Solvent-Promoted Self-Healing Epoxy Materials

Mary M. Caruso,[†] David A. Delafuente,[†] Victor Ho,[‡] Nancy R. Sottos,[§] Jeffrey S. Moore,[†,§] and Scott R. White*,[||]

Department of Chemistry and Beckman Institute, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801, Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, Department of Materials Science and Engineering and Beckman Institute, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801, and Department of Aerospace Engineering and Beckman Institute, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801

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Introduction. Epoxy-based thermosets are used in a large variety of structural composites for various applications including aerospace, automotive, and electronics among others.[1] These materials experience stresses through normal use, which can lead to cracking of the epoxy resin.[2] Microcracks are often contained deep within a structural component and are difficult to detect. If crack propagation continues, it can eventually lead to mechanical failure of the material. The ability to autonomically repair cracks within a composite is necessary to retain structural integrity and extend the lifetime of the material. Polymeric materials can be healed using light or heat based activation methods.[3] However, those approaches are restricted in that they require human intervention to trigger the healing process.

One of the earliest reports of crack healing in an epoxy resin required high-temperature conditions greater than 250 °F (121 °C).[4] After fracture of the virgin material and subsequent heating of the material above its glass transition temperature, healing was observed due to molecular diffusion and reaction of residual functionality.[5−7] Crack healing at elevated temperature was observed in a matrix consisting of EPON 828 with triethylenetetraamine (TETA) and partial recovery (ca. 50%) Izod impact strength was reported.[8] Another method of healing is the addition of a solvent to a polymer matrix. Solvents such as ethanol and methanol were used to seal the cracks of thermoplastic polymers (i.e., poly(methyl methacrylate)) when the polymer was heated.[9−14] This healing mechanism involves wetting of the polymer surface and swelling of the bulk polymer material, which leads to reptation and interlocking of the chains across the crack plane to recover virgin mechanical properties and heal a crack. More recent research has explored the effects of tetrahydrofuran (THF) in epoxy−amine polymerizations.[15−17] Raman and Palmese found that solvent molecules can influence the epoxy−amine reaction chemistry, leading to inhomogeneous thermosetting networks.[16] Additionally, the presence of THF increased the free volume in the matrix.[16] Recently, the Palmese group reported the healing capability of an epoxy−amine thermoset at temperatures above the glass transition temperature of the material.[17]

In contrast to these methods, autonomic self-healing materials can repair damage in thermosets through chemical reactions at room-temperature based on ring-opening metathesis polymerization (ROMP).[18−24] Microcapsules containing dicyclopentadiene (DCPD) and wax-protected Grubbs' catalyst are both embedded in an epoxy matrix, and upon crack propagation through the material, the capsules rupture to release DPCD into the crack plane. Poly(DCPD) is formed in the crack plane resulting from the ROMP reaction of DCPD initiated by Grubbs' catalyst to restore the original structural properties of the polymer matrix. The system takes advantage of certain desirable properties of self-healing materials including low monomer reactivity in the absence of catalyst, fast polymerization kinetics, strong adhesion, and catalyst compatibility with the matrix. Up to 90% of the material's original fracture toughness can be restored by this method. However, the present limitations of this system, including catalyst availability, cost, environmental toxicity, stability, and materials processing, have motivated the search for a simpler approach to self-healing.

To date, there is no record of using solvents to heal cracks in thermoset materials at room temperature in an autonomic fashion. Our objective in this work is to demonstrate that cracks formed in epoxy-based thermoset materials can autonomically be healed with organic solvents, preventing further crack propagation, while recovering the material's original mechanical integrity.

Experimental Section. Organic solvents for the reference tests and encapsulation experiments were purchased from Fisher Chemicals and used without purification. Solvents tested included cyclohexane, hexanes, xylenes, toluene, chlorobenzene, tetrahydrofuran (THF), methylene chloride (CH_2Cl_2), nitrobenzene, *N*-methyl pyrrolidone (NMP), dimethylacetamide (DMA), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetonitrile (CH_3CN), butanol, ethanol, and formamide. EPON 828, EPON 862, EPICURE 3046, and EPICURE 3274 were purchased from Miller-Stephenson, and diethylenetriamine (Ancamine DETA) and tetraethylenepentamine (Ancamine TEPA) curing agents were received from Air Products.

Fracture testing followed previously reported protocols[23,24] using tapered double cantilever beam (TDCB) samples prepared at the following epoxy:amine ratios (by weight) and poured into silicone rubber molds: 100:12 parts per hundred (pph) mixture of EPON 828:DETA, 100:50 pph mixture of EPON 862:EPICURE 3274, and 100:16 pph mixture of EPON 828:TEPA. The resins underwent the same cure cycle of 24 h at room temperature, followed by 24 h at 35 °C. Other than short-groove reference tests with 5 μL of chlorobenzene manually injected into the crack plane of the EPON 862:EPICURE 3274 and EPON 828:TEPA matrices, EPON 828:DETA was used as the matrix for all experiments. After a precrack was inserted with a sharp razor blade into the groove of the sample, the TDCB specimens were pin-loaded and tested to failure using an Instron load frame under displacement control at a rate of 5 μm s^{-1}. Long-groove TDCB specimens contained a 47 mm long molded groove, while the short-groove TDCB specimens had a 25 mm long molded groove.[24] For the long-groove TDCB reference tests, 30 μL of each solvent was injected onto the crack plane, the two sides were realigned, and allowed to heal for 24 h at room temperature (22 °C). The healed TDCB samples were again loaded to failure and the load-displacement curve was recorded. All healed samples were tested after 24 h, unless otherwise stated. In situ healing was assessed in a similar manner as reference specimens, except that solvent was present in microcapsules (at various weight percentages of the matrix) dispersed throughout the central insert section of the short-

[†] Department of Chemistry and Beckman Institute, University of Illinois at Urbana−Champaign.
[‡] Department of Chemical Engineering, University of Texas at Austin.
[§] Department of Materials Science and Engineering and Beckman Institute, University of Illinois at Urbana−Champaign.
[||] Department of Aerospace Engineering and Beckman Institute, University of Illinois at Urbana−Champaign.

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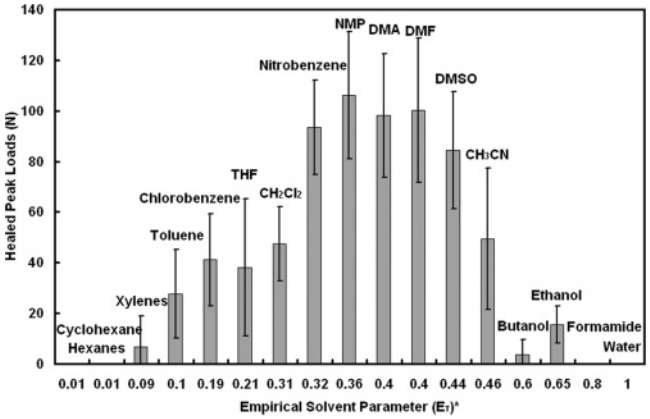

Figure 1. Summary of reference tests for various solvents. Healed peak fracture load is plotted as a function of polarity. The empirical solvent parameter (E_T) is related to polarity as described in [25]. Error bars represent standard deviation based on 5−10 samples.

groove TDCB samples (64 mm in length). Short-groove TDCB specimens were used for in situ healing because the average crack face separation is reduced from 26 μm (long-groove TDCB specimens) to 3 μm near the pin holes of the sample, allowing for intimate contact between the crack faces.[24] Healing efficiencies were defined as the ratio between the healed and the virgin fracture toughness,[18] represented as $\eta = P_{\text{healed}}/P_{\text{virgin}}$, where P and η represent the fracture peak loads of each sample and the healing efficiency, respectively. ESEM images were taken on a Philips XL30 ESEM-FEG instrument after a sputter-coating treatment with a gold−palladium source.

Results and Discussion. Solvents were screened for their healing ability by manually injecting solvent on the crack plane of a fractured epoxy test specimen. These reference tests mimic the behavior of the autonomic mechanism of solvent delivery that involves the fracture of embedded microcapsules. An extensive evaluation of common organic solvents shows a range of healing efficiencies that correlate with solvent polarity (Figure 1). The five solvents that exhibit the highest healing efficiencies are nitrobenzene, NMP, DMA, DMF, and DMSO. These solvents have dielectric constants ranging from 32 to 47 and boiling points that range from 153 to 210 °C. However, the relationship of polarity with healing efficiency remains unclear. On both extremes of the polarity spectrum, cyclohexane, hexanes, formamide, and water show no indication of recovering mechanical integrity. This behavior is consistent with control experiments for our previous self-healing system that showed no healing in the absence of catalyst.[18] Figure 1 demonstrates that polar aprotic solvents work well as healing agents, while protic solvents do not. The hydrogen bond acceptor ability of the five most efficient solvents is another possible explanation since the reacted epoxy contains a large amount of free hydroxyl groups that serve as hydrogen bond donors. The dipole−dipole interaction between hydrogen bond accepting solvents and free amines has been reported as having an influence on the epoxy−amine curing reaction.[16]

The autonomic self-healing system requires that solvent be encapsulated and the capsules embedded in the epoxy matrix. Unfortunately, the five highly efficient solvents noted above have yet to be successfully encapsulated using the urea−formaldehyde (UF) in situ polymerization method[19] due to their high degrees of polarity. Reverse-phase encapsulation procedures[26] were attempted for these solvents, but also proved unsuccessful to date. Thus, chlorobenzene emerged as a potential solvent for our initial autonomic healing experiments since it was encapsulated previously.[27] Chlorobenzene was encapsulated by the UF in situ polymerization method[19] with average

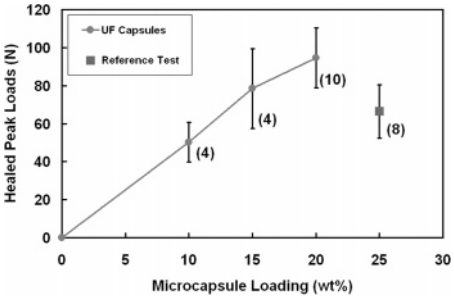

Figure 2. In situ healing with UF chlorobenzene microcapsules. Recovered peak loads were recorded 24 h after the initial fracture event. Error bars represent standard deviation based on the indicated number of samples (in parentheses). The reference test point is for manually injected chlorobenzene (5 μL) in a short groove TDCB specimen.

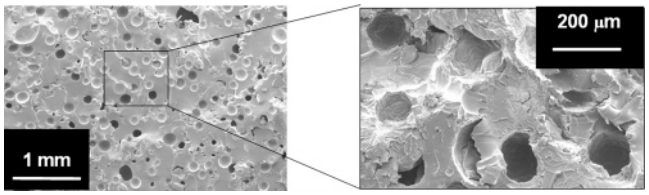

Figure 3. ESEM images of an epoxy fracture surface after healing and subsequent fracture with 20 wt % UF chlorobenzene core capsules. The inset shows a magnified region of the surface.

diameters of 160 ± 20 μm. Though a chlorobenzene system does not show the best recovery of fracture peak load (Figure 1), it serves as an adequate choice for initial demonstration of the solvent-based, autonomic healing concept. Chlorobenzene is a stable healing agent, and thus far it has remained in the interior of the microcapsules. No leakage through the shell walls is observed as indicated by no difference in mass loss measured by thermogravimetric analysis (TGA) experiments after several weeks.

When the chlorobenzene capsules are incorporated into the epoxy matrix and a crack propagates through the material, the solvent is released and wets the crack plane surface upon cleavage of the capsules. Using a short-groove TDCB specimen (25 mm in length of the crack-directed groove),[24] healed peak load increases with the amount of microcapsules in the system (Figure 2).

Intimate contact between the two crack faces is necessary for healing to occur. The fracture surface of a healed, in situ TDCB sample shows cleavage of the UF microcapsules on the surface (Figure 3). The fracture surface changes from a normally smooth surface to a more textured appearance with the addition of microcapsules. This type of morphology has been observed previously and is consistent with fracture surfaces of epoxy with embedded microcapsules.[28]

In order to assess the healing performance, we calculated a healing efficiency based on the ratio of the healed peak load to the virgin peak load.[18] Representative virgin and healed load-displacement curves for in situ fracture testing of a system with 20 wt % UF chlorobenzene capsules are shown in Figure 4a. Average healing efficiencies for this system are shown in Figure 4b, where the UF/chlorobenzene system shows 82% healing efficiency. This efficiency is comparable to the reference tests for chlorobenzene (78% healing efficiency). Nonpolar solvents such as xylenes and hexanes were also encapsulated using the UF in situ polymerization procedure to serve as controls for healing behavior. Fracture testing of specimens with microcapsules of these control solvents was performed yielding efficiencies of 38% and 0%, respectively. Additionally, hollow UF capsules were incorporated into TDCB samples and showed no healing.

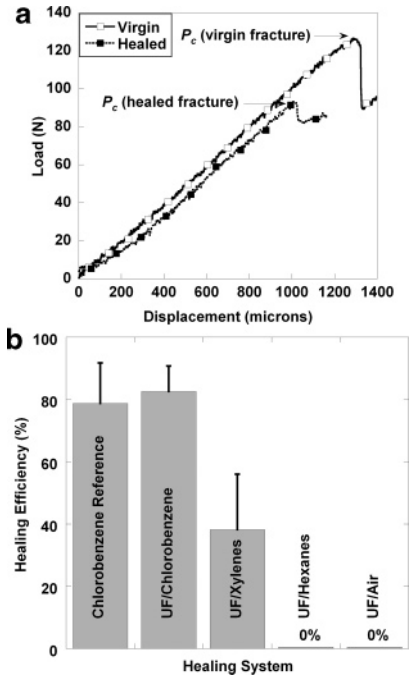

Figure 4. (a) Representative load-displacement curves for short-groove specimens demonstrating in situ healing with 20 wt % urea-formaldehyde chlorobenzene capsules. (b) Reported healing efficiencies for manually injected chlorobenzene reference tests and the in situ healing with various solvents in UF capsules.

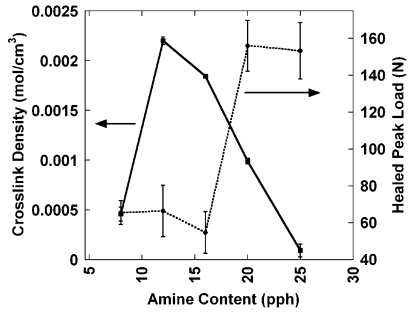

Figure 5. Healed peak load and cross-link density vs amine content for EPON 828:DETA epoxy. Samples were healed for 24 h after manually injecting 5 μL of chlorobenzene onto the fracture plane.

In an effort to explain the healing observed in the EPON 828:DETA system using chlorobenzene, the amount of amine was varied from 8 to 25 pph. Short-groove reference tests with manually injected chlorobenzene showed an increase in healed peak load with increasing amine concentration as shown in Figure 5. Conversely, healing performance appears to be inversely related to cross-link density (above the stoichiometric point). The highest cross-link density was observed at 12 pph DETA and agrees with previously published studies.[29]

Successful solvent healing was also applied to two other epoxy systems, EPON 862:EPICURE 3274 and EPON 828:TEPA. Reference tests with manually injected chlorobenzene for these matrices show significant recovery of fracture toughness, with average healed peak loads of 80 and 60 N, respectively, compared to 66 N for EPON 828:DETA. In conclusion, solvent-based healing of a thermoset at room temperature has been demonstrated with encapsulated chlorobenzene. This autonomic self-healing system recovered 82% of the materials' original fracture toughness. Healing of polymeric materials with encapsulated solvents is an economical, simple, and potentially robust alternative to the recovery of virgin properties of a material after crack damage has occurred. The mechanism of healing and effect of crosslinking in the matrix is currently under investigation. Other work involving water and epoxy resins suggests that the solvent may plasticize an epoxy matrix to allow molecular mobility that promotes further curing reactions, which could apply to the present system where solvent penetrates through the material to cause further crosslinking.[30,31] Spectroscopic evidence and thermal data will be necessary to elucidate the healing mechanism and will be reported in due course.

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