

Fabricating nature-inspired self-healing polymers

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A thermo-reversible self-healing epoxy resin based on Diels-Alder chemistry is synthesized and strength-tested as part of a fiber-reinforced composite material.

Synthetic polymers are lightweight structural materials that have revolutionized many industries, including transportation, aviation, and biomedicine. However, the development of breaks and microcracks leading to catastrophic failures in industrial components remains a significant issue for these widely used materials. Living systems have the ability to self-heal and, therefore, completely recover their material properties after damage occurs, but unlike biological materials, current synthetic polymers are unable to self-repair. Hence, the development of nature-inspired synthetic polymers that can self-heal structural failures (such as delamination) or aesthetic damage will improve maintenance and repair procedures and significantly extend the lifetimes of these industrial materials.

Self-healing synthetic polymers can be grouped into two main categories. One type uses healing agents encapsulated in hollow fibers, microspheres, or other containers,² such that when there is damage the healing agents are released and recovery occurs. The major drawback of this type is that self-repair can only occur once at each site. The other, more effective, type of self-healing involves the cleavage and reformation of the polymer's chemical bonds through an external stimulus such as heat, light, or electricity,² which could occur many times at the same site. Of these stimuli, thermal treatment is a desirable option as it can easily provide the energy required for self-repair to specific sites in the polymer. Here, we present the results of our investigation into the development of self-healing epoxy resins of the second type using Diels-Alder (D-A) chemistry.

A number of organic reaction types could be used as the reversible bonding source for self-healing polymers, and the choice of reaction depends on the desired physical and chemical properties of the resulting polymer as well as compatibility with existing material fabrication processes. Among these, D-A chemistry—in which the electrons in carbon-carbon double bonds rearrange to form new covalent bonds

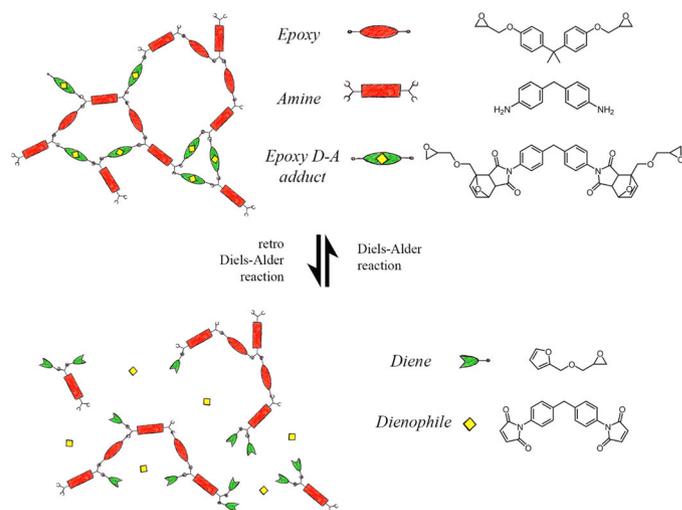


Figure 1. The hybrid polymer architecture of a self-healing epoxy resin based on Diels-Alder (D-A) chemistry. Epoxy: bisphenol A diglycidyl ether. Amine: 4,4'-diaminodiphenylmethane. Diene: glycidyl furfuryl ether. Dienophile: 1,1'-(methylenedi-4,1-phenylene)bismaleimide.

between molecules—offers unique advantages in terms of selectivity, bond strength, and easily accessible thermal treatment temperatures.

Epoxy resins with robust self-healing abilities require hybrid polymer architectures, in which stable and thermo-reversible polymer networks coexist.² We produce these hybrid architectures using a combination of the irreversible crosslinks between bifunctional epoxy compounds and tetrafunctional amines (the stable network) and D-A adducts consisting of furan-derived dienes and bismaleimide-derived dienophiles (the thermo-reversible network): see Figure 1. The thermo-reversible bonding in the D-A adducts is weaker than the other covalent bonds in the 3D polymer network, and hence when the polymer is damaged the D-A adducts are partially cleaved, generating molecular segments that are easily recombined during the thermally induced self-repair process.

Effective self-healing in these polymers requires both high overall molecular mobility and a large number of diene and dienophile

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functional groups available for D-A adduct formation. High molecular mobility is achieved by heating the polymer to the glass-transition temperature (T_g)—the temperature at which a material changes from a hard ‘glassy’ state to a rubber-like state—while heating the polymer above 120°C induces the retro D-A reaction (see Figure 1). Hence, our procedure to restore the pristine network structure involves heating the epoxy resin to 140°C for 20min, followed by a longer heat treatment at 90°C (T_g) to induce D-A adduct formation.² We verified the effectiveness of this process by observing the disappearance of fractures and microcracks in the polymer after thermal treatment (see Figure 2).

Fiber-reinforced plastics are ideal composite materials for structural applications, a result of their high specific stiffness and strength, and excellent fatigue resistance. However, there are still concerns regarding the fracture toughness of these materials. Indeed, delamination between layers is a particularly common damage type in these composites, and implies a cohesive failure of the polymer matrix. To test the ability of the self-healing epoxy resin to recover from delamination damage, we fabricated a carbon-fiber-reinforced polymer composite with this material and carried out a series of short beam shear tests—in which delamination is achieved by flexing a sample of the composite until breakage—with a self-repair thermal treatment between each test (see Figure 3). We found that this self-healing composite retains 95% of its structural integrity after one failure/restore cycle, and 68% after three cycles.²

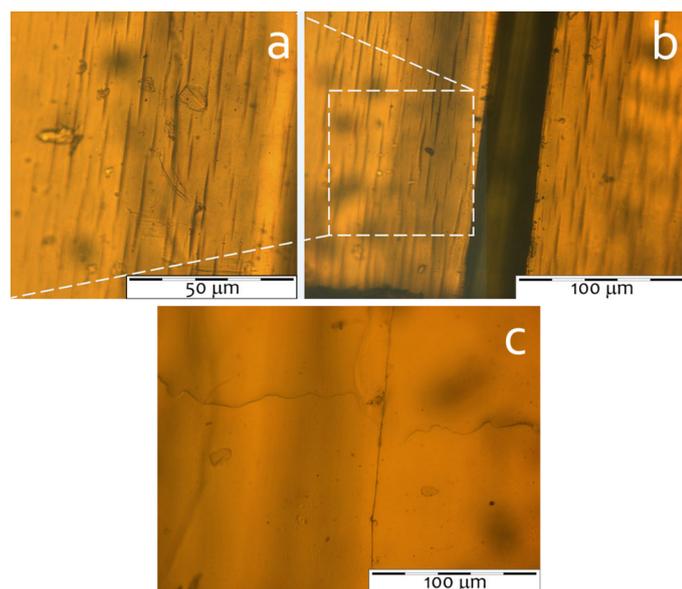


Figure 2. Microscopy images of a self-healing epoxy resin (a,b) before and (c) after thermal treatment.

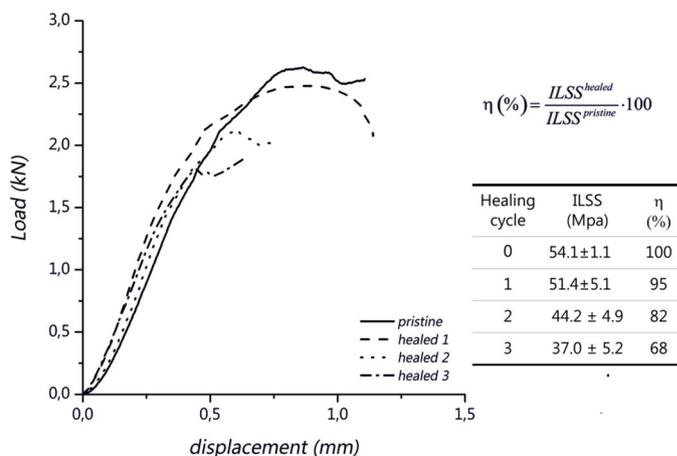


Figure 3. Results of a series of short beam shear tests on a self-healing fiber-reinforced composite material. η : Healing efficiency. ILSS: interlaminar shear strength.

In summary, nature-inspired self-healing polymers are the next step towards long-lasting, damage-tolerant industrial materials, and D-A chemistry is a very promising approach to developing these polymers. We have shown that self-healing epoxy resins with thermo-reversible network structures are able to recover from severe scratches, and can be used as the matrix for fiber-reinforced composite materials. Our test results show a 95% recovery efficiency in these composites after the first damage and only small decreases in efficiency after further damage cycles.

As ineffective healing at matrix/reinforcing fiber interfaces in self-healing composites could threaten the recovery abilities of these materials, our future work in this field includes developing surface treatments to address self-repair specifically at interfaces. In addition, we are designing self-healing polymers with a range of T_g values by selecting appropriate diene-dienophile pairs. Furthermore, we are using self-healing composite materials to develop structural aerospace components with enhanced reworking/recycling capabilities.

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