

ENGINEERING POLY(ISOBUTYLENE) AS SELF-HEALING POLYMER

W. H. Binder¹, A. Stojanovic¹, D. Döhler¹, P. Michael¹, Florian Herbst¹

¹ *Institute of Chemistry, Chair of Macromolecular Chemistry, Faculty of Natural Sciences II (Chemistry, Physics and Mathematics), Martin-Luther-University Halle-Wittenberg, von-Danckelmann-Platz 4, Halle (Saale) 06120, Germany – e-mail: wolfgang.binder@chemie.uni-halle.de*

Keywords: self healing, autocatalysis, click chemistry, multiple healing, poly(isobutylene)

ABSTRACT

All polymeric materials are subject to thermal, mechanical as well as chemical degradation and destruction during their lifetime. As new materials are designed, the quest for materials with self-healing properties (i.e.: those which can regenerate similar to living matter, especially after mechanical deformation) is increasing, culminating in the need for self-healing polymers after mechano-deformation¹⁻³. We here report on the realization of two different principles of self-healing polymers, based on either dynamic, supramolecular polymers^{4,5}, or via the use of encapsulated reagents^{3,6-8}. Whereas in the first principle either hydrogen-bonded, supramolecular polymers^{5,9} or ionomers^{10,11} are responsible for a restorative force to effect multiple self-healing, reactive liquid polymeric components are embedded into separate capsules in the second concept, subsequently reacting via “click”-reactions after rupture of the capsule by mechanical deformation and destruction. The design of the polymers, their synthesis and the underlying autocatalytic effects to achieve sufficiently fast reactivity and thus self-healing properties are discussed.

1. INTRODUCTION, RESULTS and CONCLUSIONS

Critical for a practical application of self-healing polymers is the need to achieve multiple self-healing cycles thus enabling repeated healing after repeated mechanical deformation has occurred (see Figure 1). Thus the underlying crosslinking reactions should act repeatedly and reversibly, putting supramolecular interactions in the limelight of interest. The current paper concentrates on the use of supramolecular interactions such as ionomers¹⁰⁻¹² and hydrogen bonds^{9,13-15}, both linked to polymers, to achieve reversible self-healing under reasonable time scales. Critical for the design of such processes is a deeper understanding of association dynamics in the melt-state of such polymeric liquids^{9,13}, most of them in the rubbery or partially thermoplastic state. Focus of the current talk is directed towards poly(isobutylenes) as polymers displaying a high chain mobility and high individual segment-dynamics.

Together with crosslinking as well as post-crosslinking reactions and their associated network formation the thermomechanical and physicochemical properties are thus defined. Combined with conventional crosslinking reactions, such as the azide/alkyne-“click”-reaction (CuAAC¹⁶⁻²²) as one of the most prominent “click”-type reactions reaction the kinetics of the CuAAC and the association dynamics of the supramolecular components are discussed, focussing on simple hydrogen bonding systems (such as diaminotriazine/thymine as well as more complex hydrogen bonds (such as the barbituric acid/Hamilton-receptor-moieties).²³⁻²⁵

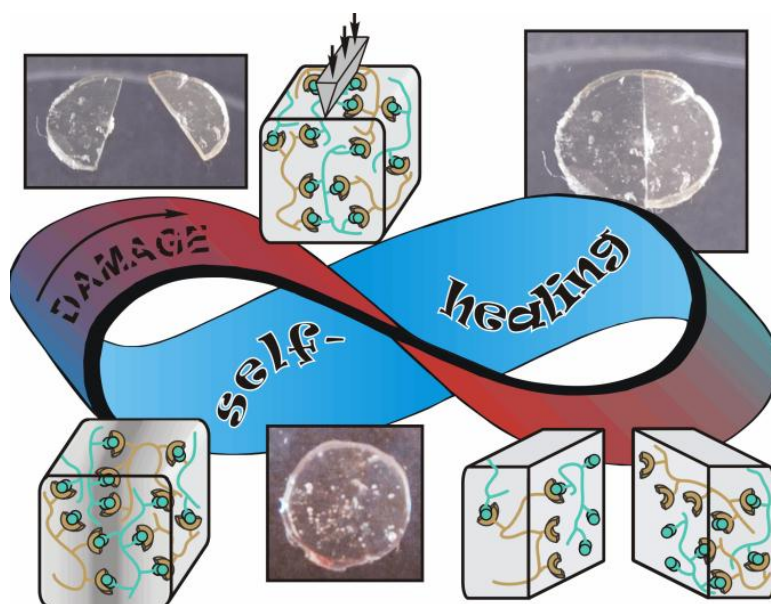


Figure 1: Multiple healing cycles of supramolecular polymers

ACKNOWLEDGEMENTS

We are grateful for the grant DFG BI 1337/8-1 (within the SPP 1568 “Design and Generic Principles of Self-Healing Materials”) and the EU-project IASS for financial support.

REFERENCES

- [1] Self-Healing Polymers. From Principles to Applications.; Binder*, W. H., Ed.; Wiley-VCH: Weinheim, 2013.
- [2] Herbst, F.; Binder*, W. H.: Self-healing polymers via supramolecular, hydrogen bonded networks. In Self Healing Polymers: from Principles to Application; Binder, W. H., Ed.: Weinheim, 2013; pp in press.
- [3] Döhler, D.; Michael, P.; Binder*, W. H.: Principles of Self Healing Polymers. In Self Healing Polymers: from Principle to Application; Binder, W. H., Ed.; Wiley VCH: Weinheim, 2013.
- [4] Herbst, F.; Döhler, D.; Michael, P.; Binder*, W. H.: Self-healing polymers via supramolecular forces. *Macromol. Rapid Commun.* in press 2013, marc.201200675
- [5] Herbst, F.; Seiffert, S.; Binder, W. H.: Dynamic supramolecular poly(isobutylene)s for self-healing materials. *Polymer Chemistry* 2012, 3, 3084-3092.
- [6] Schunack, M.; Gragert, M.; Döhler, D.; Michael, P.; Binder*, W. H.: Low-Temperature Cu(I)-Catalyzed “Click” Reactions for Self-Healing Polymers. *Macromol.Chem. Phys.* 2012, 213, 205-214.
- [7] Döhler, D.; Michael, P.; Binder*, W. H.: Autocatalysis in the Room Temperature Copper(I)-Catalyzed Alkyne–Azide “Click” Cycloaddition of Multivalent Poly(acrylate)s and Poly(isobutylene)s. *Macromolecules* 2012, 45, 3335-3345.
- [8] Gragert, M.; Schunack, M.; Binder*, W. H.: Azide/Alkyne-“Click”-Reactions of Encapsulated Reagents: Toward Self-Healing Materials. *Macromol. Rapid Commun.* 2011, 32, 419-425.
- [9] Hackethal, K.; Herbst, F.; Binder, W. H.: Synthesis and clustering of supramolecular “graft” polymers. *J. Polym. Sci., Part A: Polymer Chem.* 2012, 50, 4494-4506.

- [10] Zare, P.; Stojanovic, A.; Herbst, F.; Akbarzadeh, J.; Peterlik, H.; Binder*, W. H.: Hierarchically Nanostructured Polyisobutylene-Based Ionic Liquids. *Macromolecules* 2012, 45, 2074-2084.
- [11] Zare, P.; Mahrova, M.; Tojo, E.; Stojanovic, A.; Binder, W. H.: Ethylene glycol-based ionic liquids via azide/alkyne click chemistry. *J. Polym. Sci. Part A: Polymer Chemistry* 2013, 51, 190-202.
- [12] Pagano, F.; Gabler, C.; Zare, P.; Mahrova, M.; Dörr, N.; Bayon, R.; Fernandez, X.; Binder, W. H.; Hernaiz, M.; Tojo, E.; Igartua, A.: Dicationic ionic liquids as lubricants. *Proc. I. Mech. Eng., Part J: J. Engineering Tribology* 2012, 226, 952-964.
- [13] Herbst, F.; Schröter, K.; Gunkel, I.; Gröger, S.; Thurn-Albrecht, T.; Balbach, J.; Binder*, W. H.: Aggregation and chain dynamics in supramolecular polymers by dynamic rheology: cluster formation and self aggregation. *Macromolecules* 2010, 43, 10006–10016.
- [14] Binder, W.; Zirbs, R.: Supramolecular Polymers and Networks with Hydrogen Bonds in the Main- and Side-Chain. In *Adv. Polym. Sci.: "Hydrogen Bonded Polymers"*, 2007; pp 1-78.
- [15] Binder, W. H.: Polymeric Ordering by H-bonds. Mimicking Nature by Smart Building Blocks. *Monatsh. Chem. / Chemical Monthly* 2005, 136, 1-19.
- [16] Binder, W. H.; Sachsenhofer, R.: 'Click' Chemistry in Polymer and Materials Science. *Macromol. Rapid Commun.* 2007, 28, 15-54.
- [17] Binder, W. H.; Sachsenhofer, R.: 'Click' Chemistry in Polymer and Material Science: An Update. *Macromol. Rapid Commun.* 2008, 29, 952-981.
- [18] Binder*, W. H.; Herbst, F.: Click chemistry in polymer science. In *McGraw-Hill Yearbook of Science & Technology*; Blumel, D., Ed.; McGraw-Hill: New York, 2011; pp 46-49.
- [19] Binder, W. H.; Zirbs, R.: "'Click'-Chemistry in Macromolecular Synthesis. In *Encyclopedia of Polymer Science and Technology*; John Wiley & Sons, Inc, 2009; pp DOI: 10.1002/0471440264.pst565.
- [20] Binder, W. H.; Sachsenhofer, R.: "Click"-Chemistry in Polymer and Material Science: An Update. *Macromol. Rapid Commun.* 2008, 29, 952-981.
- [21] Binder, W. H.; Sachsenhofer, R.: "Click" Chemistry in Polymer and Materials Science. *Macromol. Rapid Commun.* 2007, 28, 15-54.
- [22] Binder, W. H.; Kluger, C.: Azide/alkyne-"click" reactions: applications in material science and organic synthesis. *Curr. Org. Chem.* 2007, 10, 1791.
- [23] Döhler, D.; Michael, P.; Binder, W. H.: Autocatalysis in the Room Temperature Copper(I)-Catalyzed Alkyne-Azide "Click" Cycloaddition of Multivalent Poly(acrylate)s and Poly(isobutylene)s. *Macromolecules* 2012, 45, 3335-3345.
- [24] Schunack, M.; Gragert, M.; Döhler, D.; Michael, P.; Binder, W. H.: Low-Temperature Cu(I)-Catalyzed "Click" Reactions for Self-Healing Polymers. *Macromol. Chem. Phys.* 2012, 213, 205-214.
- [25] Gragert, M.; Schunack, M.; Binder, W. H.: Azide/Alkyne-"Click"-Reactions of Encapsulated Reagents: Toward Self-Healing Materials. *Macromol. Rapid Commun.* 2011, 32, 419-425.