

## Development of Remendable Polymer Networks with Thermally Reversible Bonds

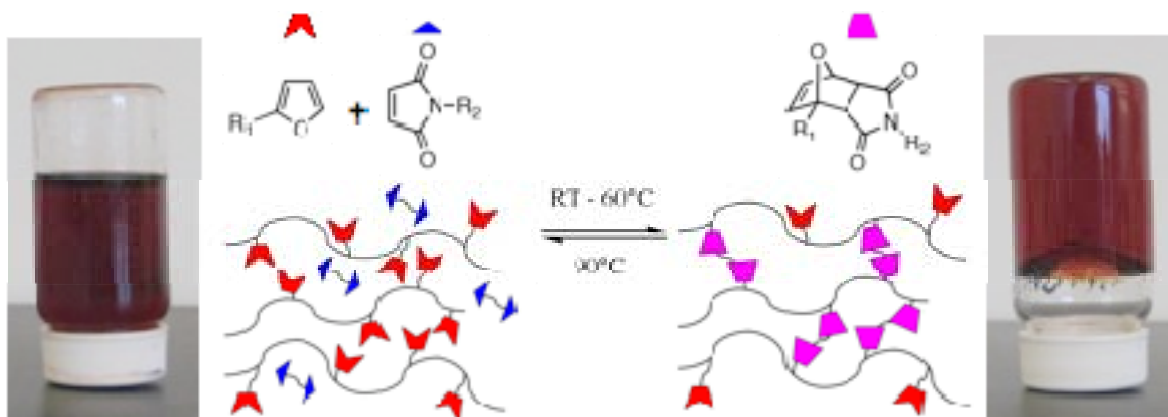
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Materials that can recover properties following mechanical failure are desirable, as they offer increased durability and safety. Mendable materials are particularly desirable for load-bearing applications in which material failure is costly and dangerous.

Inspiration for remendable materials comes from nature and there is a great interest in developing biomimetic processes by a number of functionalities can be applied to synthetic materials. Biomimicry in remendable materials has led to composites with vascular networks that “bleed” resin when a crack forms.<sup>1</sup>

Two approaches for healing polymer networks have captured much attention. In one method, polymer networks are made to self-heal by adding microcapsules filled with uncured resin<sup>2-8</sup>. Upon fracture the microcapsules rupture releasing the resin, which hardens to heal the crack. The other method relies on the inherent reversibility of bonds designed into a polymer network<sup>9-26</sup>. The reversible nature of these linkages allows for network remodeling at the damaged site. We have investigated a composite approach to self-healing that combines many advantages of healing via encapsulation and healing via reversible bonds. This methodology allows for localized healing by including a secondary phase that induces healing through thermoreversible bonding while maintaining the mechanical and physical properties of the base thermoset.

Epoxy-amine thermosets are high modulus materials that are used in composites for their mechanical strength. We report on the development of two healing systems for epoxy-amine thermosets based on the thermoreversible Diels-Alder reaction of furan and maleimide. In one, crack healing of a traditional epoxy-amine thermoset is induced by thermally reversible crosslinking of a secondary phase. In the other, furan functionalization of an epoxy-amine thermoset allows for in situ crack healing of this thermoset with a bismaleimide solution. Both phenomena occur at room temperature and minimal pressure and significant load recovery is possible multiple times in a given location.



**Figure 1.** Thermoreversible crosslinking gel: crosslinking chemistry (top center), a schematic of reversible network (bottom center), and photographs showing liquid (left) and gel (right).

In this work the thermoreversible Diels-Alder reaction of furan and maleimide was selected to impart remendability. Specifically, the crosslinks of the gel are based on the Diels-Alder reaction between maleimide groups on a bismaleimide and pendant furans on a linear polymer. A schematic

representation of this network is shown in Figure 1 with maleimide moieties as triangles, furan moieties as notched trapezoids and Diels-Alder adducts as trapezoids. Also shown in Figure 1 are the Diels-Alder reaction and pictures of vials containing the liquid system at 90°C and the gel at room temperature (RT). This form of the Diels-Alder reaction is reversible, forming a ring structure at room temperature and reforming the respective diene and dienophile between 60 and 90°C.

Load recovery in the furan-functionalized network is postulated to be the result of both physical and chemical bonding across the crack surface. Physical bonding is caused by solvent-mediated swelling and subsequent interlocking of crack surfaces, while chemical bonding results from the Diels-Alder reaction of furan and maleimide.

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