# Reversibly Cross-Linked Polymer Gels as Healing Agents for Epoxy−Amine Thermosets

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**ABSTRACT** The Diels−Alder reaction was used to develop a reversibly cross-linking gel as a healing agent for traditional epoxy−amine thermosets. Direct application of the reversibly cross-linking network to a crack surface in an epoxy−amine thermoset resulted in the recovery of 37% of the initial epoxy−amine network's strength. Composites in which the reversibly cross-linking gel was incorporated as a secondary particulate phase recovered 21% of the initial composite strength after the first healing cycle, with healing possible up to five times.

**KEYWORDS:** self-healing materials • Diels−Alder reaction • polymer composites • healing mechanism • reaction kinetics

## INTRODUCTION

Materials that can repair cracks and recover from mechanical failure are desirable. Because remendable materials both repair and prevent the propagation of cracks on the microscale, they offer the potential for increased durability, safety, and cost efficiency for many applications (1, 2). Two approaches for the healing of polymer networks have captured much attention. In one method, polymer networks are made to self-heal by incorporating microcapsules filled with uncured resin as a secondary phase (1, 3−5). Upon fracture, the microcapsules rupture and release resin, which polymerizes to heal the crack. Often, a catalyst is also included within the polymer network to initiate polymerization (1, 3, 6). The other method relies on the inherent reversibility of bonds designed in a polymer network (7−10). The reversible nature of these linkages allows for network remodeling at the damage site. However, both of these methodologies have limitations. With the encapsulation method, healing is possible only once in a given location, while reversible bonds that lead to healing in certain polymer networks dissociate at increased temperatures, detrimentally affecting the physical and mechanical properties. In theory, these limitations could be amelliorated by using thermally reversibly cross-linked particles as a secondary healing phase within a permanently cross-linked polymer network. By including a secondary phase that induces healing through thermoreversible bonding, the healing agent would remain capable of localized healing multiple times while the mechanical and physical properties of the base thermoset are maintained. We report the development of a traditional epoxy−amine thermoset made to heal with the addition of a reversibly cross-linked healing agent based on the Diels−Alder (DA) reaction of furan and maleimide. Reversibly bonded networks using this chemistry have been previously reported (9, 11−16); however, none has been used as a secondary healing phase. A schematic representation of the composite approach to healing is shown in Figure 1 with maleimide moieties as triangles, furan moieties as notched trapezoids, and DA adducts as trapezoids.

## EXPERIMENTAL SECTION

**Gel Synthesis.** An oligomer was formed through the reaction of furfurylamine (FA; Sigma-Aldrich) and diglycidyl ether of bisphenol A (DGEBA with EEW = 185−192, EPON-828, Miller-Stephenson). Stoichiometric amounts of FA and DGEBA were mixed to form a 15 wt % solution in *N*,*N*′-dimethylformamide (DMF; Sigma-Aldrich), which was allowed to react at 90 °C for 30 h. On the basis of polystyrene standards, gel permeation chromatography gave a weight-average molecular weight of 4200 $g \cdot mol^{-1}$ for the FA−DGEBA oligomer, corresponding to an average of 8.9 pendant furans per chain. A thermally reversibly cross-linking gel was then formed by the addition of a stoichiometric amount of 1,1′-(methylenedi-4,1-phenylene)bismaleimide (BMI; Sigma-Aldrich) to the oligomer solution at room temperature and allowing sufficient time for reaction. Upon heating, DA cross-links reverse and the gel becomes an oligomer−BMI solution in DMF. Reversible gels can be prepared using other solvents including dimethyl sulfoxide, but DMF was selected for its low volatility.

**Fourier Transform Near-Infrared (FT-NIR) Spectroscopy.** Characterization of the DA reaction kinetics within the gel was performed using FT-NIR spectroscopy with a Thermo Nicolet Nexus 870 FT-IR. Reversible cross-linking was observed by measuring the maleimide absorbance peak area at 4875 $cm^{-1}$ (17). A room temperature specimen was heated from room temperature to 90 °C for 1 h and subsequently cooled to room temperature in a sealed glass tube (18). After cooling for 12 h at room temperature, the heating and cooling cycles were repeated.

**Compact Tension (CT) Mechanical Testing.** The ability of the reversibly cross-linked gel to function as a healing agent was evaluated by measuring the crack healing of modified CT specimens of DGEBA and bis(*p*-aminocyclohexyl)methane (PACM; Air Products) via direct application of the healing agent to crack surfaces. DGEBA and PACM were mixed in stoichio-

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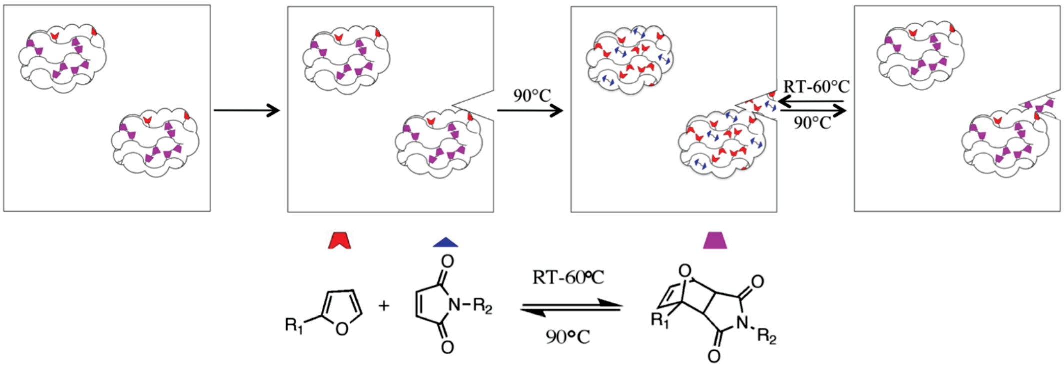

FIGURE 1. Crack healing of a polymer network using a reversibly cross-linked network as a secondary particulate healing phase. Heating causes the secondary gel phase to liquefy and flow into the crack surface. Upon cooling, cross-links re-form.

metric amounts and cured for 2 h at 85 °C and 2 h at 165 °C to ensure complete cure and a $T_g$ of 160 °C (19). Control healing studies were conducted with no healing agent, an oligomer solution in DMF, and pure DMF.

The preparation of CT specimens is explained in greater detail elsewhere (20). Specimens were loaded to failure at a rate of 0.1 mm · min$^{-1}$, and cracks were initiated by tapping a razor in the crack surface. Once CT specimens were fractured, cracks were filled with 10 $\mu$L of the healing agent (DMF, an oligomer solution, or an oligomer—BMI solution) and left to heal at room temperature under minimal pressure (~4.7 kPa) for 12 h. Prior to injection into the crack, the healing agent was heated at 90 °C for 1 h, ensuring that the reversibly cross-linked gel healing agent had liquefied to the oligomer—BMI solution. After healing, specimens were loaded to failure to determine the load recovery for the first heal (heal 1). For subsequent healing cycles, specimens were heated at 90 °C for 1 h under no pressure and healed for 12 h at room temperature under minimal pressure. This testing procedure was repeated until specimens no longer recovered load following healing.

To demonstrate the viability of the composite approach to healing, modified CT specimens were prepared in which 10 wt % gel particles were embedded within a stoichiometric DGEBA—PACM network. Diffusion of DGEBA and PACM into the reversibly cross-linked network was deemed likely, so order of magnitude calculations were performed to determine the critical diffusion length before gelation of the DGEBA—PACM network. The critical length of diffusion of the epoxy—amine reactants into gel particles based on the diffusivities of similar molecules was calculated as 807 $\mu$m (21, 22). As a result, we chose to form particles of approximately this size so as to maximize the homogeneity of the test specimens while still allowing for the presence of a mobile healing phase upon heating.

The gel was crushed to a powder possessing particles with an average diameter of approximately 660 $\mu$m as measured using a Zeiss Axioskop 2 Plus with Axi Cam. These particles were mixed into a DGEBA—PACM resin system, and the composite was cured for 2 h at 60 °C and 2 h at 90 °C because the boiling point of DMF is 153 °C. This cure cycle resulted in a partially cured system with $T_g$ of approximately 100 °C and comparable strength to DGEBA—PACM cured traditionally. Differential scanning calorimetry performed with a TA Instruments Q2000 DSC gives a degree of conversion of $X = 0.922$, which is in good agreement with the literature (23, 24).

## RESULTS AND DISCUSSION

**FT-NIR Analysis of the Gel.** Representative FT-NIR results of the reversibly cross-linking gel are shown in Figure 2. The previously described reversible cross-linking was repeatable and consistent with FT-NIR analysis. At room temperature, the cross-linked network is a DMF-swollen gel. However, after approximately 20 min at 90 °C, a sufficient number of cross-links reverse for the system to liquefy and form a polymer—bismaleimide solution in DMF. Upon cooling to ambient temperature, gelation was observed after approximately 13 h.

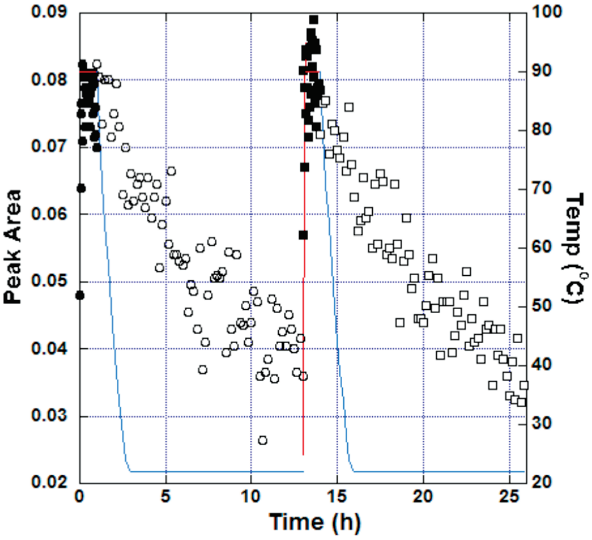

FIGURE 2. Maleimide peak area during heating (filled points) and cooling (open points).

Data show the expected increase and decrease of the maleimide peak area with increasing and decreasing temperature, respectively. The second heating and cooling cycles closely match data from the first healing cycles. Furthermore, Figure 2 shows that adduct decomposition (the reverse reaction) occurs more rapidly than adduct formation (the forward reaction). These results are consistent with the observed physical behavior. In previous work using nuclear magnetic resonance spectroscopy to characterize DA-based dendrimers, McElhanon and Wheeler also observed that adduct formation is significantly slower than decomposition (25). The forward (DA adduct formation) reaction is most likely so much slower because it is a bimolecular reaction with diffusion limitations, whereas the reverse (DA adduct decomposition) reaction is unimolecular.

**Healing Studies.** The results for strength recovery are presented in Figure 3. The oligomer and reversibly cross-linked gel are labeled as LO and CLG, respectively. The

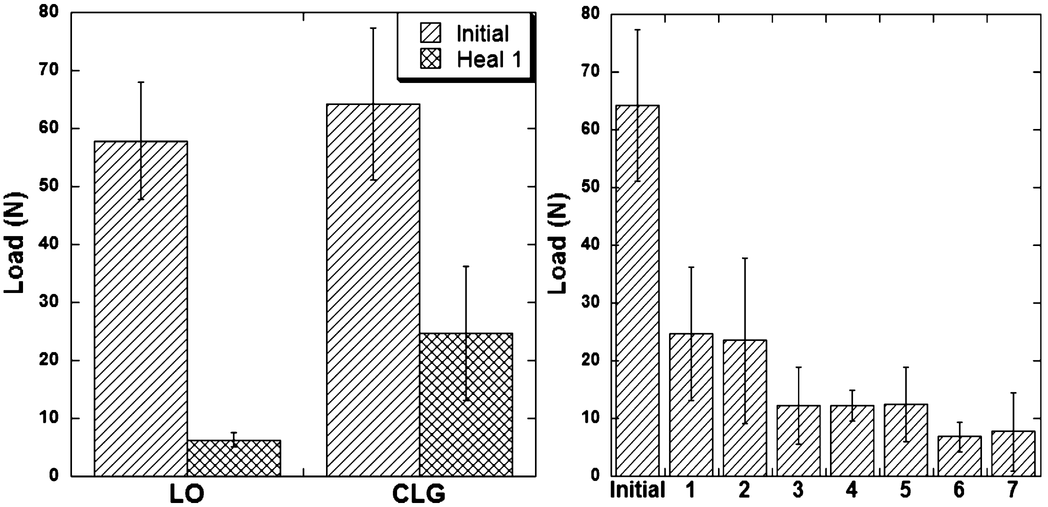

FIGURE 3. Load recovery for first heals for linear (LO) and cross-linked (CLG) healing agents (left) via direct application of the healing agent and subsequent heals for CLG (right). Error bars indicate standard deviations.

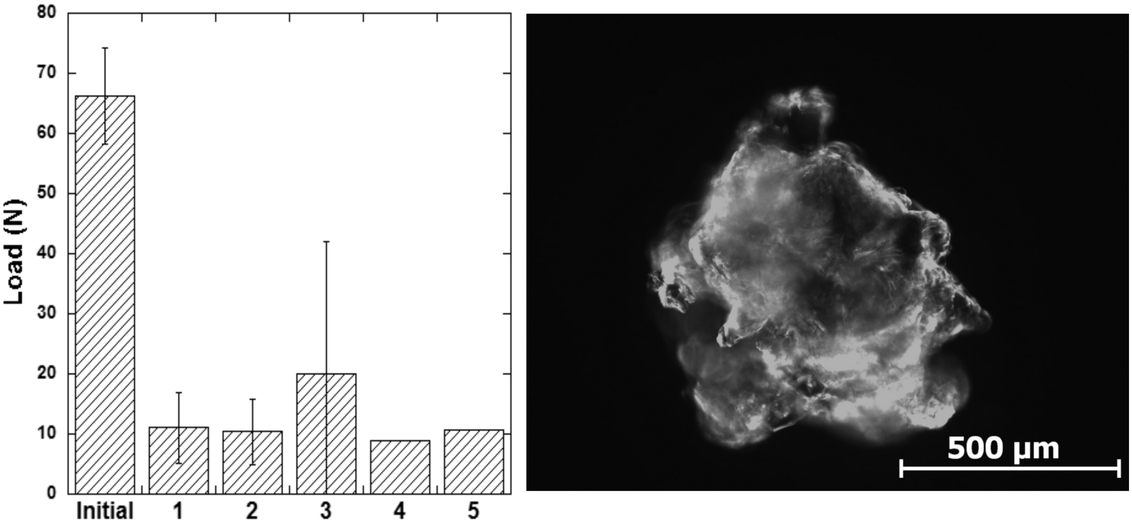

FIGURE 4. Load recovery for the DGEBA−PACM composite containing a secondary particulate CLG phase (left) and optical microscopy of a particle in suspension (right).

healing values for DMF as the healing agent and systems with no healing agent are not shown because no load was recovered.

CLG significantly outperforms LO as a healing agent for the first heal. LO recovered an average load of 6.3 ± 1.2 N (9.6 ± 3.1% healing efficiency), as compared to 25 ± 3.9 N (37 ± 8.3%) for CLG. This large difference in ability as healing agents is further evidence that healing in the cross-linking system is the result of DA bond formation. Although these healing efficiency values are relatively small, they could be improved by increasing the oligomer chain length or the concentration of the polymer in the gel or by using a higher functionality maleimide.

The healing mechanism for the CLG system is based on the DA reaction. When heated, the oligomer−BMI solution diffuses into the crack surface and the oligomer chains interdiffuse into the opposing crack surfaces. As the system cools, cross-links form as pendant furans on the oligomer chains react with the maleimides on the BMIs. Although interdiffusion plays a role in the healing of our systems, the mechanism of strength recovery is very different from that of thermoplastic healing studied by Wool, in which the strength recovery is entirely dependent upon interdiffusion and entanglement (26). In our system, healing is obtained with oligomers that are not long enough to entangle because DA cross-linking results in increasing molecular weight and network formation, which "stitches" the crack surfaces together. Additionally, the cross-linked network formed is stronger than the base oligomer system.

DMF increases the mobility of the reversibly cross-linking network. Once the system is heated and the gel's cross-links break apart, the solvent is free to diffuse throughout the system. Some of the solvent diffuses into the polymer network and causes swelling, while the rest diffuses onto the crack surface and eventually evaporates. Although swelling of the base polymer network with a solvent can be detrimental to the mechanical properties, the amount of solvent that is contained within the gel is not significant relative to the polymer mass.

**Preliminary Composite Study.** Load recoveries, which are shown in Figure 4, are appreciable and exhibit the same trends and relative values as DGEBA—PACM with direct application of the healing agent. Healing was possible up to five times with an average load recovery of 12.1 N (21% healing efficiency) for heals 1—5. To ensure that any healing observed was not the result of continued reaction of the base thermoset, the healing ability of DMF in a DGEBA—PACM system cured using this cure cycle was measured. This system did not exhibit healing; healing of the 10 wt % gel composites is therefore the result of reversible cross-linking of the healing agent across the crack surface. The inability of DMF to heal DGEBA—PACM runs counter to the work of Caruso et al. (27, 28), who observed solvent-promoted healing of another epoxy—amine network. The difference in behavior could be due to the much higher cross-link density and $T_g$ of our system.

Although the particle-containing composite is successful in healing multiple times, it does not properly demonstrate our composite approach to healing. Integral to this approach is the idea of significant mobility, which is provided through the solvent-containing gel. Studies of the mobility of the gel particles in the composite show that the reversibly cross-linked gel does not completely liquefy upon heating, presumably because of interpenetration with the epoxy—amine network during cure. Additionally, as the epoxy and amine molecules diffused into the gel, DMF flowed out, further decreasing the mobility of the healing agent. In future work, we will take advantage of the diffusion of reactants into the gel particles and develop chemistries for protective shells around the gel particles to prevent interpenetration. Because the composite with a limited-mobility healing agent had a healing efficiency of 21%, it is expected that a composite with a mobile healing agent will recover even more strength.

## CONCLUSIONS

We have developed a novel healing system based on the DA reaction that allows a traditional epoxy—amine thermoset to recover mechanical properties multiple times following failure in the same location. Thermosetting composites containing reversibly cross-linked material represent exciting new materials that combine the mechanical properties of traditional epoxy—amine thermosets with the healing of remendable polymers. Preliminary studies showed that composites of gel particles embedded in a thermosetting epoxy—amine system exhibit comparable healing to crack healing of epoxy—amine thermosets by direct application of the healing agent to the crack interface. Future work will focus on the development of epoxy—amine composites with highly mobile reversibly cross-linked secondary phases.

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