SOLVENT-BASED SELF-HEALING EPOXY MATERIALS

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

[†] Department of Chemistry and Beckman Institute
University of Illinois at Urbana-Champaign
Urbana, IL 61801
[‡] Department of Chemical Engineering
University of Texas at Austin
Austin, TX 78712
[§] Department of Materials Science and Engineering
University of Illinois at Urbana-Champaign
Urbana, IL 61801
[ǁ] Department of Aerospace Engineering
University of Illinois at Urbana-Champaign
Urbana, IL 61801

Introduction

Epoxy resins have a variety of applications in the automobile, aerospace, and adhesives industries. Within the past decade, White and co-workers have designed self-healing materials employing a ring-opening metathesis polymerization (ROMP) reaction between embedded microcapsules containing dicyclopentadiene monomer and wax-protected Grubbs' catalyst in an epoxy resin matrix.[1] This system has many limitations such as catalyst availability and cost, environmental toxicity, and stability. To overcome some of these limitations, a simple, one-component system based on common organic solvents has recently been developed, eliminating the need for the catalyst which was previously required for self-healing to be observed.

Early reports of crack healing in an epoxy resin required high temperature conditions for healing to occur.[2] This observed healing after fracture of the virgin material was due to molecular diffusion and reaction of residual functionality during subsequent heating of the material above its glass transition temperature.[3-5] Solvent addition is also responsible for some reports of healing, i.e. ethanol and methanol were used to seal the cracks of thermoplastic polymers under high temperature conditions.[6] The invoked healing mechanism involved wetting of the polymer surface and swelling of the bulk polymer material, which led to chain interlocking across the crack plane and recovery of virgin mechanical properties. More recent research has explored the effects of tetrahydrofuran (THF) in epoxy-amine polymerizations.[7-9] Thus far, there has been no record of using solvents to autonomically heal cracks in thermoset materials at ambient temperatures. Our objective in this work is to demonstrate that crack damage in epoxy-based thermosets can be healed autonomically with organic solvents, preventing further crack propagation, and recovering the material's original properties.

Experimental

Materials. Organic solvents for the reference tests and encapsulation experiments, and urea, ammonium chloride, and formaldehyde were purchased from Fisher Chemicals and used without purification. Resorcinol was received from J.T. Baker. Ethylene maleic anhydride copolymer (EMA) was purchased from Zeeland Chemicals, and 1,4-butanediol and cyclohexanone were purchased from Sigma-Aldrich and used as received. 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.

Instrumentation. Thermogravimetric Analysis (TGA) experiments were performed on a Mettler-Toledo TGA 851[e], calibrated by indium, aluminum, and zinc standards. Microcapsule samples were 5-10 mg weighed into 40 μL aluminum crucibles. Unless otherwise indicated, a heating rate of 10 ˚C/min over a temperature range of 25-650 ˚C was used in an atmosphere of nitrogen. ESEM images were taken on a Philips XL30 ESEM-FEG instrument after a sputter-coating treatment with a gold-palladium source.

Microencapsulations. The poly(urea-formaldehyde) in situ polymerization encapsulation has been presented and characterized in a previous work.[10] DCPD in the original procedure was replaced with xylenes, hexanes, and chlorobenzene in the same quantity (60 mL) as the liquid core material. All capsules were characterized using thermogravimetric analysis (TGA) and environmental scanning electron microscopy (ESEM).

Fracture Testing. Mechanical reference testing of tapered double cantilever beam (TDCB)[11] samples was conducted with long and short groove specimens[12] using an Instron load frame under displacement control at a rate of 5 μm s^{-1}. The epoxies tested include: 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 cure cycle of 24 h at room temperature, and a subsequent 24 h at 35 ˚C. EPON 828:DETA was used as the matrix for all experiments except for 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. In 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 hours, unless otherwise stated. In situ healing was assessed in a similar manner to 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-groove TDCB samples (64 mm in length). Short-groove TDCB specimens were used for in situ healing, allowing for intimate contact between the crack faces.[12] Healing efficiencies were defined as the ratio between the healed and the virgin fracture toughness,[1] represented as $\eta = P_{healed}/P_{virgin}$, where P and η represent the fracture peak loads of each sample and the healing efficiency, respectively.

Results and Discussion

Solvent Screening. 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 boiling points that range from 153-210 ˚C and E_T values ranging from 0.32-0.44. On both extremes of the polarity spectrum, cyclohexane, hexanes, formamide, and water show no indication of recovering mechanical integrity. The relationship of polarity with healing efficiency remains unclear. 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 highly efficient solvents is a possible explanation since the reacted epoxy contains a large amount of free hydroxyl groups that serve as hydrogen bond donors.

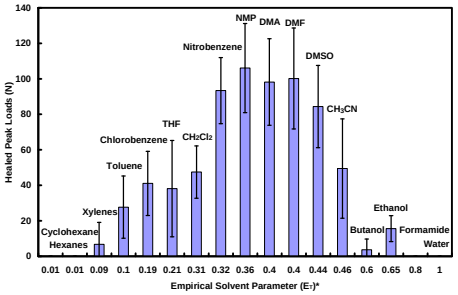

Figure 1. Reference tests for solvents exhibiting self-healing as a function of polarity. The empirical solvent parameter (E_T) is related to polarity as described in (13). Error bars represent standard deviation based on 5-10 samples.

Chlorobenzene Encapsulation. The autonomic self-healing system requires that the solvent be encapsulated and the capsules be 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 due to their high degrees of polarity. Thus, chlorobenzene emerged as a potential solvent for our initial autonomous healing experiments, since it was known that this solvent could be encapsulated.[14] Chlorobenzene was encapsulated by the UF in situ method[10] with average diameters of 160 ±

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

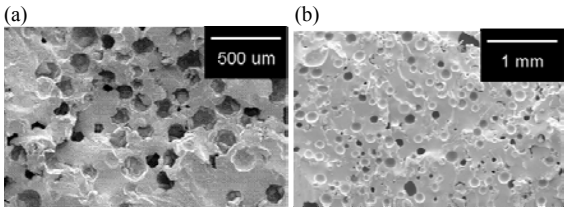

Figure 2. ESEM images of an epoxy fracture surfaces after healing and subsequent fracture with: (a) 20 wt% polyurethane chlorobenzene capsules and (b) 20 wt% UF chlorobenzene capsules.

Microcapsules having two different shell walls were studied. The difference in healing between the two shell wall capsules shown is attributed to the bonding of capsules to the epoxy as revealed by ESEM images (Figure 2). Polyurethane capsules do not form perfect spheres, but rather are shriveled in appearance while the UF capsules are more spherical. As a result of their shapes, the fracture surfaces of in situ TDCB samples appear distinct. The polyurethane capsules debond from the epoxy surface when fractured and do not release as much solvent as the UF capsules, which rupture cleanly to release the solvent and adhere well to the matrix. 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.[15] When the chlorobenzene capsules are incorporated into the epoxy matrix and a crack propagates 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),[12] the healing efficiency was found to increase with the volume fraction of microcapsules in the system (Figure 3). It is noted that intimate contact between the two crack faces is necessary for healing to occur.

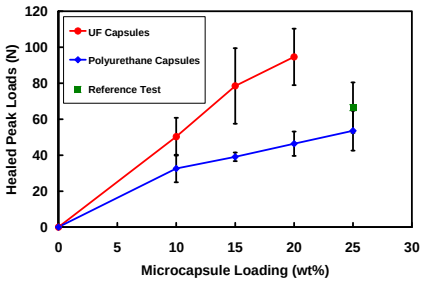

Figure 3. In situ healing with chlorobenzene microcapsules. Recovered peak loads were recorded 24 hours after the initial fracture event. Error bars represent standard deviation based on 5-10 samples. The reference test point is for manually injected chlorobenzene (5 μL) in a short-groove TDCB specimen.

Healing Efficiencies. In order to quantify the amount of healing, the virgin peak loads and healed peak loads are represented as healing efficiencies.[1] From the in situ fracture testing, an average healing efficiency of 82% was attained for a system with 20 wt% UF chlorobenzene capsules. 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 control solvents was performed yielding efficiencies of 38% and 0%, respectively (Figure 4). Additionally, hollow UF capsules were incorporated into TDCB samples and provide no healing. These control experiments show that the reference tests for nonpolar solvents correlate with in situ results of little to no healing, and healing is not attributed to the incorporation of microcapsules into the epoxy network (hollow capsules).

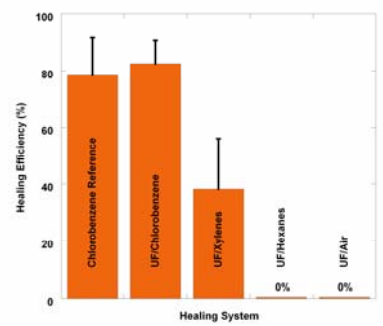

Figure 4. Observed healing efficiencies for chlorobenzene reference tests and in situ healing with various solvents in UF capsules.

Conclusions

In conclusion, solvent-based healing of a thermoset at room temperature has been achieved with chlorobenzene as a model solvent. This autonomic self-healing system recovered 82% of the materials' original fracture toughness. Using encapsulated solvents for self-healing applications is an economical, simplistic, and potentially robust alternative to restore original properties of a material after incurring crack damage. Development of a more environmentally friendly and optimal system is currently underway.

Acknowledgement. This work was supported by the Air Force Office of Scientific Research MURI (grant no. FA9550-05-1-0346) and the National Science Foundation under award number DMI 0328162 (Nano-CEMMS). The authors gratefully acknowledge Ben J. Blaiszik, Jason M. Kamphaus, and Gerald O. Wilson for their guidance and helpful discussions.

References

(1) White, S. R.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; Kessler, M. R.; Sriram, S. R.; Brown, E. N.; Viswanathan, S. *Nature* **2001**, *409*, 794.
(2) Outwater, J. O.; Gerry, D. J. *J. Adhesion* **1969**, *1*, 290.
(3) Jud, K.; Kaush, H. H. *Polym. Bull.* **1979**, *1*, 697.
(4) Wool, R. P.; O'Connor, K. M. *J. Appl. Phys.* **1981**, *54*, 5953.
(5) Raghavan, J.; Wool, R. P. *J. Appl. Polym. Sci.* **1999**, *71*, 775.
(6) (a) Jud, K.; Kausch, H. H.; Williams, J. G. *J. Mater. Sci.* **1981**, *16*, 204. (b) Wu, T.; Lee, S. *J. Polym. Sci.: Part B, Polym. Phys.* **1994**, *32*, 2055. (c) Wang, P. P.; Lee, S.; Harmon, J. P. *J. Polym. Sci. Part B, Polym. Phys.* **1994**, *32*, 1217. (d) Lin, C. B.; Lee, S.; Liu, K. S. *Poly. Eng. & Sci.* **1990**, *30*, 1399. (e) Hsieh, H.-C.; Yang, T.-J.; Lee, S. *Polymer* **2001**, *42*, 1227. (f) Shen, J.-S.; Harmon, J. P.; Lee, S. *J. Mater. Res.* **2002**, *17*, 1335.
(7) Raman, V. I.; Palmese, G. R. *Colloids Surf. A: Physicochem. Eng. Aspects* **2004**, *241*, 119.
(8) Raman, V. I.; Palmese, G. R. *Macromolecules* **2005**, *38*, 6923.
(9) Rahmathullah, A. M.; Palmese, G. R. "Healing Behavior of DGEBA Epoxy Cured with a Cycloaliphatic Diamine." Proceedings of the First International Conference on Self-Healing Materials, April 18-20, 2007, Noordwijk, The Netherlands.
(10) Brown, E. N.; Kessler, M. R.; Sottos, N. R.; White, S. R. *J. Microencapsulation* **2003,** *20*, 719.
(11) Brown, E. N.; Sottos, N. R.; White, S. R. *Exp. Mech.* **2002**, *42*, 372.
(12) Rule, J. D.; Sottos, N. R.; White, S. R. *Polymer* **2007**, *48*, 3520.
(13) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH: New York, 1988; p 407-410.
(14) Cho, S. H.; Andersson, H. M.; White, S. R.; Sottos, N. R.; Braun, P. V. *Adv. Mater.* **2006**, *18*, 997.
(15) Brown, E. N.; White, S. R.; Sottos, N. R. *J. Mater. Sci.* **2004**, *39*, 1703.