Angewandte Highlights

Adaptable Materials

DOI: 10.1002/anie.201200708

Covalent Adaptable Networks: Reversible Bond Structures Incorporated in Polymer Networks

Christopher N. Bowman and Christopher J. Kloxin**

addition–fragmentation chain transfer ·
covalent adaptable networks · exchange reactions ·
polymers · transesterification

Historically, thermosets have been exactly what their name implied—permanent, intractable, insoluble, largely inert, covalently crosslinked polymer networks. These polymers are ideal for various high-temperature, structural, or composite applications ranging from wind turbine blades to adhesives; however, their performance and implementation are limited by their irreversible chemical structure.

Recent approaches combine the desirable attributes of conventional thermosets with the dynamics of controllably reversible bond structures to yield covalent adaptable networks or CANs.[1] The combination of these two material features is broadly enabling; mending or self-healing,[2] triggerable shape change or stress reduction,[3] and recycling or reprocessing of thermosets have been achieved.[4] CANs are broadly classified into two types, the dynamic structure of which is achieved either kinetically through bond exchange or by equilibrium shifts resulting in reversible depolymerization.

Adaptive network behavior is facilitated in networks that incorporate exchangeable chemical bonds throughout the elastically active network chains. Exchangeable bonds, as illustrated in Figure 1, undergo cleavage and reformation in a manner which conserves the total number of bonds, and therefore the crosslinked structure and modulus. When the characteristic time for bond rearrangement is slower than the duration of an applied stress, the material behaves as a classical, elastic thermoset; however, when the bond exchange dynamics are sufficiently rapid relative to the duration of an applied stress, the CAN becomes viscoelastic.

While recently implemented more broadly, crosslinked networks that incorporate dynamic bond structures have been used for decades. Crosslinked rubbers with disulfide bridges have long been known to undergo bond exchange where relatively weak, unstable disulfide bonds undergo bond cleavage and reformation.[5] The result of this dynamic response is a complex rheological behavior including plastic deformation, that is, creep, of otherwise elastic networks. Figure 2 illustrates two bond exchange mechanisms implemented in CANs. Addition–fragmentation chain transfer (AFT) capable moieties such as allyl sulfides or trithiocarbonates were recently incorporated in CANs. Radical generation and the subsequent bond exchange (Figure 2a) occur upon exposure to light in the presence of a radical-based photoinitiator to achieve photoinduced plasticity,[3b] photo-

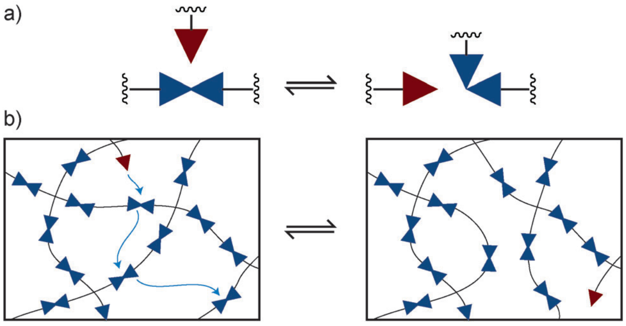

Figure 1. Bond exchange reactions within polymer networks. a) An active species undergoes an exchange reaction that results in bond exchange and formation of a new active species, which subsequently undergoes additional exchange reactions. b) When the exchange reaction occurs within the backbone of a polymer network, the effective diffusion of reaction events rearranges the overall network connectivity while preserving the total bond and crosslink density.

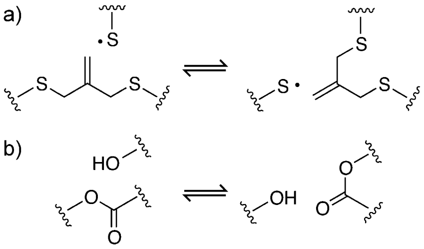

Figure 2. Two examples of bond exchange reactions. The top reaction (a) is the thiyl radical-mediated addition–fragmentation of an allyl sulfide, and the bottom reaction (b) is the transesterification reaction between hydroxy and ester functional groups. For both reactions, the reactants and products are identical and the reaction outcome is simply exchange of bond connectivity.

---

[*] Prof. C. N. Bowman
Department of Chemical and Biological Engineering
University of Colorado
ECCH 111, 424 UCB, Boulder, CO (USA)
E-mail: christopher.bowman@colorado.edu

Prof. C. J. Kloxin
Department of Materials Science and Engineering
Department of Chemical and Biomolecular Engineering
150 Academy Street, Newark, DE 19716 (USA)
E-mail: cjk@udel.edu

lithographically defined features,[3a] and even photoinduced healing.[6]

Excitingly, recent work by Montarnal et al.[4] has significantly extended and expanded the scope of the CAN approach by creating a polymer network that employs highly temperature sensitive transesterification (TE) reactions (Figure 2b) in epoxy networks. In contrast to AFT-based exchange reactions,[3b] the approach by Montarnal et al. uses a thermal stimulus to induce the bond exchange and plastic flow, is fully reversible, does not require a radical generator, and enables complete reprocessing of the network (Figure 3). The successful approach of Montarnal et al. depends on strong temperature dependence of the catalyzed TE reaction. The TE kinetics are three orders of magnitude faster at 100 °C than at ambient temperature and increase further at higher temperatures. Thus, the material flows and is processed like a thermoplastic at elevated temperatures, while performing as a nearly ideal, irreversible thermoset at ambient temperature. Critically, in both AFT and TE systems, the steady-state bond concentration does not change significantly upon application of the stimulus. In AFT the number of bonds broken at any time is on the order of the radical concentration, that is, 10^{-4}–10^{-8} M, while in the TE case, no shift in the equilibrium ester concentration was observed.

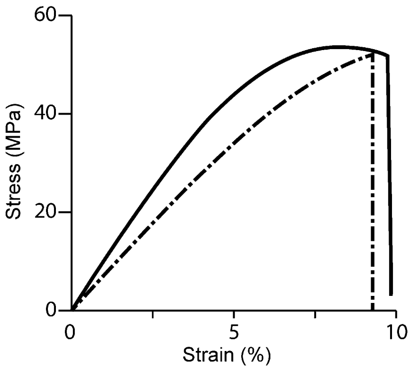

Figure 3. Tensile stress as a function of strain before (solid line) and after (dashed line) reprocessing (adapted from Montarnal et al.[4]). Montarnal et al. formed a network using diglycidylether bisphenol A and glutaric anhydride in the presence of zinc acetate (10 mol%) and subsequently performed the tensile test (solid line). The material was ground to a powder, remolded, and tested again (dashed line). Note: only two representative data sets from ref. [4] are shown.

In contrast to the bond exchange approach, Chen et al.[2] incorporated thermoreversible bond structures, particularly Diels–Alder (DA) adducts, throughout the network to achieve a temperature-sensitive polymerization–depolymerization equilibrium (Figure 4). The equilibrium extent of DA adduct formation, for example, a furan-based diene and a maleimide-based dienophile, strongly favors low-temperature adduct and network formation and high-temperature depolymerization. Crack healing and mechanical recovery were achieved in this highly crosslinked network simply by elevating the temperature. Interestingly, these DA networks are such that they are also undergoing a temperature-dependent bond exchange process resulting from the constant cleavage and reformation of the DA adduct. Thus, at a fixed temperature, both the mechanical properties and the healing behavior of these networks become time-dependent in a complex manner strongly dependent on the DA kinetics.

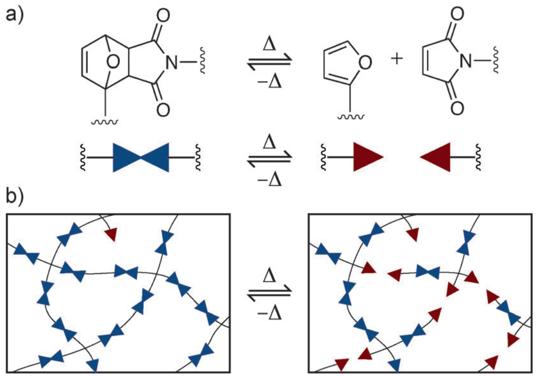

Figure 4. Reversible polymerization in a polymer network. a) The Diels–Alder reaction between furan and maleimide is an example of a reversible crosslinking reaction as the enabling depolymerization and, ultimately, b) adaptation in a covalently crosslinked network.

Specialized applications of polymer networks place an ever-increasing demand on the thermoset behavior whereas demands for recyclable and reprocessable structures are ubiquitous. In response, CANs have been synthesized and shown to achieve these desirable performance metrics by synergistically combining the formation of a crosslinked network with the ability to induce plastic deformation and/or flow upon demand. However, recent work has only scratched the surface of the potential reactions and behavior. There have been only a few reversible covalent reactions employed for either the bond exchange or depolymerization approach. As Montarnal showed, each reaction will have unique behavior and significant advantages.

In considering depolymerizing CANs, novel reactions and triggers for the depolymerization should be explored. Barner-Kowollik and co-workers[7] have recently explored a hetero-DA reaction that uses a cyclopentyl and dithiocarbamyl functional group to form the adduct where the DA kinetics were much faster than conventional maleimide–furan systems. Networks of this type would respond much more rapidly and hybrid networks containing multiple DA adduct structures would have unique mechanical and physical behavior. It would also be advantageous to develop depolymerizing systems that respond to different stimuli. For many thermosetting applications high-temperature thermal stability is critical to the overall material performance; however, it remains desirable to heal cracks or to reprocess these thermally stable systems. Other stimuli such as light of an appropriate wavelength[8] or the use of a particular solvent would enable this outcome.

Ultimately, CANs will be used in composites, adhesives, coatings, and other applications for which smart, responsive, healable, and/or recyclable materials are needed. The behavior achieved by combining reversible covalent bond structures with thermosetting polymers will drive future research into the chemistry, fundamentals, properties, and applications of these materials.

Received: January 26, 2012

---

[1] a) C. J. Kloxin, T. F. Scott, B. J. Adzima, C. N. Bowman, *Macromolecules* **2010**, *43*, 2643 – 2653; b) R. J. Wojtecki, M. A. Meador, S. J. Rowan, *Nat. Mater.* **2011**, *10*, 14 – 27.
[2] X. X. Chen, M. A. Dam, K. Ono, A. Mal, H. B. Shen, S. R. Nutt, K. Sheran, F. Wudl, *Science* **2002**, *295*, 1698 – 1702.
[3] a) C. J. Kloxin, T. F. Scott, H. Y. Park, C. N. Bowman, *Adv. Mater.* **2011**, *23*, 1977 – 1981; b) T. F. Scott, A. D. Schneider, W. D. Cook, C. N. Bowman, *Science* **2005**, *308*, 1615 – 1617.
[4] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, *Science* **2011**, *334*, 965 – 968.
[5] R. D. Andrews, A. V. Tobolsky, E. E. Hanson, *J. Appl. Phys.* **1946**, *17*, 352 – 361.
[6] a) Y. Amamoto, J. Kamada, H. Otsuka, A. Takahara, K. Matyjaszewski, *Angew. Chem.* **2011**, *123*, 1698 – 1701; *Angew. Chem. Int. Ed.* **2011**, *50*, 1660 – 1663; b) R. Nicolay, J. Kamada, A. Van Wassen, K. Matyjaszewski, *Macromolecules* **2010**, *43*, 4355 – 4361.
[7] A. J. Inglis, S. Sinnwell, M. H. Stenzel, C. Barner-Kowollik, *Angew. Chem.* **2009**, *121*, 2447 – 2450; *Angew. Chem. Int. Ed.* **2009**, *48*, 2411 – 2414.
[8] A. Lendlein, H. Y. Jiang, O. Junger, R. Langer, *Nature* **2005**, *434*, 879 – 882.