

FORCE-INDUCED POLYMER CROSS-LINKING AND IMPROVED MECHANICAL INTEGRITY IN RESPONSE TO DESTRUCTIVE MECHANICAL STRESS

Ashley L. Black Ramirez¹, Joshua A. Orlicki² and Stephen L. Craig¹

¹Duke University, Department of Chemistry and Center for Biologically Inspired Materials and Materials Systems, Durham, North Carolina, 27708-0346.
Email: Stephen.craig@duke.edu

²Rodman Materials Research Center, Macromolecular Science & Technology Branch, Army Research Laboratory, RDRL-WMM-G
4600 Deer Creek Loop, Aberdeen Proving Ground, Maryland, 21005.
Email: Joshua.orlicki@us.army.mil

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ABSTRACT

Mechanical stresses in polymers typically compromise their mechanical integrity, for example by inducing carbon-carbon bond scission reactions that degrade polymer molecular weight. [1-4] In the solid state, stress-induced bond breaking triggers the formation of microcracks that propagate and eventually cause the material to fail under load. [5-7] In solution, shear-induced bond breaking leads to a loss of viscosity. [1] A new strategy for self-strengthening and/or self-healing polymers has recently been proposed [8-10], in which stress-sensitive mechanophores in polymers might be mechanochemically triggered to undergo bond-forming reactions that repair or replace the mechanical damage (Fig. 1). This strategy differs from the use of weak, reversible bonds that reform after the stress is removed, in that the nascent polymers are not programmed to fall apart quickly, but rather have all of the strength and properties associated with a fully covalent structure. The utility of the mechanophore approach depends on the proposition (heretofore unrealized) that it is possible to engineer a polymer that, under conditions that typically degrade molecular weight, forms more stress-bearing bonds than are broken. Here we describe the behavior of a mechanophore-based polymer under chronic, destructive shear forces in solution and in the solid state. The activation of the mechanophores creates an opening for covalent bond-forming reactions that not only replace, but also outcompete the bond-breaking processes. The extent of bond forming and its effect on the ultimate structure and mechanical properties of the polymers will be discussed.

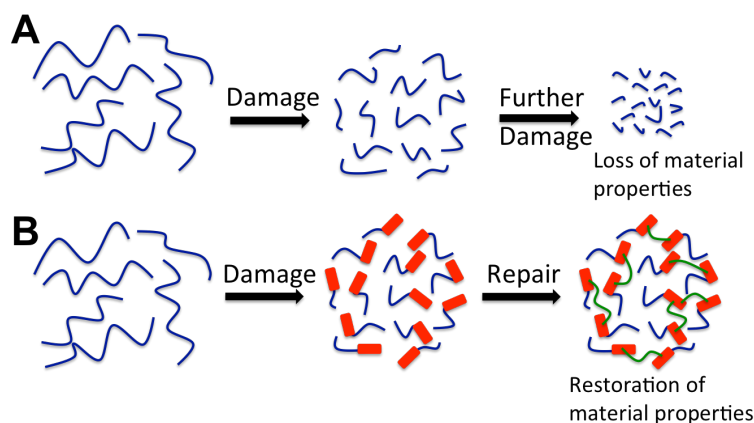


Figure 1: A. Mechanical forces lead to polymer degradation and loss of material properties through carbon-carbon bond scission reactions. B. Proposed mechanism of self-repair based on activation of a mechanophore (red) that forms cross-links (green) under stress, restoring structure and material properties.

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REFERENCES

- [1] A. M. Basedow and K. H. Ebert, Ultrasonic degradation of polymers in solution, *Advances in Polymer Science*, **22**, 1977, pp. 83-148.
- [2] A. P. Smith, J. S. Shay, R. J. Spontak, C. M. Balik, H. Ade, S. D. Smith and C. C. Koch, High-energy mechanical milling of poly(methyl methacrylate), polyisoprene and poly(ethylene-*alt*-propylene), *Polymer*, **41**, 2000, pp. 6271-6283.
- [3] J. M. Lenhardt, A. L. Black and S. L. Craig, *gem*-Dichlorocyclopropanes as abundant and efficient mechanophores in polybutadiene copolymers under mechanical stress, *Journal of the American Chemical Society*, **131**, 2009, pp. 10818-10819.
- [4] K. L. Berkowski, S. L. Potisek, C. R. Hickenboth and J. S. Moore, Ultrasound-induced site-specific cleavage of azo-functionalized poly(ethylene glycol), *Macromolecules*, **38**, 2005, pp. 8975-8978.
- [5] H. R. Brown, V. R. Deline and P. F. Green, Evidence for cleavage of polymer chains by crack propagation, *Nature*, **341**, 1989, pp. 221-222.
- [6] S. Liu and J. A. Nairn, The formation and propagation of matrix microcracks in cross-ply laminates during static loading, *Journal of Reinforced Plastics and Composites*, **11**, 1992, pp. 158-178.
- [7] B. N. Persson, O. Albohr, G. Heinrich and H. Ueba, Crack propagation in rubber-like materials, *Journal of Physics: Condensed Matter*, **17**, 2005, pp. R1071-R1142.
- [8] D. A. Davis, A. Hamilton, J. Yang, L. D. Cremar, D. Van Gough, S. L. Potisek, M. T. Ong, P. V. Braun, T. J. Martinez, S. R. White, J. S. Moore and N. R. Sottos, Force-induced activation of covalent bonds in mechanoresponsive polymeric materials, *Nature*, **459**, 2009, pp. 68-71.
- [9] A. Piermattei, S. Karthikeyan and R. P. Sijbesma, Activating catalysts with mechanical force, *Nature Chemistry*, **1**, 2009, pp. 133-137.
- [10] X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran and F. Wudl, A thermally re-mendable cross-linked polymeric material, *Science*, **295**, 2002, 1698-1702.