Colloquium on Polymer Science and Molecular Engineering Zhejiang University and the University of Chicago
12-16 April 2017

Inherently Photohealable and Thermal Shape-Memory Polydisulfide Networks[1]

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Abstract: Structurally dynamic polydisulfide networks that inherently exhibit both shape-memory and healable properties have been synthesized. These materials are semicrystalline, covalently cross-linked network polymers and as such exhibit thermal shape-memory properties. Upon heating above its melting temperature (Tm) films of the material can be deformed by a force. Subsequent cooling and removal of the force result in the material being "fixed" in this strained temporary shape through a combination of crystallinity and covalent cross-links until it is exposed to temperatures above the Tm at which point it recovers to its remembered processed shape. The incorporation of disulfide bonds, which become dynamic/reversible upon exposure to light or elevated temperatures, into these networks results in them being structurally dynamic upon exposure to the appropriate stimulus. Thus, by activating this disulfide exchange, the network reorganizes, and the material can flow and exhibit healable properties. Furthermore, exposure to light also allows the film's permanent "remembered" shape to be reprogrammed. Shape-memory experiments on these films show high degrees of both fixing and recovery (>95%), and photohealing experiments showed that the films were able to recover from a scratch whose depth is approximately half the thickness of the film. Using a combination of the thermal shape-memory behavior followed by photohealing allows wide scratches to also be efficiently healed.

Introduction

In previous work, we have shown that structurally dynamic polymers (polymers with the ability to reorganize their structure) that contain reversible metal–ligand interactions allow access to films that either have the ability to heal[3] or exhibit shape memory properties[4] upon exposure to light, but not both. In many cases, the use of light on dynamic polymers is successful due to its conversion to heat within the film and subsequent decomplexation of the dynamic motif. Unfortunately, this heat dependence creates a void in the application of these materials on heat sinks (*e.g.*, a metal or glass). Thus, a semicrystalline, covalently crosslinked polymer containing disulfide bonds as an integral component of the network was targeted as a material that would potentially exhibit both photohealing and thermal shape-memory responses.

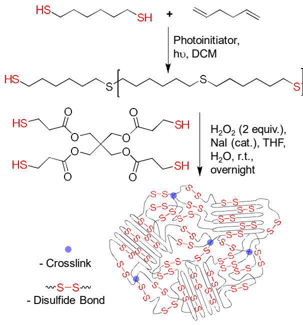

Fig. 1. *Left* Synthesis of the semicrystalline polydisulfide network.

Project Goals:

- To develop structurally dynamic polymer films that exhibit both shape-memory and healing characteristics
- Construct films that demonstrate photohealing behavior when used as a coating on a heat sink

Photohealing Behavior

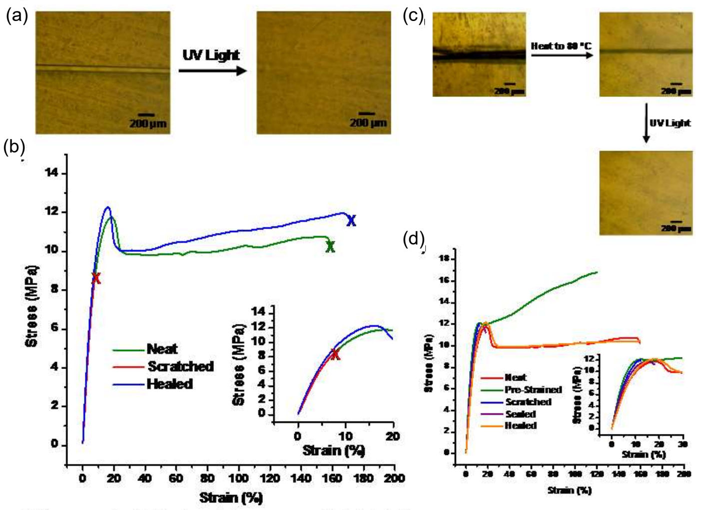

Fig. 4. Figure comparing photohealing and shape-memory assisted photohealing behavior of the films. (a) Image showing healing of a scratched film, (b) stress-strain curve for representative neat, scratched, and healed samples, (c) image showing a scratch on a strained sample that is sealed via shape recovery upon heating and healed with UV light, (d) stress-strain curve for representative neat, prestrained, scratched, sealed, and healed samples.

Shape-Memory Behavior

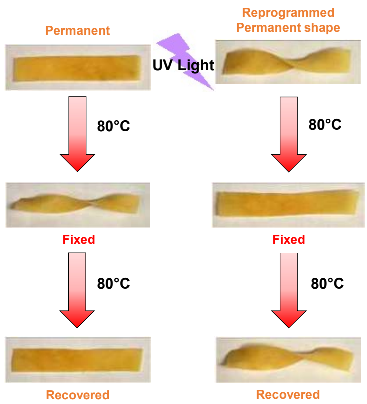

Fig. 2. Pictures showing the reprogrammable shape memory properties of the networks.

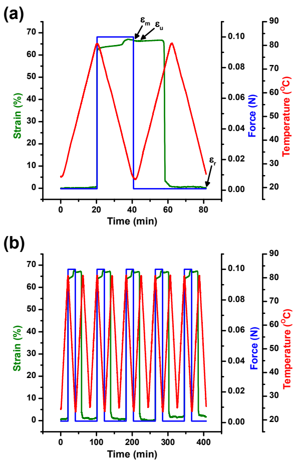

Fig. 3. *(a)* One-way shape memory cycle for a disulfide network. *(b)* Shape memory experiment for a disulfide network showing five cycles.

Shape-Memory and Healing Networks

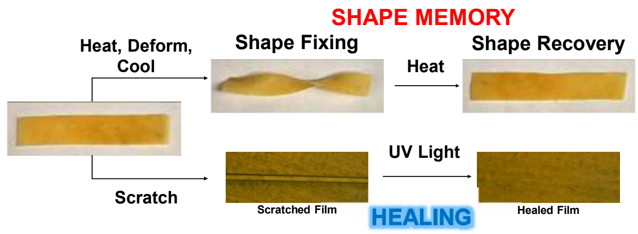

Fig. 5. Pictures showing the shape-memory and healing behavior of the disulfide networks.

Shape-Memory and Healing Adhesives

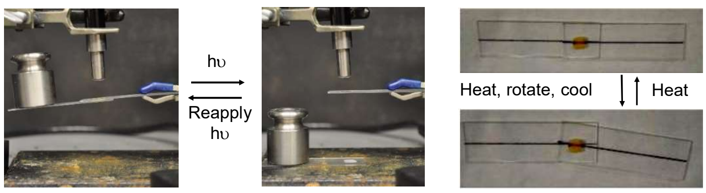

Fig. 6. Pictures showing the reversible bonding/debonding behavior and the shape-memory adhesive healing characteristics of the systems.[2]

Conclusions: In summary, semicrystalline, covalently cross-linked networks that contain disulfide bonds have been shown to form films that intrinsically exhibit both thermal (at 80 °C) shape-memory and photohealable behavior. Using these properties in combination imparts on the film the ability to heal relatively large scratches/ deformations. Furthermore, these cross-linked films also have the ability to reconfigure/reprogram their permanent, "re- membered" shape by simple exposure to light or relatively high (ca. 180 °C) temperature.

Acknowledgement:
The authors gratefully acknowledge financial support from the National Aeronautics and Space Administration (Grant no. NNX11ZA50H) and Army Research Offices (Grant no. W911NF-12-1-0339).

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