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Self-healing thermoset using encapsulated epoxy-amine healing chemistry

Henghua Jin [a,e], Chris L. Mangun [b], Dylan S. Stradley [c], Jeffrey S. Moore [d,e], Nancy R. Sottos [c,e], Scott R. White [a,e,*]

[a] Department of Aerospace Engineering, University of Illinois at Urbana-Champaign, 104 S. Wright St., Urbana, IL 61801, USA
[b] CU Aerospace, 301 N. Neil St., Suite 400, Champaign, IL 61820, USA
[c] Materials Science and Engineering, University of Illinois at Urbana-Champaign, USA
[d] Chemistry, University of Illinois at Urbana-Champaign, USA
[e] Beckman Institute, University of Illinois at Urbana-Champaign, USA

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ABSTRACT

Self-healing was achieved with a dual-microcapsule epoxy-amine chemistry in thermoset epoxy. One capsule contained a modified aliphatic polyamine (EPIKURE 3274) while the second capsule contained a diluted epoxy monomer (EPON 815C). Amine microcapsules were prepared by vacuum infiltration of EPIKURE 3274 into hollow polymeric microcapsules. Epoxy microcapsules were prepared by an *in situ* polymerization method. Both types of capsules were incorporated into an epoxy matrix (EPON 828:DETA) and recovery of mode-I fracture toughness was measured using tapered-double-cantilever-beam (TDCB) specimens. The optimal mass ratio of amine: epoxy capsules was 4: 6 and an average healing efficiency of 91% was achieved with 7 wt% amine capsules and 10.5 wt% epoxy capsules. Long-term stability of the healing system was demonstrated for six months at ambient conditions. Thermal stability was investigated by post curing samples at 121 °C and assessing healing performance.

1. Introduction

Fiber-reinforced polymeric composites are widely used in applications such as aircraft structures, wind turbine blades, and vehicles as they provide advantageous mechanical properties, e.g. high specific strength and stiffness. The polymeric matrix typically consists of a thermoset, such as epoxy, which is brittle in nature and flaw sensitive, resulting in poor resistance to crack initiation and growth. Inspired by living systems, self-healing polymers are designed to autonomically repair damage whenever and wherever it occurs, thus providing a means to significantly extend the service life and reliability of polymeric structural composites. Three primary conceptual approaches to self-healing have been explored over the past several years [1]. In the first, microcapsules containing reactive chemical species are incorporated into the native polymer matrix and, upon crack damage, release their contents and undergo a healing reaction. In the second, an embedded vascular network serves as healing agent(s) reservoir for sequestration and distribution throughout the polymer matrix. The third approach utilizes inherently reversible bonding in the matrix polymer to affect healing via thermally reversible reactions or reformation of hydrogen bonds.

Several microcapsule-based self-healing systems for polymers have been reported in the literature, including DCPD/Grubbs' catalyst [2,3], DCPD/tungsten hexachloride (WCl_6) [4], PDMS/dimethyldineodecanoate tin (DMDNT) catalyst [5], PDMS/Pt catalyst [6], epoxy/mercaptan [7], and epoxy/boron trifluoride diethyl etherate ($(C_2H_5)_2O{\cdot}BF_3$) [8]. Approaches relying on latent functionality have also attracted increasing research interest [9,10]. In this case the microencapsulated healing agent serves as a plasticizer to liberate residual reactive functionality in the host polymer matrix. For example, Caruso et al. reported solvent-promoted self-healing and demonstrated full recovery of fracture toughness [9,10]. The epoxy matrix is swollen by solvent delivered from ruptured microcapsules, which frees residual amine groups to initiate further cross-linking. However, this healing mechanism requires chain mobility within an undercured epoxy matrix, which is a substantial limitation for structural composites cured at elevated temperatures.

Autonomic damage restoration in large-scale structural composites requires chemistries that are robust, cost-effective, environmentally stable, and provide high healing efficiency. Many of the efforts on developing self-healing systems have focused on chemistries that are different from the host epoxy matrix. However,

* Corresponding author. Department of Aerospace Engineering, University of Illinois at Urbana-Champaign, 104 S. Wright St., Urbana, IL 61801, USA. Tel.: +2173331077.
E-mail address: swhite@illinois.edu (S.R. White).

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encapsulation of epoxy and its hardener provides a repair system that is chemically and mechanically compatible with host matrix. Preparations of microcapsules containing epoxy resins have been reported by several groups [11–15]. Microencapsulation of hardener for epoxy has been attempted with only modest success [7,8,16–18]. In practice, however, preparation of capsules containing a liquid amine is very difficult. Recently, McIlroy et al. reported a scheme for the encapsulation of diethylenetriamine (DETA) via interfacial polymerization using diisocyanate to create a cross-linked polymer shell around an amine-containing core [18]. However, the healing capability of these amine capsules was limited by the resulting high viscosity of core content [19].

In this paper we report a new approach to preparing amine microcapsules that constitutes a dual-microcapsule epoxy-amine self-healing system for epoxy polymers. Epoxy resin capsules are prepared by *in situ* polymerization of EPON 815C resin with a urea-formaldehyde shell wall [15], while amine capsules are produced by vacuum infiltration of EPIKURE 3274 amine into polymeric hollow microcapsules. Tapered-double-cantilever-beam (TDCB) specimens are used to assess the healing performance of this healing system. Thermal and aging stability of the system was also investigated.

2. Experiments

2.1. Materials

Epoxy monomers EPON 828 and EPON 815C as well as amine curing agents diethylenetriamine (EPIKURE 3223, DETA) and EPIKURE 3274 were purchased from Miller-Stephenson (Morton Grove, IL) and used as-received. Urea, triethanolamine, formic acid, and Formalin (37% formaldehyde in water) were obtained from Sigma–Aldrich (Saint Louis, MO). Ethylene-maleic anhydride (EMA) copolymer (Zema-400) powder with average $M_w = 400$ kDa was received from Zeeland Chemicals, and was used in a 2.5 wt% deionized water solution.

2.2. Synthesis of microcapsules

EPON 815C is a diluted EPON 828 epoxy resin containing 13.6% n-butyl glycidyl ether (BGE) with a low viscosity (5–7 P at 25 °C). Epoxy microcapsules were prepared by *in situ* polymerization of urea-formaldehyde (UF) following the procedure described by Blaiszik et al. [15] with an agitation rate of 800 RPM. Capsules were filtered and rinsed two to three times using ethanol and then sieved between 125 and 250 μm yielding an average diameter of 113 ± 48 μm.

Hollow microcapsules were prepared by a poly-condensation reaction of urea-formaldehyde pre-polymer on the surface of entrained air bubbles in a reaction vessel (Fig. 1). The pre-polymer solution was first prepared by dissolving 10.25 g of urea into 27.5 g of formalin (37% formaldehyde in water) in a 150 mL beaker and allowing the reaction to proceed at 70 °C for 1 h. The pre-polymer solution was then added to a 500 mL beaker that contained 50 mL deionized H_2O and 12.55 mL 2.5 wt% EMA. The beaker was placed in a temperature-controlled water bath, and then agitated at rates from 800 to 3000 RPM with a digital mixer (Eurostar, IKA Labortechnik) driving a three-bladed, 63.5 mm diameter, low-shear mixing propeller (Cole Parmer). The propeller was placed just beneath the solution's surface in order to entrap air bubbles. The water bath temperature was set to 35 °C with a ramp rate of 120 °C/min. When the bath temperature reached 30 °C, the pH was adjusted to 2.0 using formic acid. Once the bath temperature reached 34 °C, 25 mL warm deionized water (ca. 30 °C) was added. Thereafter, 15 mL of warm deionized water was added after an additional 15 and 30 min and 50 mL after 45 and 60 min. The water bath temperature was then set to 34 °C and the solution was allowed to react for 2 h. Hollow capsules between 75–180 μm were obtained upon air-drying and sieving.

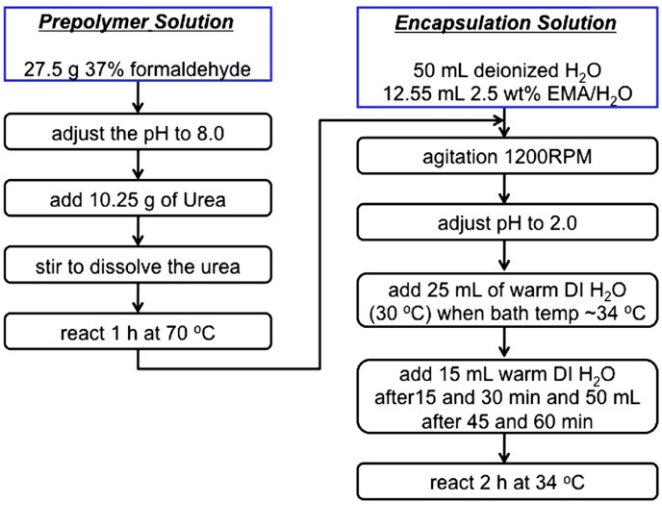

Fig. 1. Microencapsulation protocol for synthesis of poly(urea-formaldeheyde) hollow microcapsules.

2.3. Infiltration of EPIKURE 3274 modified aliphatic polyamine

Initially the hollow capsules were immersed in EPIKURE 3274 amine contained in a cylindrical vacuum jar. After vacuum infiltration for several hours, microcapsules floating on the top of the 3274 amine bath, which are still empty, were disposed while the ones at the bottom (filled with amine) were filtered and used without rinsing. The collected capsules have an average diameter of 117 ± 32 μm.

2.4. Healing performance evaluation

Localized short groove TDCB fracture specimens were used to evaluate the healing performance [20]. To prepare TDCB specimens, EPON 828 and 12 pph diethylenetriamine (DETA) were mixed, degassed to remove entrapped air, and poured into silicone rubber molds (with silicone rubber inserts) to cure overnight. The silicone rubber inserts were then removed and EPON 828:DETA (100:12) mixed with or without capsules was poured into the insert and allowed to cure 24 h at room temperature followed by 24 h at 35 °C [20]. In addition, a set of specimens were post-cured at 121 °C for various times with a ramp rate of 2.5 °C/min. Prior to testing, a pre-crack was created with a fresh razor blade into the center groove of the specimen. TDCB specimens were pin loaded using a load frame under displacement control mode at a loading rate of 5 μm/s until the crack had propagated through the insert groove section of the sample where the microcapsules reside. The samples were unloaded, allowing the crack faces to come back into contact, and then set aside to heal for 48 h at room temperature (without any external intervention, e.g. no applied heat or pressure) before again being loaded to failure. Healing efficiencies are reported as a ratio of healed to virgin fracture toughness, which for the TDCB geometry reduces to the ratio of peak loads at fracture [21],

$$\eta = \frac{K_{IC}^{Healed}}{K_{IC}^{Virgin}} = \frac{P_C^{Healed}}{P_C^{Virgin}}. \quad (1)$$

Averaged healing efficiencies are reported based on 5–9 specimens.

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Three separate types of control specimens were tested in order to investigate the effects of the individual components and delivery on healing performance. Control type I specimens contained only neat epoxy inserts. Healing was achieved by manually injecting a 0.7 μL stoichiometric amine: epoxy solution into the crack plane after virgin testing. Control type II and control type III specimens contained only epoxy microcapsules or amine microcapsules, respectively.

2.5. Characterization of microcapsules

Capsule size distributions were obtained from multiple optical images taken with a Leica DMR optical microscope interfaced with ImageJ software (version 1.42). At least 200 separate microcapsule diameters were measured to obtain the size distribution. A field emission environmental scanning electronic microscope (SEM) (Philips XL30 ESEM-FEG) was used to image the fracture surfaces of specimens and microcapsules under high magnification. Fracture surfaces of interest were sputter-coated with ca. 30 nm thick layer of gold-palladium before imaging. In order to characterize the shell wall thickness, hollow microcapsules were embedded in EPON828/DETA (weight ratio 100:12), cured for 24 h at room temperature and 24 h at 35 °C, then cleaved for imaging.

Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA851® under nitrogen flow and a heating rate of 10 °C/min. FTIR was also performed to analyze the core of 3274 amine capsules. To extract the core material, 3274 capsules were placed in a syringe filter (Millipore Millex® GP) attached to the end of a syringe. The syringe was depressed to crush the capsules, and the liquid contents of the microcapsules were collected in a vial for FTIR analysis.

3. Results and discussion

3.1. Microcapsule preparations

3.1.1. Hollow UF microcapsules

After synthesis, hollow microcapsules floated and accumulated on the surface of the reaction vessel while sediments including small urea-formaldehyde particles sank to the bottom. The yield was measured by comparing the mass of hollow capsules to the mass of shell wall materials used in capsules synthesis (i.e. urea and formaldehyde). The yields for this encapsulation procedure ranged from 9.6% to 17.7% for various agitation rates.

Hollow microcapsules with an average diameter 30–220 μm were produced by controlling the agitation rate between 800 and 3000 rpm during encapsulation, as shown in Fig. 2. Microcapsule size decreased with agitation rate in a power law fashion. A least square fit to the data yielded a slope of −1.3, a value consistent with liquid core microcapsules produced in similar manner [15,22,23].

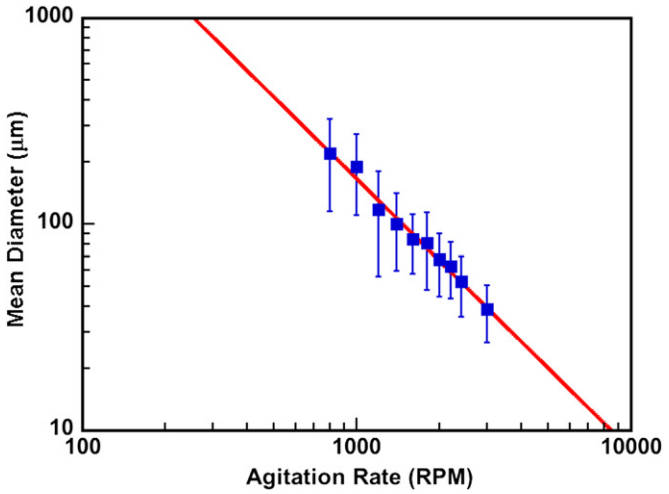

Fig. 2. Mean diameter as a function of agitation rate for hollow UF microcapsules. Error bars stand for standard deviations.

Hollow microcapsules were sieved and those between 75 and 180 μm were collected for amine infiltration (Fig. 3a). Because UF is a brittle material, the hollow capsules tended to be fragile upon air-drying due to the absence of an incompressible core material. Consequently, some of the capsules collapsed during sieving and handling. Some capsules have small holes on the surface, as shown in the inset of Fig. 3a, which could be created during the evacuation for SEM images or due to damage during handling.

Shell wall thicknesses for hollow microcapsules were measured from SEM images (Fig. 3b). Ten measurements were performed at different locations for each microcapsule. The average shell wall thickness was 1.1 ± 0.3 μm and is generally independent of the capsule diameter.

3.1.2. Amine microcapsules

Hollow UF microcapsules that were infiltrated with EPIKURE 3274 sank in the vacuum jar and were collected by filtering. Capsules tend to agglomerate due to the wet exterior surface (Fig. 4a). Nevertheless, amine capsules can be evenly dispersed when manually mixed into neat EPIKURE 3274, as shown in Fig. 4b. In addition, the filled capsules appear clear and transparent in the continuous phase (due to index matching), while hollow capsules appear black. FTIR spectra of both as-received EPIKURE 3274 and the core content of amine capsules show existence of primary amine chemical structures (N–H stretches between 3300 and 3000 cm^{-1}) as shown in Fig. 4c.

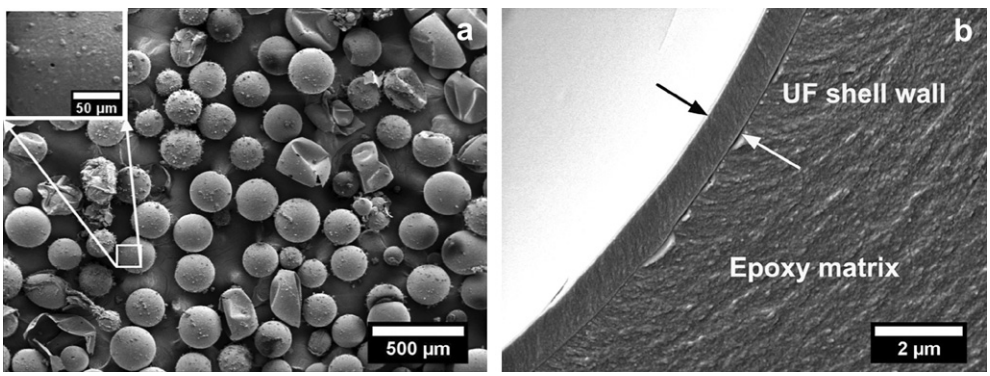

Fig. 3. Characterization of hollow UF microcapsules. (a) SEM images of hollow UF microcapsules (inset: small hole on the microcapsule surface). (b) Shell wall of a ruptured hollow microcapsule embedded in EPON 828/DETA epoxy matrix.

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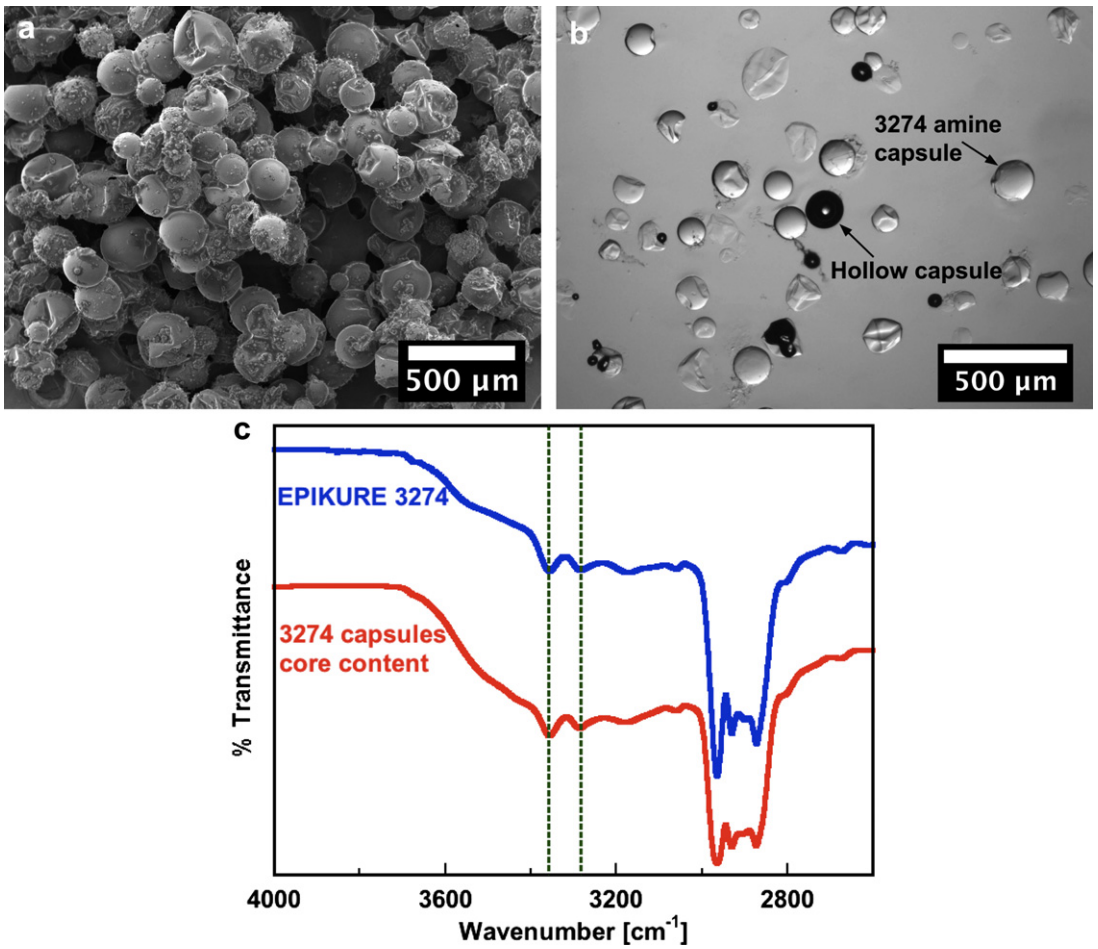

Fig. 4. Characterization of amine microcapsules. (a) SEM image of amine microcapsules after infiltration. (b) Optical micrograph of capsules immersed in EPIKURE 3274. Filled microcapsules appear clear while hollow microcapsules appear dark. (c) FTIR spectra of EPIKURE 3274 and extracted capsule core content. Primary amine N–H stretches are designated with dashed vertical lines.

The thermal stability of amine capsules as characterized by TGA is shown in Fig. 5. Both neat EPIKURE 3274 and amine capsules show very similar weight loss traces. Not surprising, the capsule shell wall provides little additional thermal stability given that the capsule core is infiltrated under vacuum pressure.

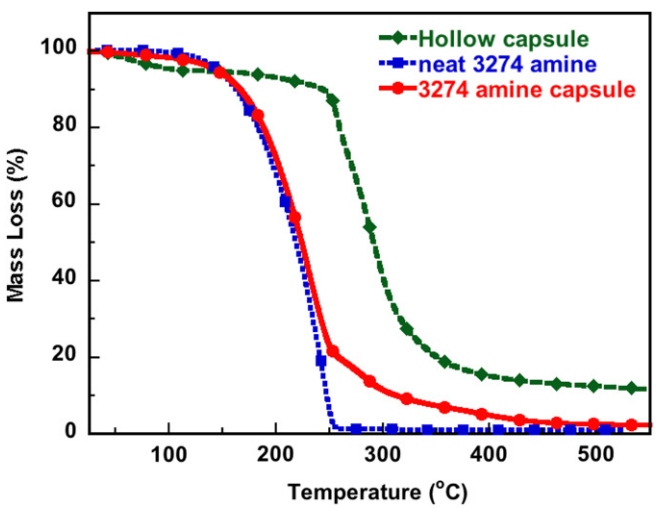

Fig. 5. TGA traces of amine capsules and neat EPIKURE 3274.

3.1.3. Epoxy microcapsules

Epoxy microcapsules containing EPON 815C resin were spherical with some UF debris adhered to the capsule surface (Fig. 6a). After drying and sieving, the epoxy capsules tended to agglomerate; however, they uniformly dispersed upon stirring into an epoxy matrix. Thermogravimetric analysis (TGA) of the capsules indicated good thermal stability to well over 200 °C (Fig. 6b). The initial mass loss at ca. 220 °C is largely associated with loss of the diluent phase (BGE) through the poly(UF) shell wall.

3.2. Fracture testing

Autonomic recovery of fracture toughness was measured by preparing and testing EPON 828:DETA (100:12) localized short groove tapered double cantilever beam (TDCB) specimens [20,21]. Fig. 7 shows representative load-displacement curves for the virgin and healed tests of a self-healing specimen. The average critical loads were determined from all of the individual propagation events (i.e. peak loads) during the virgin and healed tests (Fig. 7). For this particular specimen, the average virgin and healed critical loads were 97 N and 75 N, respectively, corresponding to a healing efficiency of $\eta = 77\%$.

Given the importance of stoichiometric ratio, we investigated the healing performance of TDCB samples in which the ratio of amine to epoxy capsules was varied while holding the total capsule loading at a constant 10 wt%. The highest average healing efficiency

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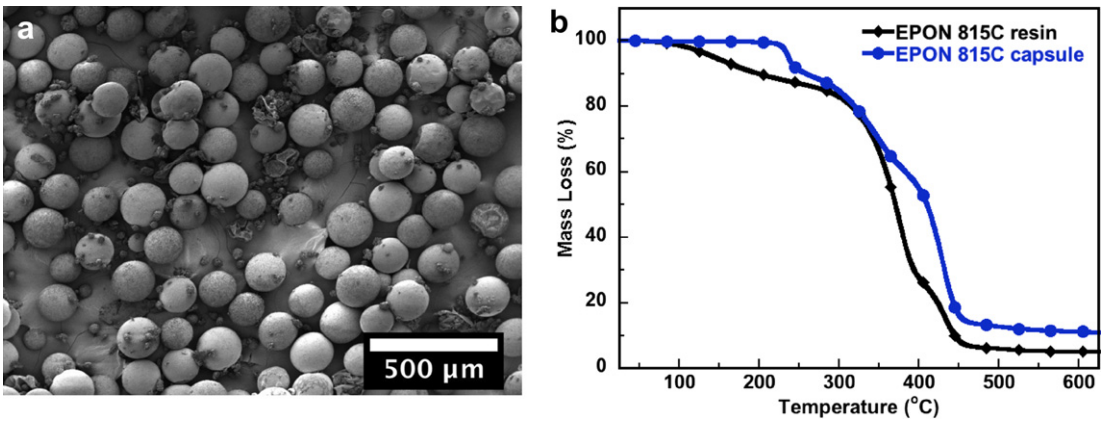

Fig. 6. Characterization of epoxy microcapsules. (a) SEM image of epoxy microcapsules. (b) TGA traces of epoxy microcapsules and neat EPON 815C resin.

(85 ± 13%) was obtained at a mass ratio of 4: 6 for amine: epoxy capsules as shown in Fig. 8a. Because the mean diameters of both capsule types were similar, the volumetric ratio of healing agents directly correlated to the capsule weight ratio [20]. This ratio deviated from the stoichiometric ratio of EPIKURE 3274 to EPON 815C (4:10) indicating some of the amine core material may be lost during specimen preparation. In addition, the total amine capsule weight included some EPIKURE 3274 coating on the capsule surface, which subsequently reacted with the surrounding epoxy matrix. Consequently, additional amine capsules (beyond stoichiometric requirements) were required to optimally react with the 815C resin to form a strong healing bond.

Once the optimal ratio of epoxy to amine capsules was established, a set of experiments was carried out to examine the effect of total capsule concentration (results shown in Fig. 8b). In general, healing efficiency increased as the total capsule concentration increased. The highest healing efficiency of 91 ± 21% was obtained with 17.5 wt% capsules. There was also a steady increase in virgin toughness with the capsule concentration due to toughening mechanisms, such as crack pinning, that have been well-documented in the literature [21]. Fractography of healed fracture surfaces reveals that the healed polymer failed cohesively (Fig. 9). This cohesive failure is indicative of *in situ* formation of epoxy and excellent bond strength to the epoxy matrix. Most importantly, this autonomic reaction leads to the high recovery of the virgin fracture toughness.

In separate experiments non-healing neat epoxy specimens (Control I) were healed by injection of 0.7 μL of pre-mixed EPIKURE 3274 and EPON 815C at a stoichiometric ratio of 4: 10. This quantity of healing agent was equivalent to the total volume of healing agent

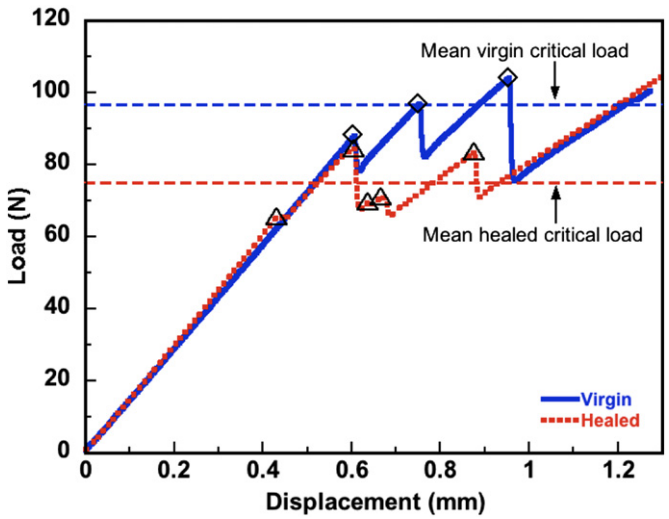

Fig. 7. Representative load versus displacement curves for self-healing TDCB fracture test. The diamonds and triangles represent the values used to calculate the mean critical loads of virgin and healed tests, respectively. The upper dashed line represents the mean virgin critical load (97 N) and the lower dashed line the mean healed critical load (75 N).

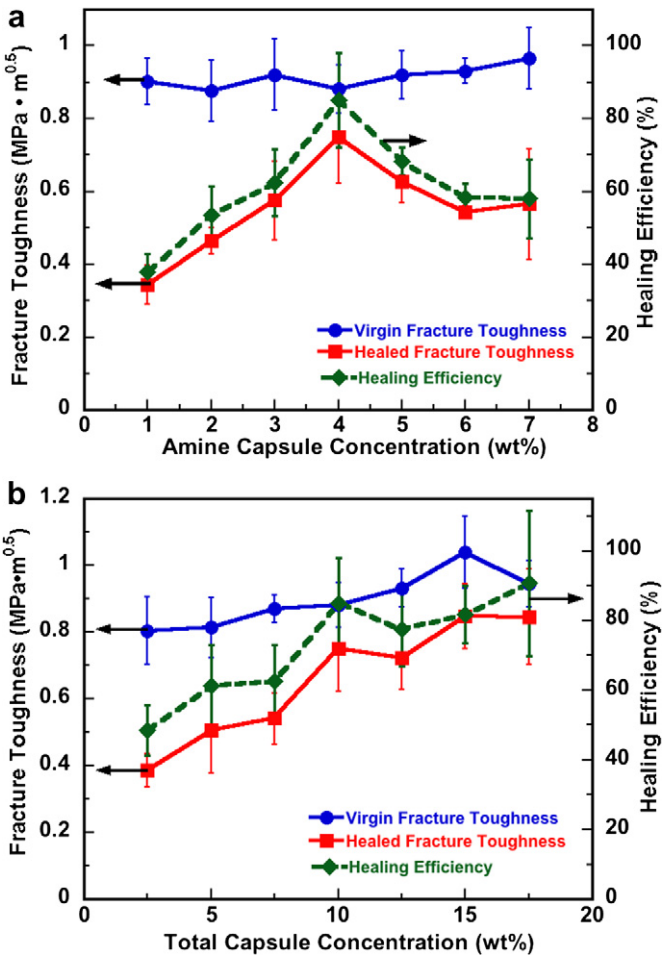

Fig. 8. Fracture toughness for virgin and healed tests of self-healing specimens with corresponding healing efficiencies. (a) Effect of amine: epoxy capsule weight ratio at a constant 10 wt% total capsule concentration. (b) Effect of total microcapsule concentration at a constant 4: 6 amine: epoxy capsule weight ratio.

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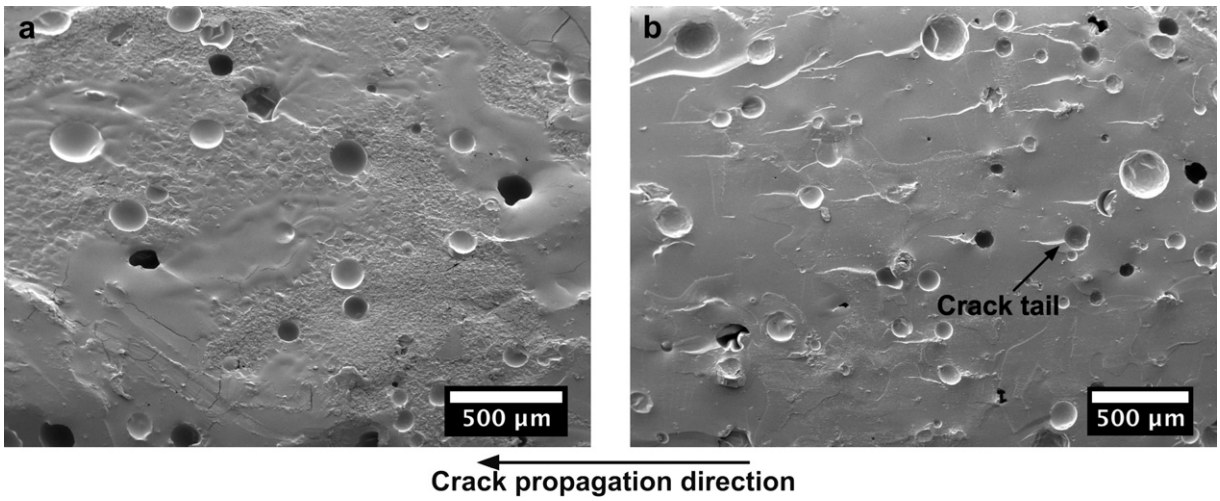

Fig. 9. SEM images of fracture surface from a self-healing specimen containing 4 wt% amine capsules and 6 wt% epoxy capsules. (a)Fracture surface after healed test. (b) Unhealed fracture surface (rinsed with ethanol immediately after fracture) revealing crack tails.

released from 10 wt% capsules during a self-healing fracture test [20]. An average healing efficiency of 136 ± 32% was measured although substantial crack deviation from the original crack plane occurred [6,7,10]. Nevertheless, the mechanical recovery provided by this healing agent system is excellent. Two other controls were tested in which only 10 wt% epoxy capsules were used (Control II) or only 10 wt% amine capsules (Control III). Both sets of controls were tested following the same protocol as self-healing tests. No healing occurred for either case, indicating that the healing for self-healing specimens is due to the reaction of epoxy and amine released from their capsules.

3.2.1. Long-term stability

The stability over time at ambient conditions of this self-healing system was also investigated. Self-healing specimens containing 4 wt% amine capsules and 6 wt% epoxy capsules were manufactured and cured and then aged at ambient conditions for various times before testing. The fracture test results are plotted in Fig. 10 and show no loss in healing efficiency after the initial drop in the first month. Importantly, up to 68% healing efficiency was obtained after aging for six months, indicating good stability of the healing system under ambient conditions. These results are a significant advancement from previous studies for solvent-based healing [9,10], in which healing efficiency decreased quickly after one month aging and decreased to zero after eight months due to the lack of residual functionality groups [24].

3.2.2. High temperature post-cure

A set of self-healing specimens containing 4 wt% amine capsules and 6 wt% epoxy epoxy capsules was prepared and then post-cured at 121 °C for various times. The results for fracture tests for these specimens are presented in Fig. 11. Healing efficiency dropped from 85% to 46% after the first hour and then remained relatively constant through 8 h. While the epoxy capsules are stable until ca. 200 °C as evident by TGA results (Fig. 6b), the reduction of healing efficiency was attributed to the leakage or instability of the amine capsules. To test this hypothesis, amine capsules were mixed with EPON 828/DETA (100:12) epoxy and placed between two glass slides and observed with optical microscopy after various heat treatments. Index refraction mismatch revealed that amine leaked out of the capsules and diffused into the matrix following the post-cure treatment (Fig. 12). Further improvements in encapsulation may lead to more thermally stable capsules, or overcompensation

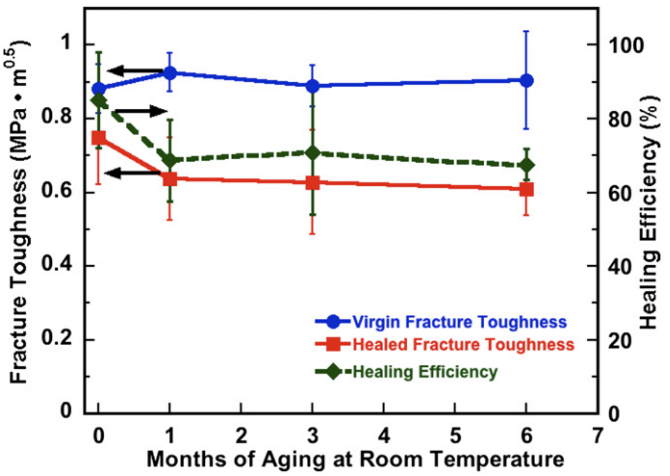

Fig. 10. Long-term stability of self-healing specimens containing 4 wt% amine capsules and 6 wt% epoxy capsules exposed to ambient conditions for various times before fracture testing.

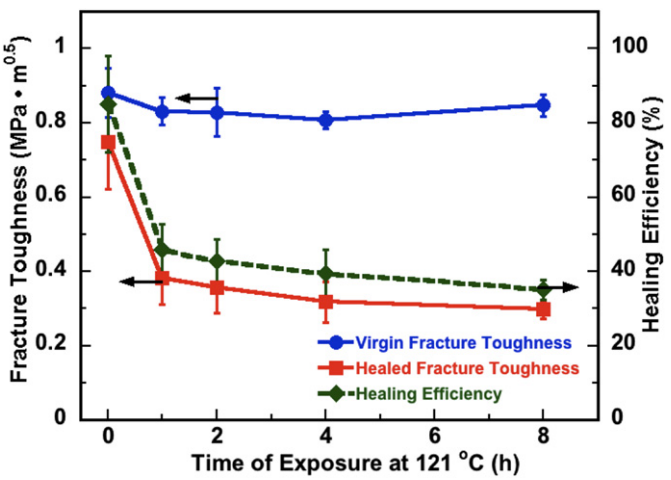

Fig. 11. Fracture testing results of self-healing specimens after post-cure at 121 °C for various times.

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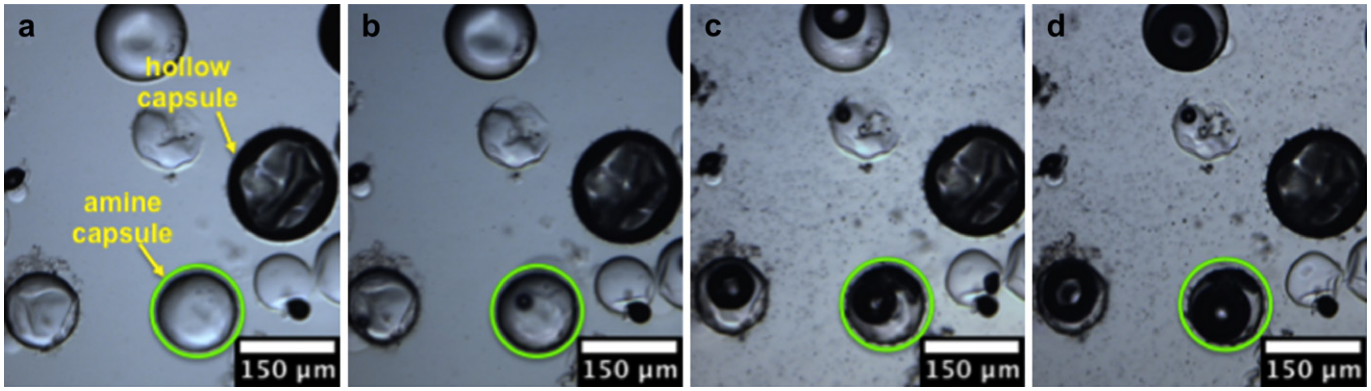

Fig. 12. Optical images of amine capsules in EPON 828:DETA (100:12) epoxy. (a) Immediately after mixing. (b) After curing at room temperature for 24 h followed by 35 °C for 24 h. (c) After post-cure for 1 h at 121 °C. (d) After post-cure for 8 h at 121 °C. Enlargement of voids in amine capsules indicates loss of core contents.

by increasing the amine capsule concentration could lead to improved healing performance at elevated temperatures.

4. Conclusion

A dual-microcapsule self-healing system was developed using epoxy resin capsules containing EPON 815C and amine capsules containing EPIKURE 3274. The optimal ratio was determined to be 4: 6 amine: epoxy capsules and an average healing efficiency of 91 ± 21% was achieved for low temperature cured specimens containing 7 wt% amine capsules and 10.5 wt% epoxy capsules. Ambient aging studies showed promising healing retention for a time period up to six months with 68% healing efficiency. Post-cure of self-healing specimens at 121 °C for 1 h decreased healing efficiency from 85% to 46% and to 35% after 8 h. This reduction of healing efficiency was traced to diffusion of amine from the capsules at elevated temperature. Future work will concentrate on protection of amine capsules rendering improvement in thermal stability and enhancement of healing efficiency for high temperature cured epoxy.

Acknowledgments

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References

[1] Blaiszik BJ, Kramer SLB, Olugebefola SC, Moore JS, Sottos NR, White SR. Annual Review of Materials Research 2010;40:179–211.
[2] White SR, Sottos NR, Moore JS, Geubelle PH, Kessler MR, Brown EN, et al. Nature 2001;409:794–7.
[3] Jackson AC, Bartelt JA, Marczewski K, Sottos NR, Braun PV. Macromolecular Rapid Communications 2011;32(1):82–7.
[4] Kamphaus JM, Rule JD, Moore JS, Sottos NR, White SR. Journal of the Royal Society Interface 2008;5:95–103.
[5] Cho SH, Andersson HM, White SR, Sottos NR, Braun PV. Advanced Materials 2006;18(8):997–1000.
[6] Keller MK, White SR, Sottos NR. Advanced Functional Materials 2007;17(14): 2399–404.
[7] Yuan YC, Rong MZ, Zhang MQ, Chen B, Yang GC, Li XM. Macromolecules 2008; 41(14):5197–202.
[8] Xiao DS, Yuan YC, Rong MZ, Zhang MQ. Polymer 2009;50:2967–75.
[9] Caruso MM, Delafuente DA, Ho V, Sottos NR, Moore JS, White SR. Macromolecules 2007;4(25):8830–2.
[10] Caruso MM, Blaiszik BJ, White SR, Sottos NR, Moore JS. Advanced Functional Materials 2008;18:1898–904.
[11] Yuan L, Liang G, Xie J, Li L, Guo J. Polymer 2006;47(15):5338–49.
[12] Yuan L, Liang G-Z, Xie J-Q, Li L, Guo J. Journal of Materials Science 2007; 42(12):4390–7.
[13] Cosco S, Ambrogi V, Musto P, Carfagna C. Macromolecular Symposia 2006; 234(1):184–92.
[14] Cosco S, Ambrogi V, Musto P, Carfagna C. Journal of Applied Polymer Science 2007;105(3):1400–11.
[15] Blaiszik BJ, Caruso MM, McIlroy DA, Moore JS, White SR, Sottos NR. Polymer 2009;50:990–7.
[16] Yuan YC, Rong MZ, Zhang MQ. Polymer 2008;49:2531–41.
[17] Xiao DS, Yuan YC, Rong MZ, Zhang MQ. Polymer 2008;50:560–8.
[18] McIlroy DA, Blaiszik BJ, Caruso MM, White SR, Moore JS, Sottos NR. Macromolecules 2010;43:1855–9.
[19] McIlroy DA, Jin H, White SR, Moore JS, Sottos NR. In preparation 2011.
[20] Rule JD, Sottos NR, White SR. Polymer 2007;48:3520–9.
[21] Brown EN, Sottos NR, White SR. Experimental Mechanics 2002;42(4):372–9.
[22] Brown EN, Kessler MR, Sottos NR, White SR. Journal of Microencapsulation 2003;20(6):719–30.
[23] Yang J, Keller MW, White SR, Sottos NR. Macromolecules 2008;41:9650–5.
[24] Caruso MM. Solvent-based self-healing polymeric materials. Department of Chemistry. vol. Ph.D. Urbana. Champaign: University of Illinois at Urbana-Champaign; 2010.

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