CANS – HOW DOES THE DYNAMIC CHEMISTRY INFLUENCE MATERIAL PROPERTIES?

NEIL LUNT, XANDER PRAET, ANDREW SLARK
Chemistry Department, University of Sheffield, UK

Abstract

We have comprehensively compared three different types of dynamic exchange reactions on the same poly(methacrylate) backbone - Diels Alder cycloaddition, transamination of vinylogous urethanes and phthalate monooester transesterification. Compositions were varied systematically to critically examine material properties in the same acrylic network. 2-ethylhexyl methacrylate (EHMA) was copolymerised with functional monomers *via* standard free-radical polymerisation techniques (FRP) to make prepolymers with similar backbones and low-moderate crosslink density comprising 5-20% comonomer and M_n=10-40 kDa.

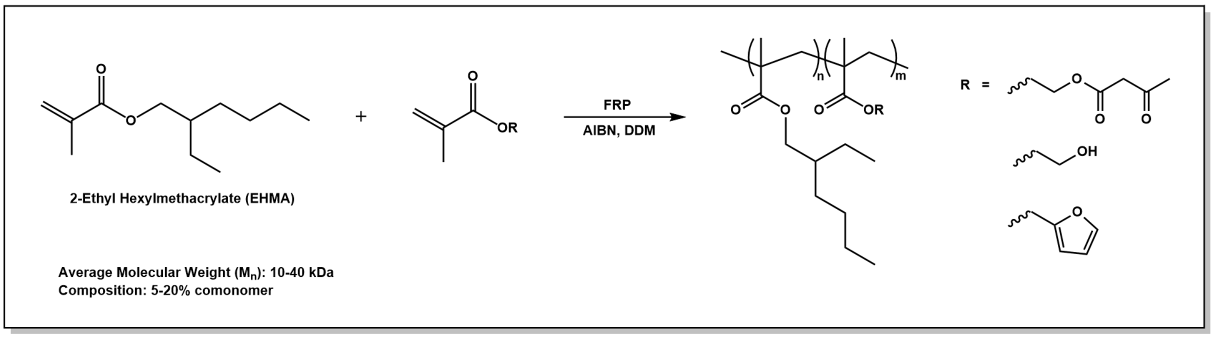


Figure 1: Copolymerisation of EHMA with functional comonomers.

Networks were then formed from the functional prepolymers and complementary flexible crosslinkers (diamines, dianhydrides and bismaleimides).

The prepolymer molecular weight, number of functional groups per chain and the specific network chemistry had a profound influence on the material behaviour, including

- curing conditions for network formation
- melt rheology
- mechanical properties
- robustness of the crosslinked network
- thermal properties
- ageing
- reprocessability

The advantages and disdvantages of the different dynamic chemistry were critically compared.

P31

REPROCESSING OF NOVEL BIOBASED THERMOSET POLYURETHANES

EDOARDO MIRAVALLE[1], GABRIELE VIADA[1], MATTEO BONOMO[1,2], CLAUDIA BAROLO[1,2,3], PIERANGIOLA BRACCO[1] AND MARCO ZANETTI[1,2]

Email: miravalle.edoardo@unito.it

[1]Department of Chemistry, NIS Interdepartmental Centre, University of Turin, via Pietro Giuria 7, 10125, Torino (Italy)
[2] INSTM Reference Centre, University of Turin, Via G. Quarello 15A, Turin, 10135, Italy
[3] ICxT Interdepartmental Centre, University of Turin, Via Lungo Dora Siena 100, Turin, 10153, Italy

Abstract

Polyurethanes (PU) can be thermoplastic and thermosetting counting for 8% of the globally produced plastic, putting them in sixth place as made and used polymer globally[1]. Due to its widespread commercial use, increasing quantities of PU waste are generated, including end-of-life waste, post-consumer waste, and processing scrap. It is estimated that only the customer-produced PUs waste ranges from 2.1 Mt to 3.6 Mt in Europe[2] by itself. Therefore, all processes involving the treatment of these wastes play a crucial role, particularly for thermoset PUs, which, differently from thermoplastic ones, are not compatible with direct industrial recycling. Since most current methodologies for recovering PUs are mainly ascribable as downgrading paths, new processes are being developed. Based on a particular stress-relaxation behavior first reported by Toblosky and Offenbach[3], which involves mechanisms of exchange of covalent bonds able to give rearrangement of the network defining a novel polymer class defined Dynamic Polymer Networks (DPN), a new mechanical recycling path for this type of polymer has been designed and investigated. The main characteristic of DPN is the preservation of the crosslink density during the exchange of bonds[4], which can be correlated with the retention of material properties, suitable for reworking purposes.

This work investigates the reprocessing abilities of a novel synthetized biobased PU. The pristine material has been obtained by combining a trifunctional polyol (Sovermol 780) and a difunctional isocyanate (Tolonate xflo100) in the presence of a catalyst, dibutyltin dilaurate. Both reagents are commercially available and are granted, respectively, 65% and 25% biobased. The reprocessing was done by finely grinding the initial network and then hot pressing it for 35 minutes at 170°C under 3 tons of pressure. Before and after the process, the material has been characterized via IR spectroscopy, TGA, and DSC analysis. No major differences in the IR spectra have been observed, which has been correlated to the preservation of all the pristine functional groups and the absence of any oxidative phenomena. Thermal analysis showed a slight decrease in T_g and thermal stability, in agreement with evidence already reported in the literature for this type of rework.

Subsequently, a process of post-synthetic insertion of components, polyols, and catalyst, has been proposed. A difference in the thermal properties and composition have been observed, symptomatic of successful inclusion process which, however, proved useful in improving reprocessing conditions.

---

[1] "Plastics - the Facts 2019," pp. 14, 35, 2019.
[2] J. Datta, *J Polym Environ*, vol. 26, no. 1, pp. 166–174, 2018.
[3] J. A. Offenbach and A. v Tobolsky, *J Colloid Sci*, vol. 11, pp. 39–47, 1956.
[4] J. Zheng *Materials Today*, vol. 51, pp. 586–625, 2021.

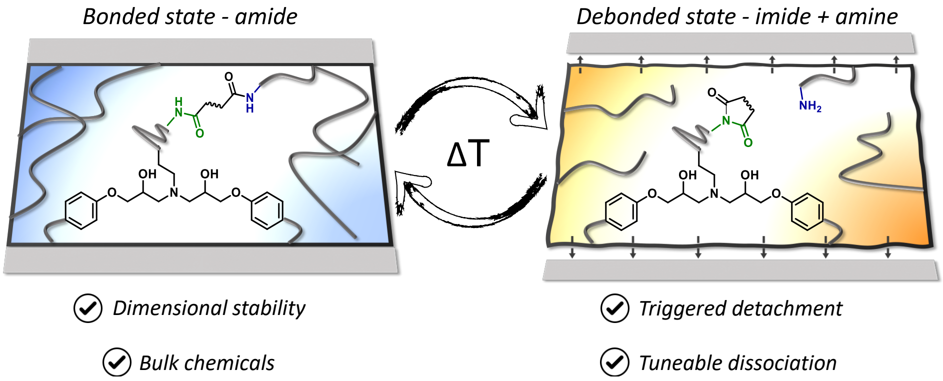
P32

EPOXY ADHESIVES WITH REVERSIBLE HARDENERS: CONTROLLABLE THERMAL DEBONDING IN BULK AND AT INTERFACES

FILIP VAN LIJSEBETTEN[1], TIM MAIHEU[1], FILIP E. DU PREZ[1]

Department of Organic and Macromolecular Chemistry, Faculty of Sciences, Ghent University,
Krijgslaan 284-S4, 9000 Ghent, Belgium
[1]Polymer Chemistry Research group, Centre of Macromolecular Chemistry (CMaC)
Email: Tim.Maiheu@UGent.be

Abstract



Adhesives are omnipresent in a myriad of materials and continue to impact our daily lives, as recognised by the continuous global growth of the adhesive market. Yet, challenging times lie ahead. Indeed, the design of adhesives with switchable properties that allow for the formation of reversibly bonded joints is highly desired as it brings the attractive feature of facilitating the disassembly of components, their structural repair, removal and aid their recycling.[1,2] On-demand adhesive dismantling has the potential to improve multi-material product recycling, but its implementation has been hampered by a critical trade-off between strong bonding and easy debonding. As a result, the temperature range in which these temporary adhesives can be used is relatively limited. Here we present the development of a new class of dynamic epoxy resins that significantly extends this upper temperature limit and still achieves fast debonding. Specifically, two types of dynamic polyamidoamine curing agents for epoxy hardening were developed, being polysuccinamides (PSA) and polyglutaramides (PGA). As the dynamic debonding/rebonding process of PSA and especially PGA linkages is more thermally demanding and at the same time more thermally robust than previously reported dynamic covalent systems, the resulting materials can be triggered at high temperatures, and at the same time remain bonded over a wide temperature range. .[3] The versatility of the PSA and PGA dynamic adhesive curing system was demonstrated in classical bulk adhesive formulations, as well as in dynamic covalent linking to a PSA- or PGA-functionalised surface. As a result, an attractive drop-in strategy was achieved for producing debondable and rebondable epoxy adhesives, with high complementarity to existing adhesive resin technologies and applicable in an industrially relevant temperature window.

References

[1] Mulcahy, K. R., Kilpatrick, A. F. R., Harper, G. D. J., Walton, A. & Abbott, A. P. Debondable adhesives and their use in recycling. *Green Chem.* **24**, 36–61 (2022).
[2] Banea, M. D. Debonding on demand of adhesively bonded joints: A critical review. *Reviews of Adhesion and Adhesives* vol. 7 33–50 (2019).
[3] Van Lijsebetten, F., De Bruycker, K., Winne, J. M., Du Prez, F. E., Masked Primary Amines for a Controlled Plastic Flow of Vitrimers. *ACS Macro Lett.* **11**, 919–924 (2022).

P33

REACTIVE PROCESSING OF POLYESTERS TO FORM VITRIMERS BASED ON DIOXABOROLANE METATHESIS

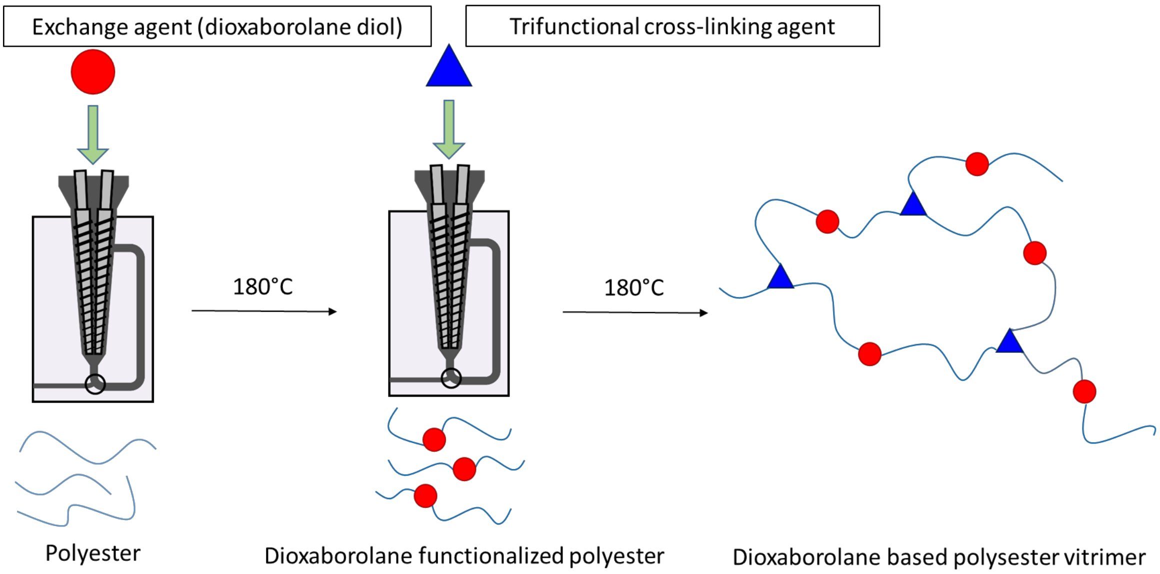
VIOLETTE MOHRING, NATHAN VAN ZEE, RENAUD NICOLAŸ

ESPCI Paris – PSL University, CNRS, 10 rue Vauquelin 75005 Paris, France– Email: violette.mohring@espci.fr

Abstract

Vitrimers relying on boronic ester metathesis were first reported in 2017.[1] Dioxaborolane chemistry presents several advantages: the exchange can take place at room temperature, without a catalyst, and is compatible with numerous grafting chemistries and polymer matrices.[1,2,3,4] In the case of polyethylene vitrimers, the chemical modification can be performed by reactive extrusion, a green and industrially relevant process.[1,2,5] Synthetizing dioxaborolane-based vitrimers from common polyester thermoplastics using reactive extrusion is therefore an interesting, yet challenging objective.

Here, we study the synthesis of polyester vitrimers obtained by reactive extrusion of glycol-modified poly(ethylene terephthalate) (PETg) and poly(lactic acid) (PLA). The synthetic pathway is composed of two main steps. First, boronic esters are introduced into the polymer chains by transesterification. The modified polymers are then crosslinked with multifunctional complementary molecules. The resulting materials have been characterized by solubility tests, DSC, TGA, DMA, and rheological measurement.



Synthesis of dioxaborolane-based polyester vitrimers by reactive extrusion

1. (1) Röttger, M.; Domenech, T.; van der Weegen, R.; Breuillac, A.; Nicolaÿ, R.; Leibler, L. *Science* **2017**, *356* (6333), 62–65.
2. (2) Caffy, F.; Nicolaÿ, R. *Polym. Chem.* **2019**, *10* (23), 3107–3115.
3. (3) Breuillac, A.; Kassalias, A.; Nicolaÿ, R. *Macromolecules* **2019**, *52*.
4. (4) Breuillac, A.; Caffy, F.; Vialon, T.; Nicolaÿ, R. *Polym. Chem.* **2020**, *11* (40), 6479–6491.
5. (5) Maaz, M.; Riba-Bremerch, A.; Guibert, C.; Van Zee, N. J.; Nicolaÿ, R. *Macromolecules* **2021**, *54* (5), 2213–2225.

P34

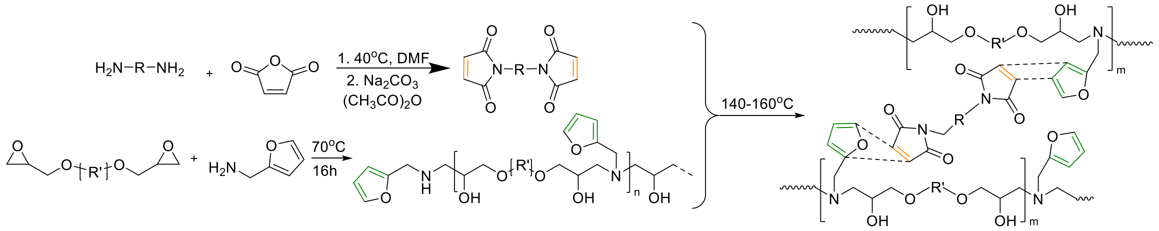
STRUCTURE-PROPERTY INVESTIGATION OF DIELS-ALDER POLYMER NETWORKS

GEORGIOS MISIAKOS, SANDRA VAN VLIERBERGHE

Polymer Chemistry and Biomaterials Group (PBM), Centre of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Ghent University, Ghent, Belgium, Georgios.Misiakos@ugent.be

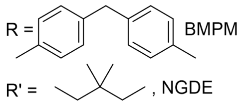
Recently, a new class of polymers based on Diels-Alder (DA) chemistry, has emerged with potential to bridge the gap between thermoplastic and thermoset materials. Harnessing the properties of dissociative chemistry mechanisms, materials that exibit thermoset-like properties while still having the ability to be reprocessed can be synthesized. In this work, the furan-maleimide pair of DA reagents is examined due to the dissociation of the DA adducts in the temperature range of Fused deposition modeling (FDM) printing temperatures. FDM has been the most widely adopted 3D printing technique, however its constructs suffer from lack of mechanical robustness and mechanical anisotropy, as a result of poor interlayer adhesion during printing with the most commonly used materials (PLA, ABS), therefore alternatives offering solutions to these deficiencies are sought. Despite several works presented in literature, a comprehensive examination of the impact of the builing block composition is lacking, thererfore, a thorough investigation of structure-property relations using a variety of backbones and crosslinkers will provide a better understanding of the behavior these networks and the interrelation between building block choice and the emerging material properties.

Scheme 1: Synthetic overview of dynamic covalent networks. Ring openiing polymerization (upper left) and bismaleimide synthesis (bottom left), formation of the dynamic covalent network (right)



By mixing bismaleimide (BM) crosslinkers in different proportions to the furan groups present, materials with a range of properties can be synthesized. This straightforward approach to the synthesis of these DPN has a lot of potential since it does not require a catalyst or even a solvent. The mechanical properties of the resulting materials will depend on the flexibility and length of the repeating unit and of the bismaleimide. Linear aliphatic BMs of increasing length and a bis-aromatic BM are used to crosslink the same polymer backbone at different ratios with respect to the furan groups of the backbone. The shift from viscoelastic to elastic behaviour with increasing length of the aliphatic BM, and the contrasting behaviour of networks crosslinked with the aromatic BM will be demonstrated. Research on a variety of building blocks is currently ongoing to produce a library of materials that will be evaluated for their mechanical and rheological properties, biocompatibility, and 3D printing potential.

R = $(CH_2)_2$, BMOE
R = $(CH_2)_3$, BMOP
R = $(CH_2)_4$, BMOB
R = $(CH_2)_6$, BMOH
R = $(CH_2)_{12}$, BMODod



Scheme 2: building blocks

References

[1] Q. Zhou, F. Gardea, Z. Sang, S. Lee, M. Pharr, S. A. Sukhishvili "A Tailorable Family of Elastomeric-to-Rigid, 3D Printable, Interbonding Polymer Networks." *Adv. Funct. Mater.* **2020**, 30, 2002374

P35

DIRECT SYNTHESIS OF TUNABLE SILICONE-BASED COVALENT ADAPTABLE NETWORKS AND THE DUAL ENHANCEMENT EFFECT OF SILICA FILLER

LOC TAN NGUYEN *1, CHIEL MERTENS 1, FILIP E. DU PREZ 1.
1 *Polymer Chemistry Research Group, Department of Organic and Macromolecular Chemistry*
Ghent University, Krijgslaan 281 (S4), 9000 Ghent, Belgium, loctan.nguyen@ugent.be

Silicones are one of the most broadly used elastomers due to their beneficial properties, including flexibility, gas permeability, hydrophobicity, and damping capacity over a broad temperature window ranging from −100 °C to 250 °C.[1] However, their synthesis involves relatively high-cost expenditure resulting in the far-more expensive price of silicone-based elastomers compared to carbon-based elastomers[2]. Besides the effort to apply green chemistry or nature-feedstock resources, the implementation of dynamic covalent bonds, which allows the crosslinked materials to be reprocessed and recycled, potentially promises to render silicone elastomer a more economically beneficial and sustainable lifetime circle. Although several dynamic chemistries have been utilized in silicone elastomers, they usually require expensive and/or tailored-made building blocks, hampering their applicability. A particularly attractive approach is the use of a Michael addition, between an acrylate and an amine to form a β-amino ester (BAE). The dynamic nature of the latter was recently demonstrated by our group[3]. Although the facile utilization of Michael Addition chemistry in silicone network synthesis has been reported [4], the dynamic nature of the formed β-amino esters bonds in bulk silicone elastomers has been overlooked.

This work describes a study of the dynamic properties of poly (dimethyl siloxane)-based networks, which were directly formed *via* aza-Michael crosslinking. Because of the reversible nature of the formed BAEs, the materials possess two dynamic bonds that can undergo associative and dissociative exchange at elevated temperatures, resulting in re-processability of up to five cycles. This concept also allows us to easily tune mechanical and dynamic properties by varying crosslinkers and/or filler content. Furthermore, the addition of fumed silica-bearing hydroxyl moieties on surfaces gave positive effects on both the mechanical and dynamic properties of materials. The effects of silica on elasticity and viscosity were also screened, and the results showed that with the appropriate level of silica fillers, they not only give four times enhancement in tensile strength but also reduce the stress relaxation time more than twice at elevated temperatures.

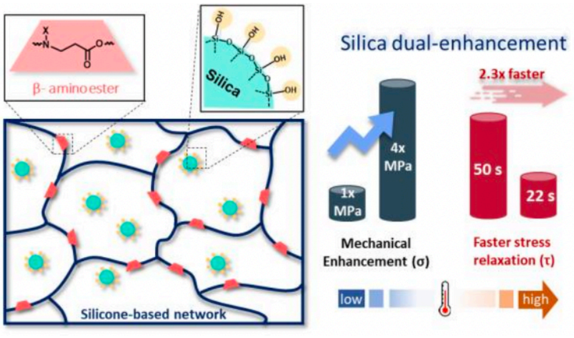


Figure 1. Graphical abstract of the silicone-based covalent adaptable network using thermally reversible β-amino ester bonds.

References

[1] P. Mazurek, S. Vudayagiri, and A.L. Skov "How to tailor flexible silicone elastomers with mechanical integrity: a tutorial review." *Chem. Soc. Rev.* **2019**, *48*, 1448-1464
[2] M. Melendez-Zamudio, et al. "Acrylated Soybean oil: A key intermediate for more sustainable elastomeric materials from silicones." *Green Chem.* **2022**,
[3] C. Taplan, M. Guerre, and F.E. Du Prez "Covalent Adaptable Networks Using β-Amino Esters as Thermally Reversible Building Blocks." *J. Am. Chem. Soc.* **2021**, *143*, 9140-9150
[4] G. Lu, et al. "Aza-Michael silicone cure is accelerated by β-hydroxyalkyl esters." *J. Polym. Sci.* **2021**, *59*, 1935- 1941

P36

VITRIMER-LIKE MATERIAL BASED ON THIOL-EPOXY-ISOCYANATE DUAL- CURING

SASAN MORADI[1], XAVIER FERNÁNDEZ-FRANCOS[1], XAVIER RAMIS[1], OSMAN KONURAY[1]

[1]Department of Machines and Heat Engines, ETSEIB, Polytechnic University of Catalonia, Avenida Diagonal 647, 08028 Barcelona (Spain) – Email: sasan.moradi@upc.edu

Abstract

Hybrid poly(thiourethane)s-poly(thiol-epoxy) fully recyclable networks were prepared by using as exchange reactions catalyst a tetraphenylborate salt derived from highly basic amine 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD)[1]. Stoichiometric ternary thiol:isocyanate:epoxy materials, with different ratios of isocyanate:epoxy groups, were prepared. Trimethylolpropane tris(3-mercaptopropionate) (S3) was mixed with bisphenol A diglycilyl ether (DG), the TBD catalyst and 1- methylimidazole, and the mixture was homogenized by mechanical stirring. Hexamethylene diisocyanate (HDI) was added at the end and the mixture was quickly stirred by hand and samples were analysed with differential scanning calorimetry (DSC) or cured in an oven before analysis. The mixtures were cured in the oven at 70 oC for 2 hours and then for 4 hours at 130 oC. Stress relaxation behaviour of the networks were studied by dynamic mechanical analysis (DMA) at 140 oC.

A complex relaxation kinetics effect was observed depending on the proportion of DG. A small fraction of DG (S3HDI0.75DG0.25) produced an increase in relaxation rate with respect to the pure poly(thiourethane) (S3HDI1.0), while further increasing the content in DG decreased the relaxation rate and led to increasing residual stress (see Figure 1). Noteworthy, complete stress relaxation could be achieved with 50 % molar ratio of DG (S3HDI0.5DG0.5). Pure thiol-epoxy network (S3DG1) also showed stress relaxation[2] but at much lower rate. Intermediate compositions (S3HDI0.25DG0.75 and S3HDI0.125DG0.875) showed a complex sequential relaxation profile. The analysis of the relaxation kinetics of S3HDI0.75DG0.25 (Figure 2) produed an activation energy of the of about 114 kJ/mol, similar to that of other poly(thiourethane)s[1]. Thermogravimetric analysis (TGA) revealed that the mass loss during stress relaxation experiments was negligible. Acording to the results of DMA the treshold límit material which completely relaxes the stress (S3HDI0.5DG0.5) was tested for its recycling ability and it was observed that it can be completely recycled within 2 hours at 140 oC.

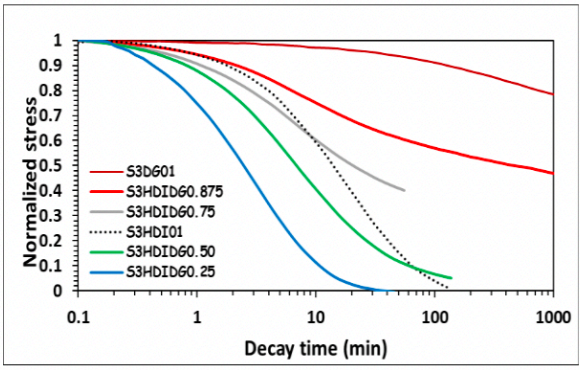


Figure 1

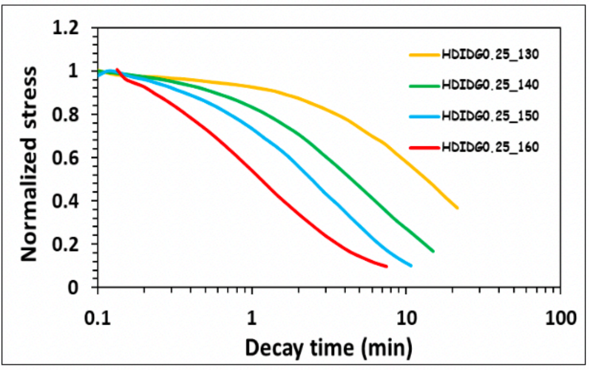


Figure 2

[1] Gamardella, F.; Muñoz, S.; De la Flor, S.; Ramis, X,; Serra, A. Recyclable organocatalyzed poly(thiourethane) covalent adaptable networks. Polymers 2020, 12, 2913; doi:10.3390/polym12122913

[2] Li, L.; Chen, X.; Jin, K.; Torkelson, J. M. Vitrimers Designed Both To Strongly Suppress Creep and To Recover Original Cross-Link Density after Reprocessing: Quantitative Theory and Experiments. Macromolecules 2018, 51 (15), 5537–5546. https://doi.org/10.1021/acs.macromol.8b00922.

P37

A PROMISING METHOD FOR POLYURETHANE RECYCLING: VITRIMERIZATION THROUGH THE ACTIVATION OF CARBAMATE EXCHANGE BY ORGANIC CATALYSTS

C. CHAMBRIAL, P. PILUSO
DRT/LITEN/DTNM/STDC/LVME-CEA, pierre.piluso@cea.fr

Abstract

Polyurethane (PU) is the sixth polymer and the first thermoset most produced (3.6 Mt in Europe in 2017).[1] PU thermoset nature makes it extremely stable, which comes out as a major issue when it comes to recycling. Indeed, PU is still mostly landfilled or incinerated. While chemical recycling processes are growing, they still fail to recover both monomers of the PU, the isocyanate being converted irreversibly to urea during the process. The vitrimer chemistry developed within the last decade offers a now possibility to recycle polyurethane through the exchange of the existing carbamate exchangeable bonds in polyurethane.

Several exchange reactions are possible in PU, namely trans-carbamoylation and urethane exchange. The latter is exclusively a dissociative mechanism, while the first one is possibly dissociative or associative.[2] Isocyanate liberation during reprocessing of activated PU can severely hampers the properties of the final polymer by leading to irreversible parasite reactions. Several papers studies the catalyst impact on the nature of the exchange mechanisms in PU during reprocessing. While good candidates for continuous reprocessing are mostly organometallic catalysts, allowing dissociative mechanisms, some promising organic catalysts favoring associative mechanisms were identified.[3,4] Those promising results paved the way to the development of a recycling method for PU that has the potential to allow closed loop recycling, through the use of selected catalysts.

In this work, we studied the effect of several organic catalysts on lab synthesized and industrial PU, and compared them to reference organometallic catalysts. We evaluated the activity of catalysts through rheology, DMA and stress-relaxation measurements with several PU formulations and the continuous reprocessing in internal mixer of the industrial PU with the best catalysts.

References

[1] R. Geyer, J. R. Jambeck, K. L. Law "Production, use, and fate of all plastics ever made." *Science advances* **2017**, *3(7)*, e1700782.
[2] C. Bakkali-Hassani, D. Berne, V. Ladmiral, S. Caillol "Transcarbamoylation in polyurethanes: underestimated exchange reactions?" *Macromolecules* **2022**, *55(18)*, 7974–7991.
[3] D. T. Sheppard, K. Jin, L. S. Hamachi, W. Dean, D. J. Fortman, C. J. Ellison, W. R. Dichtel "Reprocessing postconsumer polyurethane foam using carbamate exchange catalysis and twin-screw extrusion." *ACS Central Science* **2020**, *6(6)*, 921–927.
[4] F. Elizalde, R. H. Aguirresarobe, A. Gonzalez, H. Sardon "Dynamic polyurethane thermosets: tuning associative/dissociative behavior by catalyst selection." *Polymer Chemistry* **2020**, *11(33)*, 5386–5396.

P38

VITRIMERS FROM AZA-MICHAEL REACTION BETWEEN METHACRYLATES AND AMINES IN PRESENCE OF HYDOXY FUNCTIONALITIES

VIVIANA OSPINA[1], RICCARDO CHIARCOS[1], ERICA LAGUZZI[1], MICHELE LAUS[1],
NICOLA CUMINETTI[2], JANOSC DE BUCK[2], FEDERICA CAMPO[2].

[1] *Dipartimento di Scienze e Innovazione Tecnologica (DISIT), Università del Piemonte Orientale*
"A. Avogadro", Viale T. Michel 11, 15121 Alessandria, Italy
e.mail: viviana.ospina@uniupo.it

[2] *ELANTAS Europe S.r.l. Via San Martino 6,15028 Quattordio (AL), Italy.*

Abstract

Vitrimer materials, which exhibit mechanical properties of thermosets with processability similar to thermoplastics, have gained great interest in the perspective of plastic recycling which is fundamental in circular economy. Du Prez and collaborators[1] reported the synthesis of innovative vitrimers based on β-amino ester networks obtained using the aza-Michael addition between amine and acrylate moieties where the dynamic exchange occurs *via* both retro-aza-Michael reaction and catalyst-free transesterification. In this context, we are developing a new system in which the aza-Michael reaction occurs between sterically hindered amines and mixtures of polyfunctional methacrylic monomers. The feasibility of the process was demonstrated by evaluating the effects of both the molar ratio between monomers and the curing time at different temperatures from 90 to 120 °C. Qualitative information on the reaction conversion was obtained following the trend of the glass transition temperature (Tg) of the samples with time. Vitrimers with the higher Tg were obtained at 120 °C curing temperature with a molar ratio between methacrylic and amine functionalities of 1:0.5. In these conditions, a linear increase in the glass transition temperature with time is observed. The rheological properties of these samples were evaluated by DMTA and stress-relaxation tests at temperatures ranging from 100 °C to 180 °C. Typical stress-relaxation curves are reported in Figure 1. A full stress relaxation is observed at different temperatures thus demonstrating the effective mobility of the network crosslinking points.

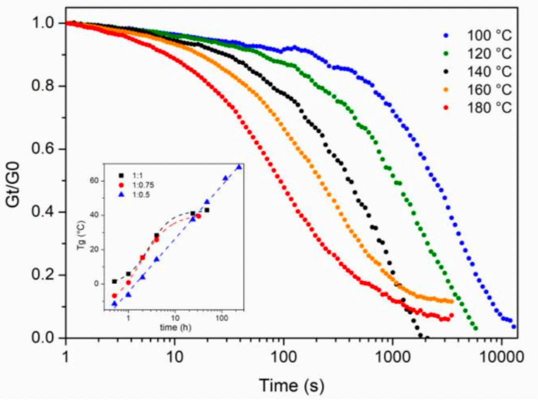


Figure 1. Stress-relaxation curves at different temperature for the sample prepared in a molar ratio metacrylic:amine functionalities 1:0.5. The evolution of Tg for the molar ratios studied is also shown.

References

1. Taplan C, Guerre M, Prez FE Du. Covalent Adaptable Networks Using β-Amino Esters as Thermally Reversible Building Blocks. Published online 2021. doi:10.1021/jacs.1c03316

P39

HIGH-PERFORMANCE, RECYCLABLE, AND DEGRADABLE BIO-BASED POLYBENZOXAZINE VITRIMERS: STRUCTURE TO PROPERTIES

A. ADJAOUD[1,2], L. PUCHOT[1], P. VERGE[1]
[1] *Luxembourg Institute of Science and Technology, Esch-sur-Alzette, Luxembourg*
[2] *University of Luxembourg, Esch-sur-Alzette, Luxembourg*

In recent decades, an important increase in the consumption of thermosets worldwide resulted in large amounts of waste that cannot be recycled or repaired. In end of life, thermosets are usually buried, disposed in landfills, or incinerated. Inspired by the work, Leibler and co-workers in 2011 [1], the introduction of reversible dissociative or associative bonds into the chemical structure of thermosets to create covalent adaptable networks (CANs) that enable self-healing or recycling has been considerably studied in the past recent years.

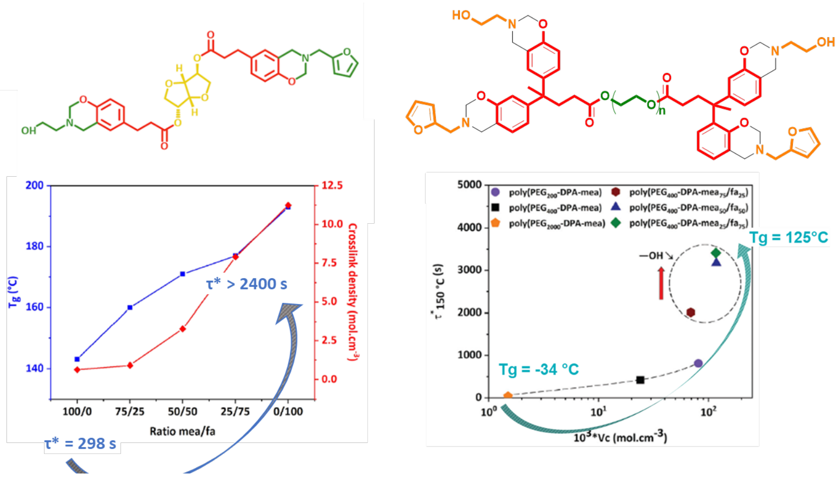


Figure 2 Representation of the relation between chemical structure and resulting properties

The poster will illustrate the synthesis and properties of innovative bio-based and catalyst-free vitrimers obtained from a benzoxazine-terminated poly-ethylene glycol or isosorbide monomers containing ester bonds and pendant aliphatic hydroxyl groups (–OH). Relying on the neighboring group participation theory, the abundant number of tertiary nitrogen groups covalently bounded into the polybenzoxazine network act as internal catalyst for transesterification reactions [2]. The effect of the structural features of the different polybenzoxazine vitrimers was investigated by tuning the network structure and thus the crosslinking density of the network and the number of –OH groups, shedding more light on the mechanism of self-catalysis and the range of properties. (Figure 1). [3][4]

References

[1] D. Montarnal, M. Capelot, F. Tournilhac and L. Leibler, Science, **2011**, 334, 965–968.
[2] J. Han, T. Liu, C. Hao, S. Zhang, B. Guo and J. Zhang, Macromolecules, **2018**, 51, 6789–6799.
[3] A. Adjaoud, A. Trejo-Machin, L. Puchot; P. Verge, et Al Polymer Chemistry **2021**, 12, 3276 - 3289.pdf
[4] A. Adjaoud, L. Puchot, P. Verge et al ACS Sus Chem Eng **2021**.

Acknowledgements

This research was supported by the Luxembourg National Research Fund (FNR) (C18/MS/12538602)

P40

PARTIALLY BIOBASED POLY(STYRENE-*B*-VANILLIN METHACRYLATE) BY ATRP: HOW THE COPOLYMER COMPOSITION INFLUENCES THE VITRIMER.

NICOLA PORCELLI, GIULIA SCURANI, NICCOLÒ BRAIDI, FABRIZIO RONCAGLIA*
Department of chemical and geological sciences, University of Modena and Reggio Emilia,
via Campi 103, Modena, Italy. e-mail: nicola.porcelli @unimore.it

Abstract

Due to increasing environmental awareness, the study of biobased and renewable monomers in the field of plastics has been encouraged by governments and pursued by enterprises. Even though industrial implementation is yet to be realized, many promising studies on the synthesis of bio-renewable monomers and polymers have been published[1a,b]. Polymers through reversible deactivation radical polymerizations (RDRPs) are considered a promising route towards the production of sustainable materials, given that these techniques allow the synthesis of pseudo-living polymeric chains with complex architectures and controlled molecular weight distributions[2].

Among plastics, thermosets are ubiquitous in manufacturing due to their crosslinked structure that provides enhanced mechanical properties, thermal and chemical resistance, and dimensional stability. However, this characteristic makes them difficult to recycle as they can neither be reformed nor depolymerized, posing increasing environmental concerns. A promising solution came with the introduction of Dynamic Covalent Chemistry into thermosets' design, giving rise to Covalent Adaptable Networks (CANs), allowing them to be reprocessable, self-healing, and/or chemically recyclable[3].

Given the high orthogonality of radical reactions, which allows a variety of functional groups to be inserted into the polymer backbone, the simultaneous involvement of CANs and RDRPs for the production of high-added value thermosets was reported[4a,b]. Herein, we present the block copolymerization of the biorenewable vanillin methacrylate via Atom Transfer Radical Polymerization (ATRP) and, subsequently, the crosslinking of the obtained polymer exploiting the pendant aldehydic groups. The chemical and mechanical properties of the vitrimeric product depend on the length of the blocks and, more generally, on the architecture of the initial copolymer.

References

[1] (a) F. L. Hatton "Recent advances in RAFT polymerization of monomers derived from renewable resources." *Polym. Chem.* **2020**, *11*, 220; (b) K. Satoh "Controlled/living polymerization of renewable vinyl monomers into bio-based polymers" *Polym. J.* **2015**, *47*, 527–536;

[2] N. Corrigan , K. Jung , G. Moad, C. J. Hawker, K. Matyjaszewski, C. Boyer "Reversible-deactivation radical polymerization (Controlled/living radical polymerization): From discovery to materials design and applications." *Prog. Polym. Sci.* **2020**, *111*, 101311;

[3] M. Guerre, C. Taplan, J. M. Winne, F. E. Du Prez "Vitrimers: directing chemical reactivity to control material properties.", *Chem. Sci.* **2020**, *11*, 4855-4870;

[4] (a) J. J. Lessard, L. F. Garcia, C. P. Easterling, M. B. Sims, K. C. Bentz, S. Arencibia, D. A. Savin, B. S. Sumerlin "Catalyst-Free Vitrimers from Vinyl Polymers." *Macromolecules* **2019**, *52*, 2105−2111; (b) S. Wang, L. Li, Q. Liu, M. W. Urban "Self-Healable Acrylic-Based Covalently Adaptable Networks.", *Macromolecules* **2022**, *55*, 4703−4709.

P41

PILLAR[5]ARENE-BASED SUPRAMOLECULAR GEL SENSOR FOR THE DETECTION OF NITRILES

MAKSIM RODIN, DIRK KUCKLING
Paderborn University, Paderborn, Germany; dirk.kuckling@uni-paderborn.de

Being important precursors in industrial production of various synthetic polymers, organic nitriles present a highly toxic class of substances, which makes it crucial to be able to monitor the nitriles levels in industrial wastes [1]. Pillar[5]arenes (P5As) is a class of macrocyclic compounds which are characterized by a distinguished ability to form host-guest complexes with neutral (such as nitriles) and positively charged species. Host-guest complexes with P5As attached to polymer chains were reported to act as reversible stimuli responsive cross-links [2] affording a fabrication of smart materials such as actuators and sensors. Recently in our group a dually crosslinked gel sensor for ovarian cancer biomarker was developed based on cyclodextrin. [3, 4] The present work is devoted to the fabrication of a gel sensor containing P5A-based supramolecular crosslinks for the detection of nitriles (Figure 1).

Copolymer poly(DMAAm-co-VDMA) (DMAAm = dimethyl acrylamide; VDMA = 4,4-dimethyl-2-vinylazlactone) was modified with pendant P5A (HM) and quaternary ammonium (GM) groups as well as with photo-crosslinker moieties to obtain host (HP) or guest (GP) polymers, respectively. A dually crosslinked sensor chip was obtained on a quartz wafer from HP/GP solution by spin-coating and subsequent UV-irradiation. In a flow cell, the chip was swollen in CHCl$_3$ and in the solutions of adiponitrile of different concentrations. Using SPR spectroscopy the dependence of the gel layer thickness (h$_1$ vs. h$_0$) from the analyte concentration was established.

Figure 1. The concept of the dually crosslinked gel sensor.

References

[1] C.-C. Wang, C.-M. Lee, L.-J. Chen "Removal of Nitriles from Synthetic Wastewater by Acrylonitrile Utilizing Bacteria." *Journal of Environmental Science and Health, Part A* **2004**, *39(7)*, 1767–1779.
[2] J. Chang, Q. Zhao, L. Kang, H. Li, M. Xie, X. Liao "Multiresponsive Supramolecular Gel Based on Pillararene-Containing Polymers." *Macromolecules* **2016**, *49*, 2814–2820.
[3] J. Li, C. Ji, B. Lü, M. Rodin, J. Paradies, M. Yin, D. Kuckling "Dually Crosslinked Supramolecular Hydrogel for Cancer Biomarker Sensing." *ACS Appl. Mater. Interfaces* **2020**, *12(33)*, 36873–36881.
[4] M. Rodin, J. Li, D. Kuckling "Dually cross-linked single networks: Structures and applications." *Chem. Soc. Rev.* **2021**, *50*, 8147–8177.

P42

EFFECTS OF ZN BASED CATALYSTS ON THE TOPOLOGY FREEZING TEMPERATURE (TV) OF EPOXIDIZED CANOLA OIL-LACTIC ACID VITRIMERS

JOÃO GABRIEL PASSOS RODRIGUES[1], SANTIAGO ARIAS[2], JOSE GERALDO A. PACHECO[2] AND MARCOS LOPES DIAS[1]

[1] Universidade Federal do Rio de Janeiro (UFRJ), Instituto de Macromolécules Professora Eloisa Mano (IMA), jgprodrigues@ima.ufrj.br and mldias@ima.ufrj.br
[2] Universidade Federal de Pernambuco (UFPE), Departamento de Engenharia Química, ariashenao@gmail.com and jose.pacheco@ufpe.br

Abstract

Vitrimers based on epoxidized canola oil cured with lactic acid were synthesized. The effects of two different types of catalysts: zinc Acetate (AcZn) and zinc Aluminate (AlZn) on the topology freezing temperature (Tv) were investigated, varying the concentrations of the catalysts (1 and 2 wt%). Vitrimers produced were characterized by Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR) and Thermomechanical Analyzer (TMA). DSC analyses revealed a small decrease in the glass transition temperature (Tg) of the vitrimers in relation to the material cured without a catalyst when concentration was increased. Without any catalyst, the network had a Tg of approximately -15°C, while materials cured with 1 and 2 wt%. ZnAc had a Tg of -16°C and -18°C, respectively. Material cured with 1 and 2 wt%. AlZn showed a Tg of -21°C and -23°C, respectively, indicating that the catalysts possibly act as a plasticizing agent in the material. The FTIR analyzes revealed that the vitrimers present higher relative intensities of the hydroxyl and ester groups bands in relation to the material obtained without a catalyst, indicating that the catalysts facilitate the cure reaction and the formation of hydroxy-ester bonds. TMA data showed that the increase in the catalyst concentration in the material promoted a decrease in Tv. The Tv of the material cured with 1 wt% of AcZn was 235°C and with 2 wt% was 195 °C. For the AlZn catalyst, a Tv of 221°C was found for 1%wt and 200 °C for 2 wt%. The Tv results of these canola oil- acid lactic networks show that these materials can be reprocessed at high temperatures, making them potential materials for application in plastic packaging obtained by thermoforming.

References

[1] Chang Li, Benzhi Ju, Shufen Zhang "Fully bio-based hydroxy ester vitrimer synthesized by crosslinking epoxidized soybean oil with doubly esterified starch." *C P* **120442**, *302*, 0144–8617.
[2] Yu-Yao Liu, Jia He, Yi-Dong Li, Xiao-Li Zhao, Jian-Bing Zeng "Biobased, reprocessable and weldable epoxy vitrimers from epoxidized soybean oil." I *C P* **112576**, *153*, 0926–6690.

P43

SUPRAMOLECULAR UPY-INTERACTIONS IN PHOTOPOLYMER NETWORKS FOR ADDITIVE MANUFACTURING

LARISSA RUPPITSCH[1], JAKOB EGGER[1], KATHARINA EHRMANN[1], THOMAS KOCH[2], JÜRGEN STRAMPFL[2], ROBERT LISKA[1]
[1] *Institute for Applied Synthetic Chemistry, Technische Universität Wien, Getreidemarkt 9, 1060 Vienna*
[2] *Institute of Materials Science and Technology, Technische Universität Wien, Getreidemarkt 9, 1060 Vienna*

Abstract

Photoresists for SLA-based 3D-printing usually depend on the formation of covalent photopolymer networks, which prohibits their reprocessing or recycling. With the rise of vitrimers, supramolecular interactions have been identified as a versatile tool to introduce such lacking reprocessability or recyclability in polymer networks. However, their use in photopolymers for additive manufacturing is still limited due to the unique challenges for such photoresists: Form-stable specimens have to be produced within only short reaction times, and the photoresist has to be a low-viscous liquid. Here we investigate the potential of Hot Lithography, an SLA-process at elevated temperatures, to process photoresists combining methacrylate and ureidopyrimidione (UPy) motifs as non-covalent crosslinking (Figure 1). Therefore, we introduce the first liquid methacrylic UPy-based monomer in a methacrylic matrix system. The formulation properties and polymerization behavior at room and elevated temperatures have been characterized in depth with RT-NIR photorheology. The materials' thermomechanical performance at varying UPy contents has been probed with DMTA and tensile tests. Finally, we demonstrate the printability of such a resist with a Hot Lithography process and its thermal reprocessing *via* a hot press to underline the potential of this system.

Figure 1: Structure of a ureidopyrimidone-containing photopolymer network at room temperature and 120 °C and reprocessing of a printed part

P44

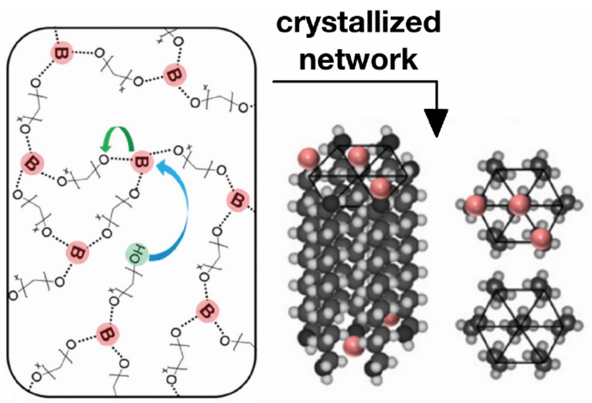
CRYSTALLINITY IN ETHYLENE VITRIMERS PROBED BY TIME-DOMAIN NMR, CALORIMETRY AND X-RAY SCATTERING

KAY SAALWÄCHTER,[1] BHASKAR SOMAN,[2] CHRISTOPHER M. EVANS[2]

[1]Institut für Physik – NMR, Martin-Luther-Universität Halle-Wittenberg, 06099 Halle (Germany) – Email: kay.saalwaechter@physik.uni-halle.de
[2]University of Illinois, Urbana-Champaign, IL (United States)

Abstract

Vitrimers, a new class of reconfigurable polymer networks based upon dynamic bonds, are considered a sustainable alternative to conventional thermosets. A potential partial crystallization can aid in further improving the mechanical properties, yet a balance with the degree of crosslinking (that normally impedes crystallization) has to be considered.[1,2,3] Here, we focus on a recently developed class of "ethylene vitrimers" made from (α,ω)-diamino alkanes and boric acid.[2] The samples were known to exhibit polymorphic crystal structures, which we now show to be distinguishable by proton NMR via their dipolar line width, enabling simple time-domain experiments based upon the related differences in transverse (T_2) relaxation.[4],[5] We can thus obtain absolute degrees of crystallinity in excess of 90%, which thus has to include the boric acid crosslinks. We can follow the kinetics of crystallization and crystal-crystal transformations in real time and elucidate the conditions under which the polymorphs form and interconvert, with a focus on recrystallization after full and partial melting. A notable increase of the melting point as well as the DSC-detected heat of melting upon long-time annealing is found to be not accompanied by an increase in crystallinity; rather, it takes place at nearly constant crystallinity (of order 90%). Therefore, T_m as well as the melting enthalpy are largely governed by the crystal perfection, which can also be followed in our NMR experiments.



DSC experiments are used to clarify an unexpected superheating effect, which challenges the determination of actual melting points. We further identify a strong memory effect in isothermal (re)crystallization. Implications of the dynamic nature of the vitrimers in relation to the kinetics of crystallization are discussed.

---

[1] Golitsyn, Y.; Pulst, M.; Samiullah, M.H.; Busse, K.; Kressler, J.; Reichert, D. *Polymer* **165,** 72 (2019)

[2] Soman, B.; Evans, C.M. *Soft Matter* **17,** 3569 (2022).

[3] Kuenstler, A.S.; Bowman, C.N. *ACS Macro Lett.* **12**, 133 (2023)

[4] Maus, A.; Hertlein, C.; Saalwächter, K. *Macromol. Chem.Phys*. **207**, 1150 (2006);

[5] Schäler, K.; Roos, M.; Micke, P.; Golitsyn, Y.; Seidlitz, A.; Thurn-Albrecht, T.; Schneider, H.; Hempel, G.; Saalwächter, K. *Solid State Nucl. Magn. Reson*. **72**, 50 (2015)

P45

UNDERSTANDING THE MODE OF ACTION OF 2,4,6-TRIS(DIMETHYLAMINOMETHYL)PHENOL AS CURING AGENT IN EPOXY-AMINE FORMULATIONS

VIKTOR SCHALLERT AND CHRISTIAN SLUGOVC

Christian Doppler Laboratory for Organocatalysis in Polymerization and Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria, viktor.schallert@tugraz.at

Abstract

2,4,6-Tris(dimethylaminomethyl)phenol (Ancamine K54) is a widely used curing agent in epoxy-amine chemistry. However, its mode of action is still not fully understood. To further the understanding, we herein study K54 and related model compounds in curing stoichiometric and substoichiometric epoxy-amine formulations.

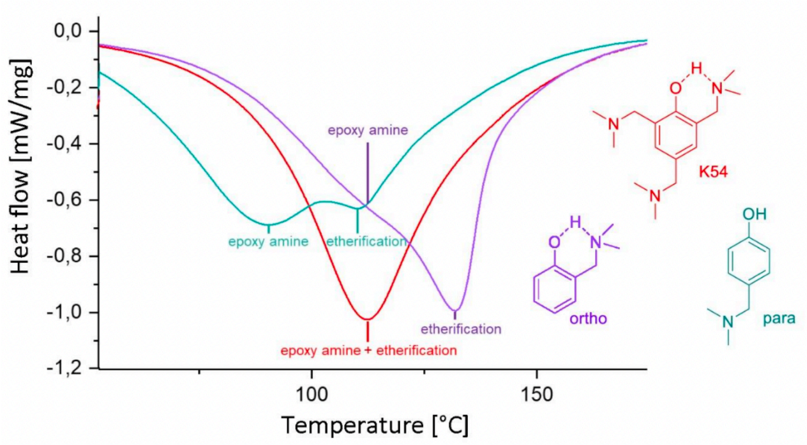


Figure 1. Performance of K54 and related compounds in curing substoichiometric epoxy-amine formulations as revealed by dynamic DSC

By a combination of dynamic DSC (Figure), NMR and IR experiments it can be shown, that the hydroxyl group of K54 interacts with one of its neighboring tertiary amines, deactivating both groups for catalysis. The residual tertiary amine-groups initiate the etherification reaction, which is particularly important for obtaining high oxirane-conversions when using formulations with substoichiometric amine content.

P46

RECYCLABLE AND REPROCESSABLE EPOXY VITRIMER ADHESIVES

Santiago, D.[1,2]; Guzmán, D.[1]; Padilla, J.[3]; Verdugo, P.[1,3]; De la Flor, S.[2]; Serra, À.[3]

1 Eurecat - Chemical Technologies Unit. C/Marcel·lí Domingo 2, 43007 Tarragona, Spain.
2 Department of Mechanical Engineering. Universitat Rovira i Virgili, Tarragona, Spain.
3 Department of Analytical and Organic Chemistry. University Rovira i Virgili, Tarragona, Spain

Abstract

Epoxy-based vitrimers represent a promising option towards sustainability and circular economy in automotive structural applications. In this work[1], a series of vitrimer materials is presented to be used as recyclable and reprocessable adhesives for such applications. Similar to those from Liu *et al.*[2], these formulations consist of diglycidyl ether of Bisphenol A- anhydride systems with glutaric anhydride and glycerol as co-curing agents in several proportions and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) or 1-methylimidazole (1MI) as catalysts. The materials obtained revealed relatively high *Tg*s, up to 85 oC, as well as a homogeneous network structure (Fig. 1a). They also showed complete stress relaxation in times as short as just 3.6 min at 180oC (Fig. 1b), shorter than usual in this type of networks[3]. Thanks to their excellent vitrimeric behavior, these thermosets were recycled and reprocessed through alcoholysis and mechanical grinding.

These formulations were also applied as adhesives for mono- and multi-material joints showing values of single-lap shear stress as high as those shown by commercial adhesives. Reversible adhesion was also studied after joint failure and after debonding without failure. In summary, the materials and methodology presented here represent a comprehensive study of recyclable and reprocessable epoxy-based vitrimers.

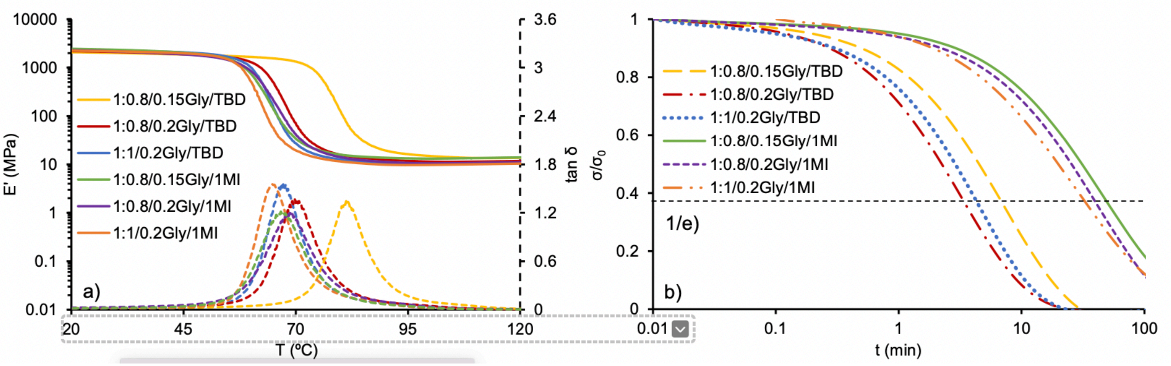


Figure 1. (a) E' modulus and tanδ as a function of the temperature of the formulations studied. (b) Normalized stress relaxation as a function of time at 180 oC for each formulation studied.

References

[1] Santiago, D.; Guzmán, D.; Padilla, J.; Verdugo, P.; De la Flor, S.; Serra, À. "Recyclable and reprocessable epoxy vitrimer adhesives". ACS Appl. Polym. Mater. DOI: https://doi.org/10.1021/acsapm.2c02063.
[2] Liu, T.; Zhang, S.; Hao, C.; Verdi, C.; Liu, W.; Liu, H.; Zhang, J. "Glycerol Induced Catalyst-Free Curing of Epoxy and Vitrimer Preparation". Macromol. Rapid Commun. 2019, 40 (7), 1–6.
[3] Han, J.; Liu, T.; Hao, C.; Zhang, S.; Guo, B.; Zhang, J. "A Catalyst-Free Epoxy Vitrimer System Based on Multifunctional Hyperbranched Polymer". Macromolecules 2018, 51 (17), 6789–6799.

P47

DISULFIDE VITRIMERIC MATERIALS BASED ON CYSTAMINE AND DIEPOXY EUGENOL AS BIO-BASED MONOMERS

Adrià Roig,[1] Marco Agizza,[2] Xavier Ramis,[3] Silvia De la Flor,[2] Àngels Serra[1]

[1]*Universitat Rovira i Virgili, Department of Analytical and Organic Chemistry, C/ Marcel·lí Domingo 1, Edif. N4, 43007 Tarragona, Spain.*
[2]*Universitat Rovira i Virgili, Department of Mechanical Engineering, Av. Països Catalans 26, 43007 Tarragona, Spain,*
[3]*Universitat Politècnica de Catalunya, Thermodynamics Laboratory ETSEIB, Av. Diagonal 647, 08028 Barcelona, Spain)*

Abstract

A series of bio-based disulfide vitrimers was obtained from diepoxy eugenol, previously synthesized, and cystamine, by an epoxy-amine polycondensation process. TREN was added to the initial formulation in different proportions to increase the crosslinking density. The materials prepared were characterized by FTIR, TGA and thermomechanical analysis. The $T_{tan□}$'s of the materials determined by DMA varied between 88.2 and 106.4 °C, on increasing the proportion of TREN in the formulation. In the same sense increased moduli in the glassy and rubbery state.

The addition of TREN, although leads to a reduction of disulfide groups in the vitrimer, increased the relaxation rate up to a maximum, at a proportion of 4 % w/w of TREN. The disulfide vitrimers prepared reached a $□_{0.37}$ at 180 °C between 1.03 and 5.80 min, and the complete relaxation in times lower than 30 min. The presence of TREN in the formulation act as a catalyst of the exchange reaction mechanism, proving that the N in the center of this structure participates in the exchange mechanism of the -S-S- metathesis. However, when the amount of TREN in the formulation overpass a certain percentage (4 % w/w), the proportion of cystamine is reduced, and the crosslinking density increases, both affecting negatively the relaxation ability.

References

[1] S. J. Tonkin, C. T. Gibson, J. A. Campbell, D. A. Lewis, A. Karton, T. Hasell, J. M. Chalker. *Chem. Sci.,* **2020,** *11*, 5537-5546

P48

A TRIFUNCTIONAL ATRP INITIATOR BEARING ADAPTABLE BONDS

GIULIA SCURANI[1], NICCOLÒ BRAIDI[1], NICOLA PORCELLI[1], FRANCESCO TASSINARI[1],
FRANCESCA PARENTI[1]

[1]Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, via Campi 103, 41125 Modena (Italy) – Email: giulia.scurani@unimore.it

Abstract

Polymers with well-defined molecular weight, dispersity, topology, composition, and functionality can be obtained by Atom Transfer Radical Polymerization.[1] This is achieved through a transition metal complex that reversibly cleaves the halogenated chain-end(s), thus allowing the controlled growth of vinyl polymers (**a**, **Figure 1**). Functional groups can be introduced into the polymer by post-functionalization of the halogenated moieties lying on the chain-end(s), or on the alkyl residue of the initiator, or by direct introduction of punctually functionalized (co)monomers – greatly enhancing the targetable applications.[2,3] In addition, the desired functional group can also be carried by the ATRP initiator, provided that the functionality is impervious to radical reactions. Some authors even explored the use of initiators containing hydrolysis- or heat-sensitive functionalities such that the final polymer exhibits self-healing properties.[4] Unfortunately, the aliphatic halide esters typically used as initiators have shown poor thermal stability.[5] For this reason, we recently synthetized a novel bifunctional benzamide-containing initiator which was successfully employed in the Activators Regenerated by Electron Transfer (ARGET) ATRP of styrene, demonstrating enhanced thermal stability.

Covalent Adaptable Networks have attracted growing interest as a promising solution to the poor recyclability of thermoset materials. When thermally treated, CANs can reorganize the connectivity between chains making reprocessing possible.[6] Our goal is now to modify the structure of benzamide-containing initiator to develop a trifunctional initiator that contains adaptable bonds. This way, the product of ATRP (inevitably crosslinked) would be recyclable, unlike the vastly more common styrene/divinylbenzene copolymeric networks (**b**, **Figure 1**).

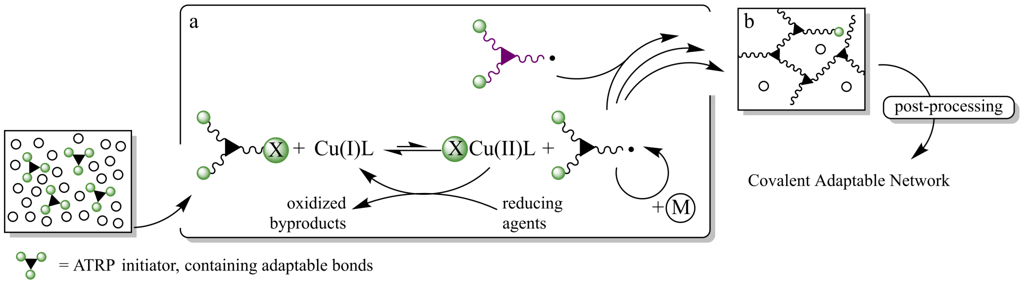


Figure 3 – a) ARGET ATRP of a vinyl monomer (M), b) resulting crosslinked polymer containing dynamic covalent bonds.

---

[1] K. Matyjaszewski, "Atom Transfer Radical Polymerization: From Mechanisms to Applications", *Isr. J. Che.* **2012**, 52, 206 – 220.

[2] Y. Yagci et al., "Telechelic polymers by living and controlled/living polymerization methods", Prog. Polym. Sci., **2011**, 36, 4, 455-567.

[3] K. Matyjaszewski, N. V. Tsarevsky, "Macromolecular Engineering by Atom Transfer Radical Polymerization", *J. Am. Chem. Soc.*, **2014**, 136, 18, 6513-6533.

[4] D. Haddleton et al., "Self-healing polymers prepared via living radical polymerisation", *Polym. Chem.*, **2010**, 1, 1, 102.

[5] O. Altintas et al. "ATRP-based polymers with modular ligation points under thermal and thermomechanical stress", *Polym. Chem.*, **2015**, 6, 15, 2854-2868.

[6] F. Van Lijsebetten et al., "Internal catalysis for dynamic covalent chemistry applications and polymer science" *Chem. Soc. Rev.*, **2020**, 49, 8425.

P49

SYNTHESIS AND CHARACTERIZATION OF A BIO-BASED TRANSESTERIFICATION CATALYST FOR GREEN PHOTOPOLYMERS

BERNHARD SÖLLE[1], SANDRA SCHLÖGL, ELISABETH ROSSEGGER[1]

[1]Polymer Competence Center Leoben GmbH, Roseggerstrasse 12, 8700 Leoben, Austria
**bernhard.soelle@pccl.at*

Abstract

In DLP (digital light processing) 3D printing, photosensitive resins are usually characterized by low viscosity, fast curing rates, high resolutions and adjustable mechanical properties. After curing, they usually behave like classic thermosets and therefore cannot be reprocessed or recycled. Since plastic pollution is one of the biggest challenges facing our society, ways to obtain sustainable materials are important. Therefore, not only bio-based monomers can be used, but also dynamic covalent bonds can be introduced into the photopolymer. A well- known example is the transesterification reaction between carboxylic acid ester bonds and free hydroxyl groups. The commonly used transesterification catalysts for such covalent adaptive networks have some drawbacks, such as their poor solubility and compromised curing speed, as well as reduced pot life. To overcome these problems, phosphate esters have been used as catalysts.[1] However, all organic phosphate esters mentioned in the literature are petroleum-based. To further improve the environmental footprint, we synthesized a new eugenol-based phosphate ester (EUGP) as a new transesterification catalyst. The catalyst is liquid and mixes well with the resin. Owing to the vinyl group, it can be covalently attached to the network and no migration takes place. Furthermore, we synthesized two different bio- based acrylates, bearing free OH- and ester moieties, based on lineseed oil and eugenol. The acrylated lineseed oil (AELO) is characterized by a high viscosity, therefore we synthesized acrylated eugenol (AEUG) which acts as a reactive diluent in our system.

To the best of our knowledge, we have successfully developed the first fully bio-based vitrimeric acrylate system for 3D printing applications. The photocurable network containing AELO and AEUG in a 1:1 ratio and 5 wt% of EUGP, exhibited high thermal stability (> 250 °C) and was able to relax 63% of the original stress within 50 minutes at 200 °C. This enables advanced applications, such as self-healing and re-shaping after 3D-printing.

References

[1] a) E. Rossegger, R. Höller, D. Reisinger, J. Strasser, M. Fleisch, T. Griesser, S. Schlögl, "Digital light processing 3D printing with thiol-Acrylate vitrimers." *Polym. Chem.*, **2021**, *12*, 639. b) E. Rossegger, R. Höller, D. Reisinger, M. Fleisch, J. Strasser, V. Wieser, T. Griesser, S. Schlögl, "High resolution additive manufacturing with acrylate based vitrimers using organic phosphates as transesterification catalyst." *Polymer*, **2021**, *221*, 123631

P50

BLENDED VINYLOGOUS URETHANE/UREA VITRIMERS DERIVED FROM AROMATIC ALCOHOLS

PHILIPP HAIDA,[1] GLORIA SIGNORATO,[1] VOLKER ABETZ [1,2]

[1] Institute of Physical Chemistry, Universität Hamburg, Grindelallee 117, 20146 Hamburg, Germany.
[2] Institute of Membrane Research, Helmholtz-Zentrum Hereon, Max-Planck-Straße 1, 21502 Geesthacht, Germany.
E-mail: gloria.signorato@studium.uni-hamburg.de

Abstract

The outstanding properties of thermosets, in terms of mechanical stability and chemical resistance, make this class of polymers attractive for various applications. However, these commercially established materials, *e.g.*, epoxy resins, phenolic resins, and polyester networks, are generally not reprocessable or recyclable due to their permanent cross-linked networks. The presented vitrimers provide reprocessable alternatives with good mechanical properties to these materials, also introducing 2,7-naphthalenediol and 1,1,1-tris(4-hydroxyphenyl)ethane as less toxic substitutes to the widely established toxic and carcinogenic bisphenol-A and resorcin-based polymers, which are increasingly being avoided and replaced in industry.

These widely used and commercially relevant aromatic alcohols were modified by fast and facile acetoacetylation with 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one to obtain acetoacetylated monomers as raw materials for vinylogous urethane/urea vitrimers. They were then cured with the commercially available poly(propylene oxide)-based trifunctional amine jeffamine T-403 and tris(2-aminoethyl)amine.

Model studies with monofunctional compounds show that aromatic acetoacetates undergo fast condensation and substitution reactions with primary amines, leading to mixtures of vinylogous urethane and vinylogous urea bonds. Both groups represent dynamic covalent bonds for thermally induced transamination reactions. Furthermore, the urethane/urea ratio can be adjusted by the solvent and/or catalyst used, and it can be shifted entirely either to vinylogous urethane or vinylogous urea bonds.

The elastomeric and thermosetting blended poly(vinylogous urethane/urea) networks derived from aromatic alcohols show short stress-relaxation times of up to 0.7 s at 130 °C and activation energies of 45-150 kJ mol^{-1} with a broad range of material properties. Moreover, the materials show remarkable reprocessing, reshaping, shape-memory and self-healing properties.

References

[1] W. Denissen, G. Rivero, R. Nicolaÿ, L. Leibler, J.M. Winne, F.E. Du Prez "Vinylogous Urethane Vitrimers" *Adv. Funct. Mater.*, **2015**, *25*, 2451-2457.

[2] A.M. Nelson, T.E. Long, "A perspective on emerging polymer technologies for bisphenol-A replacement" *Polym. Int.*, **2012**, *61*, 1485-1491.

[3] P. Haida, G. Signorato, V. Abetz "Blended vinylogous urethane/urea vitrimers derived from aromatic alcohols" *Polym. Chem.*, **2022**, *13*, 946-958.

P51

TRAPPING THE KEY INTERMEDIATE IN NUCLEOPHILE-INITIATED MICHAEL REACTIONS

MATTHIAS STEINER, ASSOC.PROF. CHRISTIAN SLUGOVC

Christian Doppler Laboratory for Organocatalysis in Polymerization, Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse. 9, 8010 Graz, Austria;
matthias.steiner@tugraz.at

Abstract

Phosphines are strong, versatile nucleophiles that are able to catalyze numerous reactions giving access to a wide variety of organic products. One reaction prominently catalyzed by phosphines is the oxa-Michael reaction, where alcohols react with Michael acceptors to form ethers. In our recent studies, we focused on oxa-Michael polymerization as a green alternative to aza- and thia-Michael reactions that employ toxic and environmentally unfriendly amines and thioles, respectively[1]. The first step in catalysis is the formation of a zwitterion, generated from a nucleophile and the Michael-acceptor.

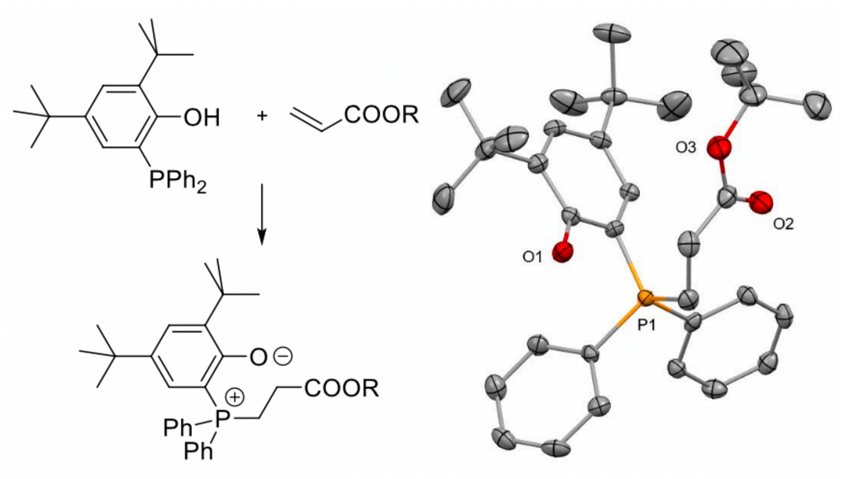


Figure 1: Zwitterion formation under investigation and XRD derived structure of a zwitterion

In our research, ortho hydroxy substituted phosphines are reacted with Michael acceptors generating zwitterions that are highly stabilized through the interaction of the alkoxide and the phosphonium ions. The reaction of 2,4-di-*tert*-butyl-6-diphenylphosphino-phenol (**1**) with Michael acceptors proceeds in good to near quantitative yields and the obtained zwitterions are air and moisture stable. The crystal structures of some of the zwitterions were obtained as well.

Investigations into the kinetics of zwitterion formation are carried out in order to generate further understanding of the governing factors of phosphine-based Michael reaction catalysis. Thereby, we seek to improve catalysis in polymerization and additional investigations will also be focused on zwitterionic polymers from these stabilized charged compounds.

References

Fischer, S. M.; Renner, S.; Boese, A. D.; Slugovc, C. "Electron-rich triarylphosphines as nucleophilic catalysts for oxa-Michael reactions." *Beilstein J. Org. Chem.* **2021**, *17*, 1689–1697.

P52

DISULFIDE-CONTAINING MONOMERS FOR REVERSIBLE UV-CURED NETWORKS

ALBERTO SPESSA[1], ROBERTA BONGIOVANNI[1], ANDREAS MÖCK[2], KURT TROCH[2], ANNA DI GIANNI[2], ALESSANDRA VITALE[1]

*[1]Department of Applied Science and Technology, Politecnico di Torino,
Corso Duca degli Abruzzi 24, 10129 Torino (Italy) – Email: alberto.spessa@polito.it*
[2] RadLab AG, Industriestrasse 1, 8956 Killwangen (Switzerland)

Abstract

Photopolymerization is a well-established technology which has gained importance over the past years for its environmental-friendly and sustainable features. Thanks to the low-energy need and fast-curing processes, UV-curable materials are nowadays one of the main choices in applications such as inks and coatings production. Despite excellent surface and bulk properties, the non-recyclability of the crosslinked coatings has been recognised as an issue by several organizations, due to the increasing attention to environmental regulations. Dynamic covalent networks (DCN), combining the benefits of thermosets and the re-processability of thermoplastics, have acquired relevance during the last few years as a possible solution to overcome the recyclability issue. Recently, dynamically crosslinked linear disulfide networks have attracted a lot of interest, in sectors like self-healing and targeting applications[1,2]. Indeed, disulfide bonds are known to be responsive to plenty of external stimuli, like pH, light, temperature, and redox conditions[3], and cleavage of disulfide with the formation of thiyl radicals could be easily achieved.

Based on these distinctive features, the introduction of disulfide-containing crosslinkers into UV-curable networks was studied as a first step for developing a reversible photopolymerizable coating. Due to the wide field of application of photopolymers, both cationic and radical photocrosslinking mechanisms were tested. In the former case, 2-hydroxyethyl disulfide (HEDS) was added in an epoxy formulation, exploiting the addition mechanism between the diol and the epoxy ring for the creation of a polymeric network. Then in the latter, following the work of Zhang *et al.*[4], a disulfide-containing diacrylate monomer was synthesized starting from HEDS and crosslinked through a radical photopolymerization reaction.

Figure 4: Possible reversible crosslinking mechanism designed for disulfide-containing networks

---

[1] Maes S. *et al.*, *Macromol. Chem. Phys.*, **2022**, 2100445.
[2] Li X. *et al.*, *ACS Macro Lett.*, **2019**, 8, 1511-1516.
[3] Deng G. *et al.*, *ACS Macro Lett.*, **2012**, 1, 275-279.
[4] Zhang M. *et al.*, Chem. Eng. J., **2020**, 390, 124625.

P53

INFLUENCE OF IMPURITIES OF "TECHNICAL" GRADE CHEMICALS ON VITRIMER NETWORK CHARACTERISTICS

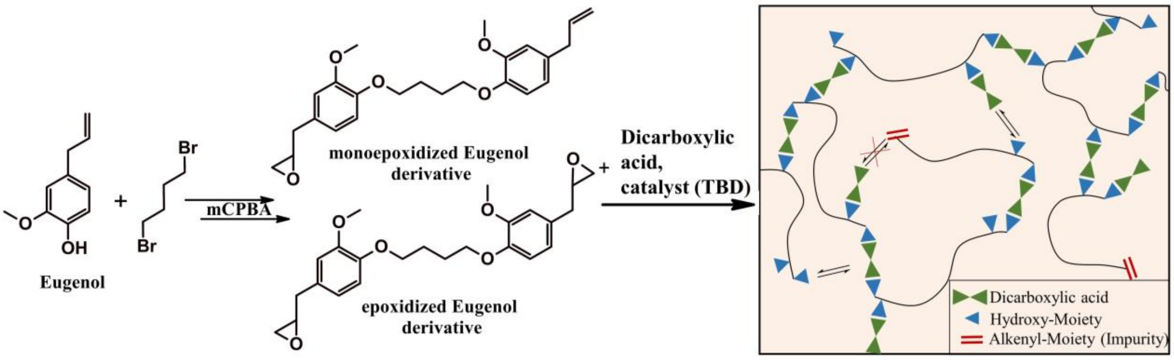
ROBIN TANNERT[1], ANDREAS TAUBERT[2], JENS WEBER[1]
[1]ZIRKON, University of Applied Science Zittau/Görlitz, Theodor-Körner-Allee 16, 02763 Zittau (Germany) – Email: robin.tannert@hszg.de
[2]Institute of Chemistry, University of Potsdam, Karl-Liebknecht-Straße 24-25, 14476 Potsdam OT Golm, Germany

Abstract

The recent introduction of vitrimers (covalent adaptable networks with constant network density) by Leibler and coworkers gave accesss to a new class of thermosets. It is a finding, which does enable significant improvements of the sustainability of polymer networks as recycling und reuse is possible more easily[1]. Functional groups, which are able to cleave and reconnect their bonds, triggered by an external stimulus, allow the network to readopt its structural and morphological properties.

For a potential scale up into technical applications of vitrimers, their processing conditions need to be attractive, as in particular high costs will impede the launch into the market. Here, the processing time plays a key role. Therefore, numerous efforts have been made to determine the impact of parameters such as temperature, catalyst, catalyst concentration, availability of reactive moieties, etc. on the necessary processing times[2][3]. In technical scale chemicals do often possess some impurities compared to laboratory scale, which leads to the integration of non or less reactive species and therewith a changed processing behaviour. This might change the stoichiometry of the reaction and hence the network properties and is hence of interest.

Starting from eugenol we synthesized a diepoxy eugenol derivative via a PRILEZHAEV reaction and combined the monomer with different dicarboxylic acids. To integrate impurities in a defined amount we changed synthesis conditions to obtain a product mix of mono- and diepoxidized eugenol derivatives. The remaining, unreacted double bond should be seen as an impurity in a technical grade chemical whose effects on the network characteristics were determined. We investigate the changes in thermal and mechanical network properties as well as the vitrimer reprocessing ability in dependence on a varying content of impurities.



Acknowledgments

Financial Support from the German Federal Ministry of Education and Research (BMBF, FKZ: 13FH2I06IA) is highly acknowledged.

[1] Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Science 2011, 334, 965-968
[2] Capelot, M.; Unterlass, M. M.; Tournilhac, F.; Leibler, L. ACS Macro. Lett. 2012, 1, 789-792
[3] Van Lijsebetten, F.; Debsharma, T.; Winne, J. M.; Du Prez, F. E. Angew. Chem. Int. Ed. 2022

P54

DESIGNING BIOBASED POLYESTER-IMINES FOR CHEMICAL RECYCLABITY AND ENZYMATIC DEGRADABILITY

SATHIYARAJ SUBRAMANIYAN[1,2], ANNA LIGUORI[1], PER-OLOF SYRÉN[1,2,3], MINNA HAKKARAINEN[1,2]*

[1] *KTH Royal Institute of Technology, Department of Fibre and Polymer Technology, Teknikringen 58, 100 44 Stockholm, Sweden*
[2] *KTH Royal Institute of Technology, Wallenberg Wood Science Center (WWSC), Teknikringen 58, 100 44 Stockholm, Sweden*
[3]*KTH Royal Institute of Technology, Biotechnology and Health, Science for Life Laboratory, Teknikringen 58, 100 44 Stockholm, Sweden*
*Email: satsub@kth.se

The development of bio-based plastics has the potential to bring many positive environmental impacts, however, to be truly effective, materials should be designed for sustainable end-of-life management, enabling a truly circular flow of plastics. Due to the presence of reversible ester bonds, polyesters are well-suited for circular material flows. Chemical recovery can be further facilitated by utilizing other dynamic covalent chemistries to include a second, more easily reversible bond, such as a Schiff base/imine bond, allowing depolymerization back to the monomeric or oligomeric products under mild conditions.[1-3]

Here we present, the synthesis and characterisation of three vanillin-derived Schiff-base (SB) monomers by utilizing three different diamines and a simple two-step process, involving a nucleophilic substitution reaction followed by Schiff base formations. The monomers were further polymerized with potentially bio-sourced aliphatic and aromatic diesters by using conventional two step bulk polycondensation protocol (transesterification and polycondensation) in the presence of metal catalyst (e.g. dibutyltin oxide) to yield six different polyester-imines with different aliphatic-aromatic contents. All the monomers and polymers were characterized for structure and thermal properties by 1D and 2D NMR, FTIR, DSC and TGA. Moreover, the chemical recyclability and hydrolytic degradability of the synthesized polyester-imines were evaluated under mild conditions in acidic medium and by utilizing ^{1}H NMR spectroscopy for the product identification. Finally, the susceptibility of the synthesized polyester-imines to enzymatic degradation by PETase was demonstrated.

Acknowledgements
Authors are grateful for the financial support from the Wallenberg Wood Science Center (WWSC) financed by Knut and Alice Wallenberg Foundation.

---

[1] Xu, Y.; Odelius, K.; Hakkarainen, M. Photocurable, thermally reprocessable and chemically recyclable vanillin-based imine thermosets. *ACS Sustainable Chem. Eng.*, **2020**, *8*, 17272-17279.
[2] Liguori, A.; Hakkarainen, M. Designed from biobased for recycling: Imine-based covalent adaptable networks, *Macromol. Rapid Commun.*, **2022**, 2100816.
[3] Liguori, A.; Subramaniyan, S.; Yao, J. G.; Hakkarainen, M. Photocurable Extended Vanillin-Based Resin for Mechanically and Chemically Recyclable, Self-Healable and Digital Light Processing 3D Printable Thermosets. *Eur. Polym. J.* **2022**, *178*, 111489.

P55

FROM DEPOLYMERIZATION OF UNSATURATED POLYESTER RESINS TO VITRIMERS

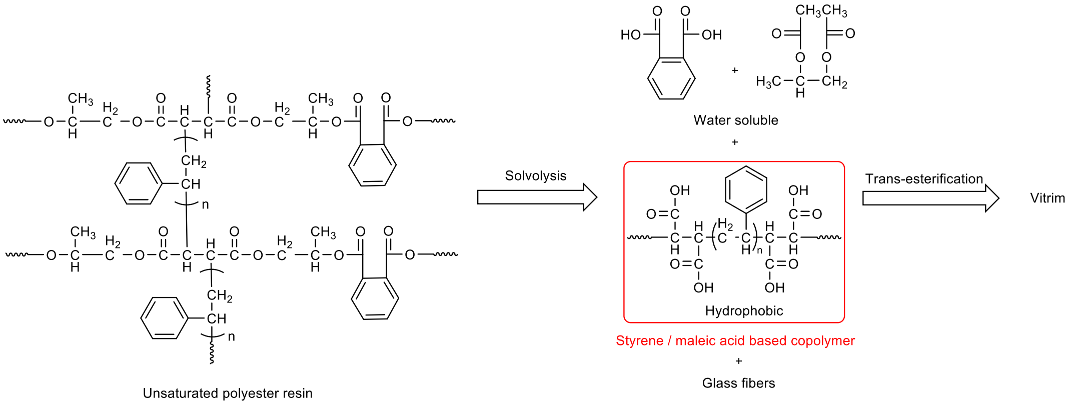
C. TRIBOUT[1,2,3], T. FAHLER[3], A. BEIGBEDER[3], L. VILCOCQ[1], E. DROCKENMULLER[2*], D. MONTARNAL[1*]

[1]Catalyse, Polymérisation, Procédés et Matériaux (CP2M), UMR 5128, CNRS, CPE, Université Lyon 1, France
[2]Ingénierie des Matériaux Polymères (IMP), UMR 5223, CNRS, Polytech, Université Lyon 1, France
[3]Centre Technique Industriel de la Plasturgie et des Composites (IPC), Bellignat, France.
eric.drockenmuller@univ-lyon1.fr, damien.montarnal@univ-lyon1.fr

Composite materials with unsaturated polyester resin (UPR) matrices are widely spread industrially and are used, among other things, in the construction of boat hulls. They are mostly composed of glass fibers and thermosetting resins like unsaturated polyesters cross-linked with styrene, allowing to obtain light materials, with good mechanical properties and inexpensive.[1] Waste from end-of-life composites is barely recycled, since they are mostly buried, abandoned, or burned. However, the practice of landfilling is set to disappear by 2030-2040 given national, european and international directives. The deconstruction of nearly 140,000 boats per year is expected before 2030-2040.[2] It is therefore necessary to find new ways in accordance with a more sustainable circular economy to recycle composite parts including the ones made of unsaturated polyester resins.

In this context, we are interested in valorizing UPR waste into new vitrimer resins with comparable mechanical features, and that can be recycled and reused following a sustainable and economical circular lifespan.[3]

We will present our strategy that includes catalyzed solvolysis of model UPR in mild conditions, that enables to isolate poly(styrene-*co*-maleic acid) copolymers in good yields. These copolymers are used as primary resources to synthesize vitrimer networks with high glass transition temperatures.



References

[1] Zaske, O. C.; Goodman, S. H.; "Unsaturated Polyester and Vinyl Ester Resins" *Handbook of Thermoset Plastics*; *Elsevier* **1998**, 97–168.

[2] Monier, V.; Hestin, M.; Trarieux, M.; Lemeillet, A.; Laroche, M.; Dupont, V.; Maumenee, G.; "Etude préalable à la mise en place de la filière de collecte et de traitement des navires de plaisance ou de sport hors d'usage sous la responsabilité des producteurs (REP)" **2016**

[3] Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. "Silica-like malleable materials from permanent organic networks" *Science* **2011**, *334*, 965–968.

P56

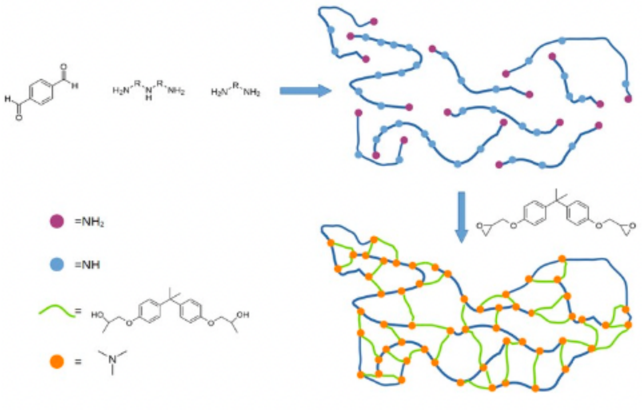
NOVEL EPOXY-POLYIMINE VITRIMER NETWORKS FOR CARBON FIBER REINFORCED COMPOSTES

TOMMASO TELATIN[a], XAVIER MONTANÉ[a*], SILVIA DE LA FLOR[b], ÀNGELS SERRA[a*]

[a] Universitat Rovira i Virgili (URV), Dept. of Analytical and Organic Chemistry, C/ Marcel·lí Domingo s/n, 43007, Tarragona, Spain. [b.] Universitat Rovira i Virgili, Department of Mechanical Engineering, Av. Països Catalans 26, 43007 Tarragona, Spain.

Abstract

Typically epoxy thermosets are used as binders to produce high-performance Carbon Fibers Reinforced Composites (CFRC) with superior mechanical properties. The main drawback of these materials regards their intrinsic non-repairability and the difficulties on the carbon fibers recover at the end of the object's life. Indeed, for CFRCs made with common epoxy thermosets, the fiber recovery often occurs through a mechanical process in which the material is ground, with the consequent reduction of the length of the fibers [1]. Of course, it represents a critical limit for fibers reuse. From this point of view, using vitrimers as a binder in CFRCs introduces the possibility of making these materials repairable and recyclable, ensuring the recovery of the carbon fibers through a chemical process that preserves the integrity of the fibers avoiding any grinding process that could damage them [2]. Vitrimers, as part of the family of Covalent Adaptable Networks (CANs), exhibit covalent cross-links that become reversible under specific stimuli. Moreover, the rate of bond exchange exhibits an Arrhenius-like temperature dependence, enabling molding, welding, and recycling of the pure polymeric materials while maintaining constant the cross-link density of the network [3]. This work focuses on developing vitrimeric materials that take advantage of the imine chemistry to introduce reversible bonds in the network. In particular, commercially available monomers have been used because of their wide availability and low price. Amine-terminated poly-imines containing unreacted secondary amine groups have been firstly synthesized and then cross-linked through reaction with an epoxy resin. The strategy employed to explore the properties of the obtained materials involves thermal and thermo-mechanical characterization by using Differential Scanning Calorimetry and Dynamic Mechanical Thermal Analysis, respectively.



Scheme 1. Synthesis of the epoxy-polyimine vitrimeric compounds.

References

[1] A. Dorigato, Adv. Ind. Eng. Polym. 2021, 4, 116-132.
[2] P. Taynton, H. Ni, C. Zhu, K. Yu, S. Loob, Y. Jin, H. Qi, W. Zhang Adv. Mater. 2016, 28, 2904-2909.
[3] J. Zheng, Z.M. Png, S.H. Ng, G.X. Tham, E. Ye, S.S. Goh, X.J. Loh, Z. Li Mater. Today 2021, 51, 586-625.

P57

METHOD DEVELOPMENT FOR MONITORING FAST CURING POLYMER NETWORKS WITH BIO-BASED COMPONENTS

PAULINE VOIGT[1], BRIGITTE VOIT[1,2]

[1] *Institute of Macromolecular Chemistry, Leibniz Institute of Polymer Research Dresden (IPF), Hohe Str. 6, 01069 Dresden, Germany.* voigt@ipfdd.de

[2] *Institute of Macromolecular Chemistry, Chair of Organic Chemistry of Polymers, Technical University Dresden, 01069 Dresden, Germany.*

Abstract

Taking responsibility for the future and becoming a sustainable society will depend on the chemical industry investing in processes and products to make “green chemistry” available. Establishing sustainability as part of the material development and performance is a pressing issue of our time, requiring fundamental changes in the materials and manufacturing industry. This issue opens a new topic, the investigation of sustainable chemicals and formulations, which are not comparable to the oil-based resources and thus, newly require system-design to begin at the molecular level, leaving a positive footprint.

The study of the network formation of fast curing polymers like methacrylate resins is still a challenge. But a crucial aspect in the material and product development for the application. So far, the study of the network formation of radical curing methacrylate resins as tertiary systems has been neglected, which is rather challenging due to the speed of the curing reaction nature of thermosets. Understanding the reaction mechanism is essential to effectively adapt the composition incorporating bio-based compounds.

A regime of analytical methods has been implemented to investigate the polymerization reaction and the crosslinked polymer material. Monitoring the reaction is done by common methods, such as near infrared spectroscopy and isotherm differential scanning calorimetry to follow the conversion.[1] For the investigation with vibrational spectroscopy a homogenous resin model system was developed. Fast sampling rheology was utilized to evolve an in-situ measurement procedure for the curing reaction of low viscous systems. Thus, the change of mechanical properties during the reaction is monitored. Those analytical methods had to be developed for the rapid radical polymerization and required adjustment to various properties of the changing state of matter. The network structure is investigated through swelling experiments and dynamical mechanical analysis.

Structural changes by implementing bio-based compounds are to be compared to the oil-based reference system to understand secondary interactions, as well as specific functionalities. This study will allow more effective experimenting for sustainable material development. Prospectively the implementation of dynamic crosslinker, like cyclic Triazine structures would be the next step to form a dynamic methacrylate network, which concludes a sustainable life cycle.

References

[1] D. Tenzer, Curing kinetics of two component methacrylate resins with inhibitors: Reaction monitoring and simulation, TU Darmstadt, 2018.

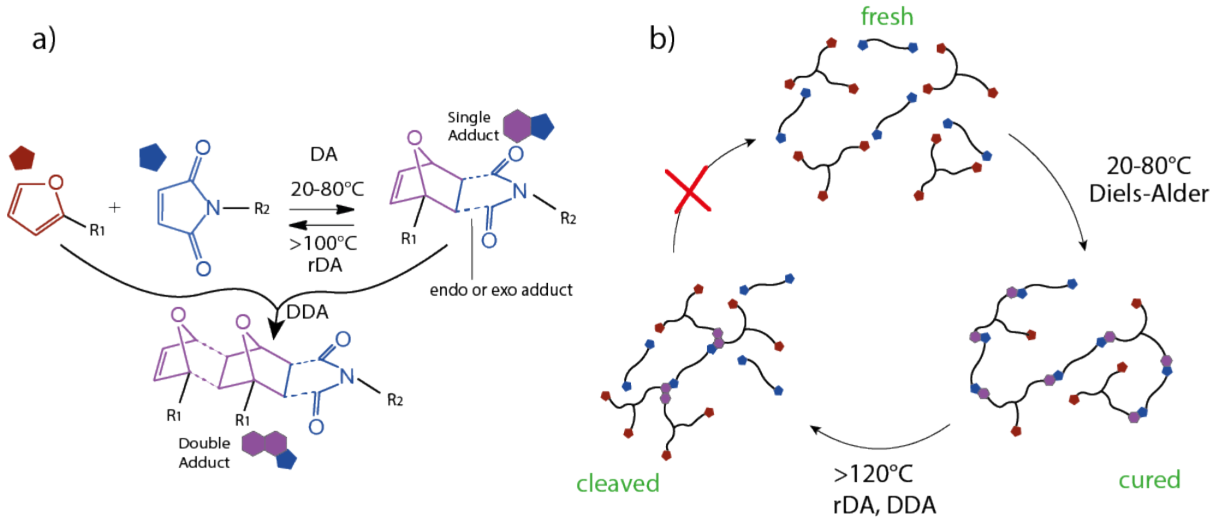
P58

BEYOND DIELS-ALDER: DOMINO REACTIONS IN FURAN-MALEIMIDE CLICK NETWORKS

PAUL VAN DEN TEMPEL, JOZEF G.M. WINKELMAN, ANTONINA. V. KRASNIKOVA, PETER J. DEUSS, FRANCESCO PICCHIONI, RANJITA K. BOSE
University of Groningen, Engineering and Technology institute Groningen (ENTEG), Nijenborgh 4, Groningen 9747 AG, The Netherlands. Email: p.van.den.tempel@rug.nl

Abstract

The furan-maleimide Diels-Alder chemistry has emerged as an important tool to design thermo-reversible click networks. This not only preserves the strong and robust properties of thermo-sets and rubbers, but also makes it possible to cleave crosslinks at non-degradative temperatures, or in other words to recycle them. In this work a new reaction is reported in furan-maleimide click networks, which is the Double-Diels-Alder reaction (DDA), also known as domino Diels-Alder. Current work shows with nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC) and kinetic studies that the DDA reaction can occur both in intramolecular and intermolecular fashion between an adduct and a furan. DDA opens up a path to tune product strength by introducing a thermal treatment step that allows the domino adducts to form with good control, or can be prevented by avoiding a surplus of mobile furan molecules, if complete reversibility of these materials is desired.
.



References

[1] G. Mali, A. N. S. Chauhan, K. A Chavan, R.D. Earned "Development and Applications of Double Diels-Alder Reaction in Organic Synthesis." *Asian Journal of Organic Chemistry* **2021**, 10. 15, 2848–2868.
[2] A. Gandini, "The furan/maleimide Diels-Alder reaction: A versatile click-unclick tool in macromolecular synthesis" *Prog. Polym. Sci.* **2013**, 38, 1, 1–29, 2013

P59

POLYHYDROXYURETHANE-BASED VITRIMERS WITH NON-URETHANE DYNAMIC COVALENT BONDS

SERGEI V. ZUBKEVICH, ALEXANDER S. SHAPLOV, DANIEL F. SCHMIDT

Luxembourg Institute of Science and Technology, 5, Avenue des Hauts-Fourneaux, L-4362 Esch-sur- Alzette,Luxembourg.

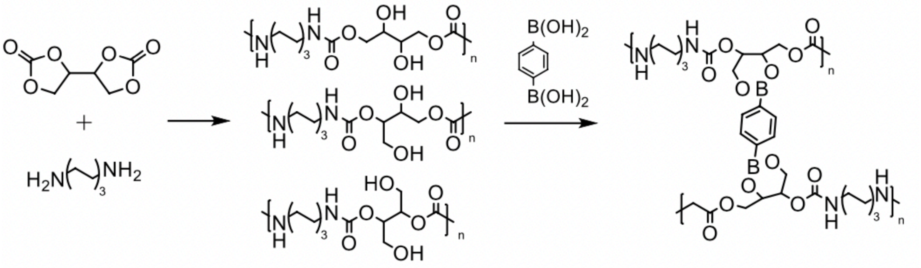
sergei.zubkevich@list.lu; alexander.shaplov@list.lu;daniel.schmidt@list.lu

Abstract

Non-isocyanate polyurethanes (NIPUs) or more specifically, their sub-class – polyhydroxyurethanes (PHUs) are extensively investigated [1] as a “green” alternative to conventional polyurethanes (PUs), which are produced with the use of hazardous and toxic isocyanates. However, the molecular weights of PHUs are generally limited to 20000 Da due to side reactions and strong hydrogen bonding between growing polymer chains [2]. This results in reduced mechanical properties of these polymers and thus limits further practical application of thermoplastic PHUs.

Different approaches to solve this problem, such as chain extension or formation of hybrid PHU-based polymers [3] have been suggested, but none of them achieved the desirable effect to date. In this study for the first time, we report another alternative approach consisting in one-pot synthesis of PHUs and their cross-linking via formation of cyclic boron esters capable of dynamic bond exchange to form a PHU-based vitrimeric material (see figure).

The first step in vitrimer preparation relates to the synthesis of tailored PHUs containing two adjacent hydroxyl groups separated by 2 to 4 carbon atoms via the reactive extrusion (see figure). Further on PHUs were converted to the respective vitrimers using the reaction between 1,4-benzenediboronic acid and the adjacent hydroxyl groups in polymer backbone. The rapid exchange of B-O bonds allows to perform this modification directly in the microcompounder without the isolation of the PHU polymer and further remold the vitrimeric material in the desired shape.



This work was supported by European Commission’s project 101066839 (SPRUT) under HORIZON-TMA-MSCA-PF-EF action.

References

[1] Gomez-Lopez, A.; Elizalde, F.; Calvo, I.; Sardon, H. Trends in Non-Isocyanate Polyurethane (NIPU) Development. *Chem. Commun.* **2021**, *57* (92), 12254–12265. https://doi.org/10.1039/D1CC05009E.
[2] Blain, M.; Cornille, A.; Boutevin, B.; Auvergne, R.; Benazet, D.; Andrioletti, B.; Caillol, S. Hydrogen Bonds Prevent Obtaining High Molar Mass PHUs. *J. Appl. Polym. Sci.* **2017**, *134* (45), 44958. https://doi.org/10.1002/app.44958.
[3] Bizet, B.; Grau, E.; Asua, J. M.; Cramail, H. Hybrid Nonisocyanate Polyurethanes (H-NIPUs): A Pathway towards a Broad Range of Novel Materials. *Macromol. Chem. Phys.* **2022**, *223* (13), 2100437. https://doi.org/10.1002/macp.202100437.

P60

ARGET-ATRP SYNTHESIS OF THERMOPLASTIC ELASTOMERS FROM RENEWABLE SOURCES

ANIELLO VITTORE,[A] ORLANDO SANTORO,[A] ROSITA LA PENTA,[B] MICHELA CAPRIO,[B] LORELLA IZZO,[A] MASSIMO MELLA[C].
[a] Dipartimento di Biotecnologie e Scienze della Vita, Università degli Studi dell'Insubria, Via J.H. Dunant 3, 21100, Varese, Italy; [b] Prometeon Tyre Groups srl, viale Sarca 222, 20126, Milano, Italy; [c] Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, Via Valleggio 11, 22100, Como, Italy, avittore@uninsubria.it

Thermoplastic elastomers (TPEs) are a class of copolymers characterized by dynamic polymer networks, i.e. physical and reversible chains-entanglements, which bestow them with the property of both being processable and recyclable like thermoplastics, and elastic like elastomers. Nowadays, the most common and used TPEs find application in many industries such as electronics, adhesives, and automotive components [1]. In view of switching from the current economic model to a circular one, TPEs represent promising materials; in fact, they may fulfil the need for products life cycle extension and waste prevention. Additional research efforts appear, however, desirable if one wishes to lighten the need for oil derived chemicals, as well as the overall economic and environmental impact of the synthetic processes.

In this scenario, our contribution reports on the synthesis of TPEs by ARGET-ATRP, a *living* polymerization that employs low amount of metal catalyst and organic solvent [2]. As for the copolymer composition, either dihydroeugenol (DEu) or carvacrol (Ca) methacrylates were used to form the *hard* part (i.e. high T_g, **A**) of the TPE, while dodecylmethacrylate (DMA) was employed to generate the *soft* entangled block (i.e. low T_g, **B**) [3].

A series of **A-B-A** copolymers have been successfully synthesized from a bifunctional macroinitiator based on polyDMA. Materials containing different lengths of the *soft* part (about 50 or 100 kDa) and a weight fraction of the *hard* part in the range 20-40% have been obtained in presence of ppm of catalyst. They have been characterized by ^{1}H-NMR and ATR-IR spectroscopy, GPC and DSC.

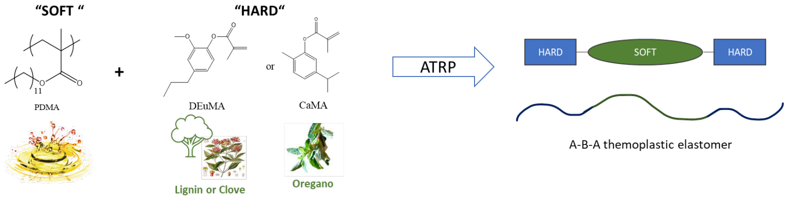


Figure 1: Graphical abstract of sustainable TPEs synthesis from renewable materials.

References

[1] J. G. Drobny, "Handbook of thermoplastic elastomers" *Elsevier*, **2014**.
[2] X. Pan, M. Fantin, F. Yuan, K. Matyjaszewski "Externally controlled atom transfer radical polymerization" *Chemical Society Reviews* **2018**, 47(14), 5457.
[3] A. L. Holmberg, J. F. Stanzione, R. P. Wool, T. H. Epps, "A Facile Method for Generating Designer Block Copolymers from Functionalized Lignin Model Compounds" *ACS Sust. Chem. Eng.* **2014**, *2*, 569–573.

P61

ENR BASED SELF-HEALING ELASTOMERS WITH FAST ELASTIC RETURN FOR SOFT ROBOTICS

Jakob Langenbach,[1] Camille Bakkali-Hassani, [1] Seppe Terryn, [2] Bram Vanderborght, [2] François Tournilhac[1] and Sophie Norvez[1]
[1]Molecular, Macromolecular Chemistry, and Materials, C3M, ESPCI Paris, PSL University, CNRS UMR7167, 75005 Paris, France
[2] Brubotics, Vrije Universiteit Brussel and Imec, Pleinlaan 2, Elsene 1050, Belgium

Addition of soft materials into robotic devices allows better flexibility and adaptability to the environment than when robots are made of hard and rigid components. However, soft materials are also more prone to damage than their rigid counterparts, what is a major disadvantage for soft-bodies robotic systems, that must be capable to handle sharp objects or work in unpredictable environments. Therefore, incorporation of self-healing (SH) materials into soft robots has the advantage that damage can be repaired and thus the robot lifetime prolonged [1]. Dynamic covalent chemistry has allowed the emergence of elastomers showing remarkable self-healing properties. Nevertheless, the speed of the elastic response of SH materials has been rarely discussed. Still, this parameter is very important when the elastomer has to be implemented into fast responsive actuators.

In this work, self-healing elastomer networks exhibiting fast return and full recovery are prepared from commercially available epoxidized natural rubber (ENR) and H-bonds functionalized fatty acids, in a two-step process using up to 98 wt % of bio-sourced material. At high deformations, the material presents an ultimate tensile strength of 2.5 MPa at 1000% strain, and full recovery of these static properties after cut and 1 h self-healing at 180 °C. Under cyclic experiments, the material is capable of following 10-60% deformation at 5 Hz over more than 100 cycles, only when hydrogen bonds are present (Figure 1). The fast dynamic response is fully restored after cutting the sample in half and healing it at room temperature for only 1 min. Diverse experiments demonstrated that the transesterification reaction has a minor influence compared with H-bonding and crosslink density on the autonomous healing at ambient temperature [2]. The potential of this sustainable SH material (renewable feedstock, no solvent, no by-product) was supported by successful implementation into an operative inflatable soft finger prototype.

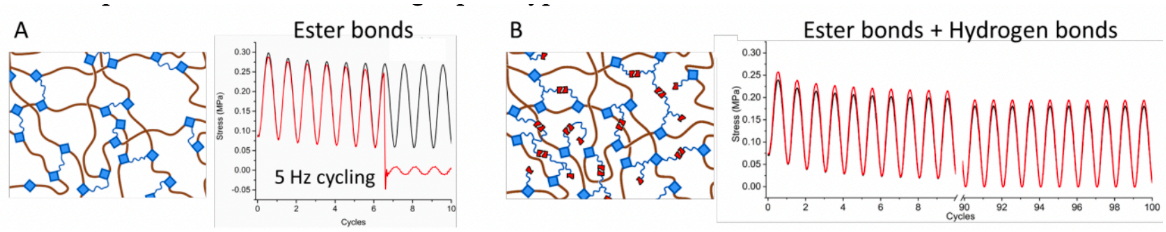


Figure 1. Tensile cycles within 10-60% strain amplitude at 5 Hz frequency, on pristine samples (black); on samples self-healed for 1 min at RT (red). ENR samples cross linked with A: ester bonds; B. ester and H-bonds.

[1] S. Terryn et al, A review on self-healing polymers for soft robotics, Materials Today, 47, 187-205
[2] J. Langenbach et al, Adhesion and stiffness matching in epoxy-vitrimers/strain sensor fiber laminates, ACS Appl Polym Mater 2022, 4, 1264-1275

P62

HYDROLYTICALLY STABLE, RNA-INSPIRED NEIGHBORING GROUP ASSISTED REARRANGEMENT IN DYNAMIC COVALENT NETWORKS

ROY WINK*, SOUMABRATA MAJUMDAR, ROLF A.T.M. VAN BENTHEM, JOHAN P.A. HEUTS, RINT P. SIJBESMA

* Department of Chemical Engineering & Chemistry and Institute for Complex Molecular Systems, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands.

Email: r.wink@tue.nl

Abstract

Recently, our group has introduced catalyst-free transesterification in phosphate triesters as new chemistry in Dynamic Covalent Networks. [**1**] The observed stress relaxation of this network was comparable to externally catalyzed carboxylate ester networks. Soon after, an associative network based on efficient β-hydroxy phosphate exchange in phosphate triesters was published, [**2**] yet the mechanism of this networks was left unstudied. The effect in these networks, where neighboring groups actively participate in the exchange mechanism, leads to relatively fast rearrangement without the use for external catalysts, and is therefore widely researched by our group and others. [**3**, **4**] We later showed that the exchange mechanism in the β-hydroxy phosphate exchange also goes via this internally catalyzed, dissociative mechanism. [**5**] The developed material showed very efficient exchange, making reprocessing via extrusion possible, which is highly interesting for applications like 3D-printing. Still, this material was yet to be optimized due to relatively fast hydrolytic degradation.

Phosphate esters self-cleaving via beta-hydroxyl internal catalysis is a process observed in nature with the self-cleavage of RNA, with the major structural difference in the fact that the RNA backbone consists of phosphate diester anions, instead of phosphate triesters. Phosphate diesters, especially in their anionic form, are generally hydrolytically more stable than phosphate triesters, due to the high negative charge density on the phosphorus center. [**6**] In an effort to arrest the hydrolytic instability of our previous networks, inspiration was taken from nature, and a dynamic covalent network containing phosphate diester anion-based crosslinks was developed and researched. The most recent results will be presented

References

[1] Majumdar, S.; Zhang, H.; Soleimani, M.; van Benthem, R. A. T. M.; Heuts, J. P. A.; Sijbesma, R. P. Phosphate Triester Dynamic Covalent Networks. ACS Macro Lett. **2020**, *9* (12), 1753–1758.
[2] Feng, X.; Li, G. Catalyst-Free Beta-Hydroxy Phosphate Ester Exchange for Robust Fire-Proof Vitrimers. J. Chem. Eng. **2021**, *417*, 129132.
[3] Delahaye, M.; Winne, J. M.; Du Prez, F. E. Internal Catalysis in Covalent Adaptable Networks: Phthalate Monoester Transesterification As a Versatile Dynamic Cross-Linking Chemistry. J. Am. Chem. Soc. **2019**, *141* (38), 15277–15287.
[4] Zhang, H.; Majumdar, S.; van Benthem, R. A. T. M.; Sijbesma, R. P.; Heuts, J. P. A. Intramolecularly Catalyzed Dynamic Polyester Networks Using Neighboring Carboxylic and Sulfonic Acid Groups. ACS Macro Lett. **2020**, *9* (2), 272–277.
[5] Majumdar, S.; Mezari, B.; Zhang, H.; van Aart, J.; van Benthem, R. A. T. M.; Heuts, J. P. A.; Sijbesma, R. P. Efficient Exchange in a Bioinspired Dynamic Covalent Polymer Network via a Cyclic Phosphate Triester Intermediate. Macromolecules **2021**, *54* (17), 7955–7962
[6] Kirby, A. J.; Nome, F. Fundamentals of Phosphate Transfer. Acc. Chem. Res. **2015**, *48* (7), 1806–1814.

P63

THIOMETHACRYLATES AS DEGRADABLE CROSSLINKERS IN POLYMER NETWORKS

MATTHEW LAUREL,[1] DANIEL MACKINNON,[1] JONAS BECKER,[1] ROBERTO TERRACCIANO,[1]
BEN DRAIN,[1] HANNES H. HOUCK[1,2] AND C. REMZI BECER[1]

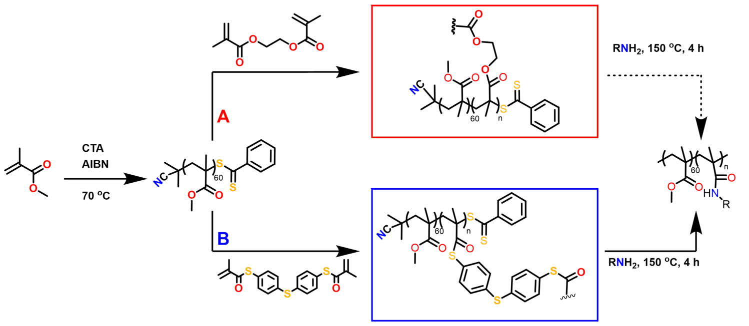
[1]Department of Chemistry, University of Warwick, Coventry, CV4 7SH, UK
[2]Institute of Advanced Study, University of Warwick, Coventry, CV4 7SH, UK
Email: M.Laurel@warwick.ac.uk

Abstract

Thioesters offer advantages over their oxo-ester analogues due to their increased reactive nature,. The poorer orbital overlap between the carbon and sulfur of the thioester results in the latter being more prone to nucleophilic attack. This improved reactivity is utilised both in nature, and increasingly in polymer networks in the search for degradable, dynamic, and more sustainable materials.[1]

Whilst thioesters have been extensively studied within the backbones of polymers, the use of thioacrylates and thiomethacrylates have been limited. Hadjichristidis et al. synthesised thiomethacrylates in a one-step synthesis of a thiol with methacryloyl chloride in aqueous base, before the monomers were polymerised via free radical polymerisation.[2] In more recent years, Becer and co-workers have applied thio(meth)acrylates in the field of living radical polymerisation.[1]

In this talk, the reactivity of thioesters compared to their oxygen analogues will be discussed with the aim to design polymer materials that are degradable under are more accessible conditions. Specifically, the aminolysis of the carbonyl moieties within poly(thiomethacrylates) and poly(methacrylates) have been studied and contrasted. Based on the swift aminolysis of thiomethacrylates, a bisfunctional crosslinkinker derivative has been synthesised, and used for the preparation of degradable core-crosslinked star-shaped polymers. The thiomethacrylate crosslinker could be copolymerised with conventional methacrylates via RAFT, thereby introducing programmed degradability of covalently crosslinked materials.[3] Understanding the contrasting reactivity of the thioesters within these polymers, compared to esters, along with the straightforward and scalable synthesis of a thiomethacrylate crosslinker is believed to allow for a wide range of thioester-containing polymer networks to be formed, potentially opening new opportunities in the synthesis of dynamic covalent materials.



Scheme 1- The selective degradation of thiomethacrylate-crosslinked star-shaped polymers.

---

[1] S. Aksakal, R. Aksakal and C. R. Becer "Thioester functional polymers". *Polym. Chem.,* **2018,** 9, 4507-4516

[2] N. Hadjichristidis, C. Touloupis and L. J. Fetters "Solution properties and chain flexibility of poly(thiolmethacrylates). 2. Poly(cyclohexyl thiolmethacrylate)". *Macromolecules*, **1981,** 14, 128-130

[3] M. Laurel, D. MacKinnon, J. Becker, R. Terracciano, B. Drain, H. A. Houck and C. R. Becer " Degradable thioester core-crosslinked star-shaped polymers". *Polym. Chem.,* **2022,** 13, 5579-5589.

P64

STIMULI RESPONSIVE POLYMERS VIA MOLECULAR RECOGNITION

Francesco Rispoli, Anjali Devi Das, G. Mannoni, A. E. Früh, Roberta Pinalli, and Enrico Dalcanale

Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Parma, Italy

Molecular recognition is the most sophisticated form of weak interaction in terms of precise responsiveness, since it requires a well-defined arrangement of complementary non-covalent interactions to operate at its best. Macrocyclic receptors, like cucurbiturils (CB[n]) and cavitands are particularly suited for the fine tuning of weak interactions due to their synthetic modularity and multiple binding modes. The ability to detect early damage is of great significance in load bearing composite materials used for high performance applications. Microdamages, if left unchecked, can grow under subsequent stress, leading to catastrophic structural failure. The sensing of early stage damage via nondestructive methods is therefore critically important for the safe use of these materials. Herein a supramolecular approach to self-diagnosis of early stage damage in a carbon fiber epoxy composite material, via the incorporation of a CB[8] based ternary complex as an additive is reported.

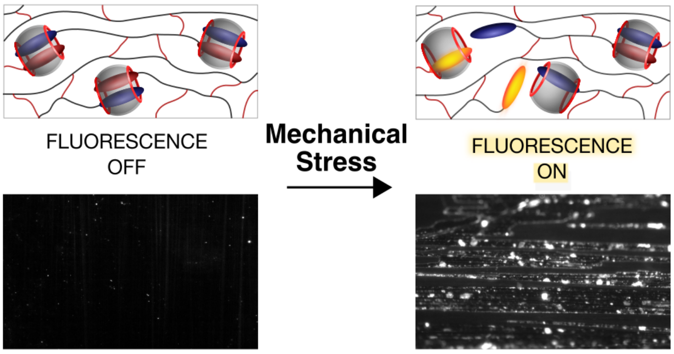


Figure 1: Schematic representation of the supramolecular self-diagnostic mode

Early stage damage detection in a carbon fiber reinforced composite is obtained by incorporating supramolecular cross-links within the matrix. CB[8] encapsulates two molecules in the matrix, a fluorophore and a quencher forming a ternary complex wherein the emission of the probe is suppressed. Under the application of stress, the weak supramolecular links within the matrix break apart, and the fluorescence of the probe is reinstated, assisting in the visualization of microscopic damage in the composite material (Figure 1). In addition, to tensile and compressive stress, the system shows the ability to detect fatigue damage. Compared to existing supramolecular damage reporting methodologies, the proposed system is specifically tailored for structural composites. Overall, this approach offers an innovative, technologically viable solution to the quest of simple and effective methods of monitoring the structural integrity in composites.[1]

References

[1] A. D. Das, G. Mannoni, A. E. Früh, D. Orsi, R. Pinalli,E. Dalcanale, "Damage-Reporting Carbon Fiber Epoxy Composites", *ACS Appl. Polym. Mater.* **2019**, 1, *11*, 2990–2997

AUTHOR INDEX

AUTHOR INDEX