

AZIDE/ALKYNE-"CLICK"-REACTIONS OF ENCAPSULATED LIQUID POLYMERS: TOWARDS SELF-HEALING MATERIALS

W. H. Binder¹, M. Gragert¹, M. Schunack¹, D. Döhler¹, P. Michael¹

¹University of Halle-Wittenberg, Faculty of Natural Sciences II, Institute of Chemistry, Chair of Macromolecular Chemistry, von Danckelmannplatz 4, D-06114 Halle (Saale).

Email: wolfgang.binder@chemie.uni-halle.de

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ABSTRACT

Most 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 and crack-formation) is increasing, culminating in the need for self-healing polymers after mechano-deformation[1]. First steps towards this endeavor have been accomplished by a variety of different concepts, among them encapsulation[2] of reactive components.

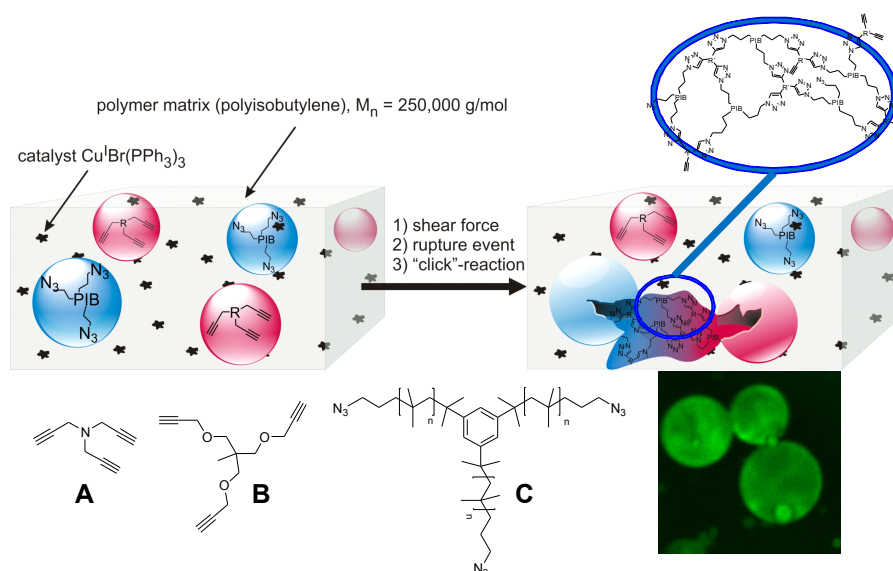


Figure 1: Concept of the self-healing materials based on liquid polymers. Crosslinking is achieved via the azide/alkyne-"click"-reaction.

In capsule-based self-healing systems a chemical reaction (i.e.: cycloaddition reaction[3], cycloreversion[4-7], crosslinking reaction via epoxides[8-10], mechanochemical catalyst activation[11]) is taking place, based on the separate embedding of two reactive components (such as dicyclopentadiene (DCPD)[2, 12] in a capsule. Mechanistically an important requirement lies in the use of ("reactive") components displaying sufficient (high) molecular mobility to allow subsequent formation of a supramolecular or covalent network. Thus usually liquid components (DCPD or derivatives, liquid epoxides) or molecules with low molecular weights (corresponding to high mobility) are used, so that the time-scale of the diffusion is sufficiently low as to allow physical contact between the interacting molecules.

We report [13] on a chemical self-healing polymer (see Figure 1), where two reactive liquid (polymeric) components are embedded into separate capsules, subsequently reacting after rupture of the capsule by mechanical deformation and destruction. In contrast to similar reported systems, our

approach uses (a) the azide/alkyne-"click"-reaction[14-16] as the underlying chemical "addition" reaction to effect crosslinking between a trivalent alkyne (**A**, **B**) and a trivalent azide **C** and (b) uses an encapsulated liquid polymer (three-arm star azido-telechelic-poly(isobutylene) **C**) as one of the reactive components. To effect the encapsulation of polymer **C** an emulsion method was developed, generating urea/formaldehyde-capsules with embedded (fluorescently) labeled polymer (see Figure 1). The two different capsules were then embedded into a polymeric matrix of high molecular weight (PIB, $M_n \sim 100\,000\text{ g}\cdot\text{mol}^{-1}$, containing added Cu(I)-catalyst), leading to effect a separate location of the capsules in the matrix, which release their contents after mechanically induced rupture and subsequent crosslinking reaction. The "click"-reaction leads to a reasonable, but small reaction rate of several days at temperatures of 40 °C as proven by DMTA- and rheology-measurements. Further structurally related polymers bearing multivalent azide/alkyne-units are discussed in terms of crosslinking efficiency and self-healing effects.

REFERENCES

- [1] M. M. Caruso, D. A. Davis, Q. Shen *et al.*, "Mechanically-Induced Chemical Changes in Polymeric Materials," *Chem. Rev.*, vol. 109, no. 11, 2009 pp. 5755-5798.
- [2] S. R. White, N. R. Sottos, P. H. Geubelle *et al.*, "Autonomic healing of polymer composites," *Nature*, vol. 409, 2001 pp. 794-817.
- [3] C. M. Chung, Y. S. Roh, S. Y. Cho *et al.*, "Crack Healing in Polymeric Materials via Photochemical [2+2] Cycloaddition," *Chem. Mater.*, vol. 16, no. 21, 2004 pp. 3982-3984.
- [4] M. J. Kryger, M. T. Ong, S. A. Odom *et al.*, "Masked Cyanoacrylates Unveiled by Mechanical Force," *J. Am. Chem. Soc.*, vol. 132, no. 13, 2010 pp. 4558-4559.
- [5] D. A. Davis, A. Hamilton, J. Yang *et al.*, "Force-induced activation of covalent bonds in mechanoresponsive polymeric materials," *Nature*, vol. 459, no. 7243, 2009 pp. 68-72.
- [6] C. R. Hickenboth, J. D. Rule, and J. S. Moore, "Preparation of enediyne-crosslinked networks and their reactivity under thermal and mechanical conditions," *Tetrahedron*, vol. 64, no. 36, 2008 pp. 8435-8448.
- [7] C. R. Hickenboth, J. S. Moore, S. R. White *et al.*, "Biasing reaction pathways with mechanical force," *Nature*, vol. 446, 2007 pp. 423-427.
- [8] B. J. Blaiszik, M. M. Caruso, D. A. McIlroy *et al.*, "Microcapsules filled with reactive solutions for self-healing materials," *Polymer*, vol. 50, no. 4, 2009 pp. 990-997.
- [9] Y. C. Yuan, M. Z. Rong, M. Q. Zhang *et al.*, "Self-Healing Polymeric Materials Using Epoxy/Mercaptan as the Healanant," *Macromolecules*, vol. 41, no. 14, 2008 pp. 5197-5202.
- [10] D. A. McIlroy, B. J. Blaiszik, M. M. Caruso *et al.*, "Microencapsulation of a Reactive Liquid-Phase Amine for Self-Healing Epoxy Composites," *Macromolecules*, vol. 43, no. 4, 2010 pp. 1855-1859.
- [11] S. Karthikeyan, and R. P. Sijbesma, "Mechanochemistry: Forcing a molecule's hand," *Nat Chem*, vol. 2, no. 6, 2010 pp. 436-437.
- [12] A. S. Jones, J. D. Rule, J. S. Moore *et al.*, "Catalyst Morphology and Dissolution Kinetics of Self-Healing Polymers," *Chem. Mater.*, vol. 18, no. 5, 2006 pp. 1312-1317.
- [13] M. Gragert, M. Schunack, and W. H. Binder, "Azide/Alkyne-"Click"-Reactions of Encapsulated Reagents: Toward Self-Healing Materials," *macromo.. Rapid Commun.*, vol. 32, no. 5, 2011 pp. 419-425.
- [14] W. H. Binder, and R. Zirbs, ""Click"-Chemistry in Macromolecular Synthesis," *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, Inc, 2009, p. DOI: 10.1002/0471440264.pst565.
- [15] W. H. Binder, and R. Sachsenhofer, ""Click"-Chemistry in Polymer and Material Science: An Update," *Macromol. Rapid Commun.*, vol. 29, no. 12-13, 2007 pp. 952-981.
- [16] W. H. Binder, and R. Sachsenhofer, ""Click" Chemistry in Polymer and Materials Science," *Macromol. Rapid Commun.*, vol. 28, no. 1, pp. 15-54, 2007.