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FULL PAPER

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Full Recovery of Fracture Toughness Using a Nontoxic Solvent-Based Self-Healing System**

By *Mary M. Caruso, Benjamin J. Blaiszik, Scott R. White, Nancy R. Sottos,* and *Jeffrey S. Moore**

Two significant advances are reported for solvent-based self-healing of epoxy materials. First, an autonomic system yielding complete recovery of fracture toughness after crack propagation was achieved by embedding microcapsules containing a mixture of epoxy monomer and solvent into an epoxy matrix. Healing with epoxy-solvent microcapsules is superior to capsules that contain solvent alone, and multiple healing events are reported for this system. Second, efficient healing is reported for new solvents, including aromatic esters, which are significantly less toxic than the previously employed solvent, chlorobenzene. Preliminary aging studies using either chlorobenzene or ethyl phenylacetate as the solvent demonstrate the stability of the epoxy-solvent system under ambient conditions for at least one month.

1. Introduction

Epoxy is one of the most widely used components of polymers in composites for diverse applications such as wind turbine blades, aircraft structures, sporting goods, and protective coatings. Most epoxy thermosets consist of a two-part system that when cured, creates a glassy polymer network with advantageous mechanical properties such as strength and stiffness.[1] However, epoxy matrix composites are inherently brittle and prone to matrix microcracking under service loading conditions. Incorporating fillers such as polymeric microcapsules into epoxy matrices increases the toughness and prevents crack growth under certain conditions.[2] Microcapsules not only enhance the inherent toughness of the material, but they can also provide self-healing functionality when crack damage is experienced.[3–16] Designed to mimic the human body's ability to repair damaged wounds, self-healing materials release a healing agent into the crack plane upon damage, and through subsequent chemical and physical processes, restore the initial fracture properties.[3]

Our initial self-healing epoxy materials contained microcapsules filled with the monomer dicyclopentadiene (DCPD) and used an epoxy matrix in which Grubbs' catalyst was embedded.[3] Extensive experimentation revealed how parameters such as microcapsule size,[4–6] matrix environments,[7–9] and catalyst,[10,11] as well as external stimuli such as temperature,[10,12] and fatigue[13–16] loading conditions affect healing performance. Most recently, certain common organic solvents were found to heal epoxy materials. Specifically, chlorobenzene was the first encapsulated solvent to exhibit autonomic self-healing in epoxy resins with healing efficiency based on the recovery of fracture toughness (η) of 82% at 20 wt% capsule loading.[17]

This one-capsule-material design (Fig. 1a) eliminated the need for a metal catalyst and avoids issues such as catalyst dissolution, deactivation, and high cost.[12] However, the toxicity of chlorobenzene served as a limitation to commercialization of this greatly simplified self-healing materials system. In this paper, we expand the solvent-based autonomic healing system to two additional ''greener'' solvents, phenylacetate (PA) and ethyl phenylacetate (EPA).[18] These solvents have been used in applications where low toxicity is of paramount importance. For example, PA has been used as an agent to cure nitrogen accumulation disorders associated

[*] Prof. J. S. Moore, M. M. Caruso
Department of Chemistry
University of Illinois at Urbana-Champaign
600 S. Mathews Ave., Urbana, IL 61801 (USA)
E-mail: jsmoore@uiuc.edu
Prof. J. S. Moore, M. M. Caruso, B. J. Blaiszik, Prof. S. R. White
Prof. N. R. Sottos
Beckman Institute, University of Illinois at Urbana-Champaign
405 N. Mathews Ave., Urbana, IL 61801 (USA)
B. J. Blaiszik
Department of Mechanical Science and Engineering
University of Illinois at Urbana-Champaign
1206 W. Green Street, Urbana, IL 61801 (USA)
Prof. S. R. White
Department of Aerospace Engineering
University of Illinois at Urbana-Champaign
104 S. Wright St., Urbana, IL 61801 (USA)
Prof. N. R. Sottos
Department of Materials Science and Engineering
University of Illinois at Urbana-Champaign
1304 W. Green St., Urbana, IL 61801 (USA)

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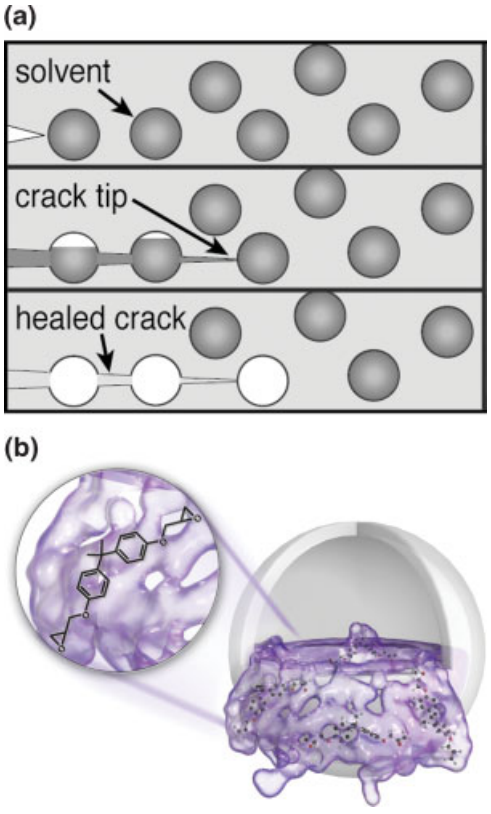


Figure 1. a) Simplified self-healing polymer system containing microencapsulated solvent. Upon crack damage, the microcapsules release their liquid core material into the crack plane and heal the crack [17]. b) 3D representation of polymeric microcapsule rupturing to release the healing agent. The liquid is comprised of an epoxy monomer, EPON 828, whose chemical structure is shown in the inset and solvent (depicted as the purple liquid) into a damaged fracture plane.

with cancer and anemia,[19] while EPA has been shown to be non-mutagenic and is a certified Kosher food additive.[20]

We also describe a way to further improve the healing ability of the solvent-based system using an epoxy monomer co-encapsulated with solvents (Fig. 1b). Several groups have reported the success and ease of making microcapsules containing epoxy resins.[21–24] We selected the epoxide functionality as a coencapsulant to test our mechanistic hypothesis that solvents swell the epoxy matrix and transport the residual amines in the matrix sol, making them available for further curing. As reported below, an improvement in the healing efficiencies (ca. 100%) is observed for samples containing epoxy-solvent microcapsules when compared to healing efficiencies (ca. 82%) for the system that consisted of microcapsules containing solvent only.[17] We show that additional thermoset material is deposited in the crack plane which presumably is the reason for the improved healing response.

2. Results and Discussion

Given our proposed mechanism that sol-extracted residual amine functionality present in a partially cured epoxy matrix is the dominant contributor to the chemistry of solvent-based self-healing systems,[25] it was reasoned that the delivery of excess epoxy to the matrix might facilitate the repair process. In an effort to test this hypothesis, microcapsules were initially prepared containing varying amounts of epoxy monomer dissolved in chlorobenzene. A first attempt incorporated a solution of 20 wt% epoxy in chlorobenzene into urea-formaldehyde (UF) microcapsules. Healing efficiency was measured for the 100:12 pph EPON 828:DETA using a short groove tapered double cantilever beam (TDCB) specimen.[5,17,26] In short groove TDCB specimens, the crack propagates through the 25 mm insert groove section of the sample where the microcapsules reside. A lower healing efficiency was measured compared to prior samples containing pure solvent capsules ($\eta_{20\%\ \mathrm{epoxy}} = 0.30$ versus $\eta_{\mathrm{chlorobenzene}} = 0.82$). From these initial studies, we further reasoned that the decreased healing behavior may have resulted from excess epoxy compared to the amount of residual amines in the sol and matrix. Indeed, by increasing the amine content of the matrix (20 pph instead of the stoichiometric 12 pph) and incorporating these same microcapsules, improved healing was observed ($\eta = 0.81 \pm 0.13$) relative to the prior results ($\eta_{20\%\ \mathrm{epoxy}} = 0.30$). Likewise, we expected that decreasing the amount of epoxy monomer in the microcapsules might also provide more desirable results for the epoxy matrix fixed at the original stoichiometry.

UF microcapsules 200 μm in diameter were prepared containing a core solution of 5 wt% epoxy-chlorobenzene.[27] In situ fracture testing with short groove TDCB specimens embedded with 5–20 wt% loadings of the epoxy-containing microcapsules demonstrated healing efficiencies up to 100% (Fig. 2). As shown in Figure 2b, healing efficiency increased proportionately with capsule loading. Complete recovery of fracture toughness was obtained at 15 wt% capsule loading and above. A low 5 wt% loading of these epoxy-chlorobenzene capsules exhibits healing efficiencies of ca. 80%. In comparison, this same degree of healing was previously achieved by a 20 wt% loading of pure chlorobenzene capsules.[17]

Full recovery of fracture toughness is explained within the context of the postulated mechanism for solvent healing.[25] When the microcapsules are ruptured by an incoming crack, the solvent locally swells the matrix, allowing accessibility of residual amines and further crosslinking with residual epoxy functionality. However, the additional epoxy delivered to the crack plane from the ruptured capsules improves the chance for additional crosslinking and helps bond new thermoset material to the original matrix interface. This new thermoset is identified by SEM on the crack plane surface of healed samples (Fig. 3), and was not previously observed on the crack faces of samples containing pure solvent capsules.[17] Since this new thermoset consists of the same epoxy material as the matrix, it is difficult to unambiguously distinguish between the original matrix and the new thermoset material.

Using surface characterization techniques, the healed film formed in the crack plane of fracture specimens was attributed to the encapsulated epoxy curing on the surface. Specifically, a

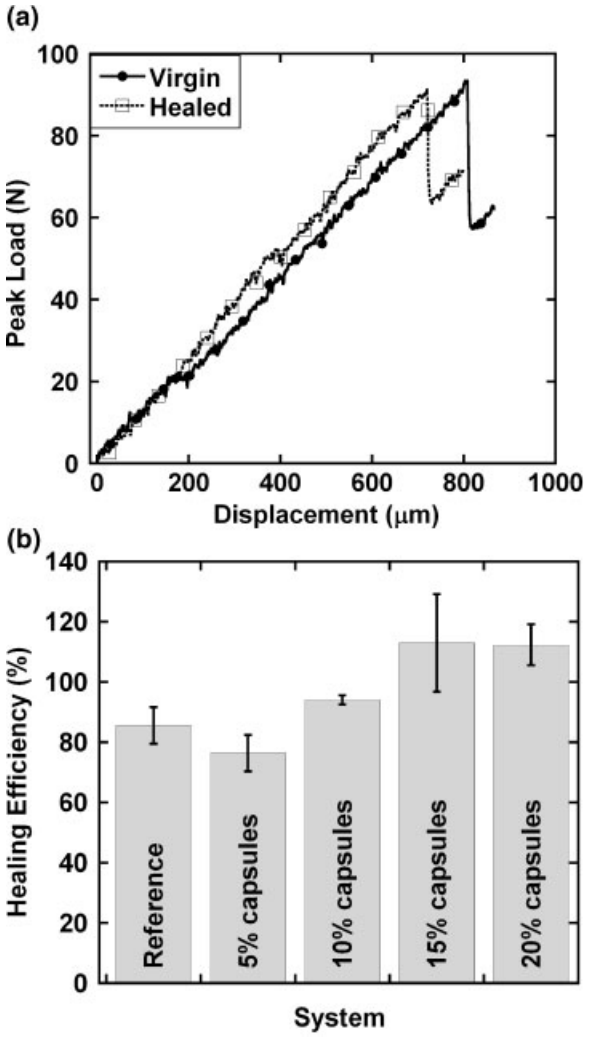


Figure 2. a) Representative load-displacement curve for short groove TDCB specimens containing 15 wt% epoxy-chlorobenzene microcapsules. b) Healing efficiency, defined as the recovery of fracture toughness ($\eta = P_{healed}/P_{virgin}$) [3], for epoxy-chlorobenzene microcapsules as a function of microcapsule loading (by weight percent). The reference test point is for a manually injected solution of 5 wt% epoxy-chlorobenzene (5 μL) and error bars indicate standard deviation based on 5 samples.

brominated epoxy (EPON 1163) shown in Scheme 1 was encapsulated with chlorobenzene using the UF in situ polymerization method at a concentration of 0.447 M (epoxide molar ratio equivalent to 13% by weight of EPON 828). Short groove TDCB fracture samples were prepared with 15 wt% capsules and demonstrated comparable healing efficiencies to the EPON 828-chlorobenzene system ($\eta = 0.81 \pm 0.21$). The fracture surfaces were analyzed by SEM to reveal the healed film (Fig. 4a). Previously, this film was indistinguishable from the matrix, but by using the brominated epoxy in microcapsules, the film is clearly visible by energy dispersive X-ray spectroscopy (EDS) mapping of the fracture surface (Fig. 4b). Additionally, time-of-flight secondary ion mass spectrometry (TOF-SIMS) was used to confirm the presence of a bromine-containing epoxy film on the fracture surface. This technique has previously been used on epoxy-amine surfaces to characterize the chemical components.[28] Results produced from the spectrometer indicate a high degree of bromine ($m/z = 79$ and 81) on the entire surface, confirming release of the brominated epoxy monomer from the microcapsules leading to formation of a new film on the surface.

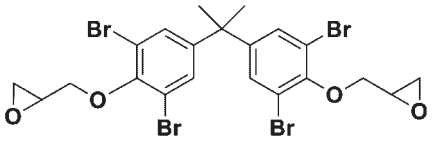
Given the important role of stoichiometry, we quantified the healing response as a function of mass of epoxy delivered, while holding the amount of solvent constant. The total mass of fluid healing agent delivered to the crack plane ($M_{\text{Healing Agent}}$) was calculated according to the derivation of Rule et al.[5] as

$$M_{\text{Healing Agent}} = \rho_s \varphi D_c \tag{1}$$

where ρ_s is the density of the matrix, φ the mass fraction of microcapsules, and D_c the mean diameter of the microcapsules. Equation 1 was modified to separate the mass of healing agent delivered (mg cm^{-2}) into the two components used in our capsules,

$$M_{\text{Epoxy}} = \rho_s \varphi D_c \xi \tag{2}$$

$$M_{\text{Solvent}} = \rho_s \varphi D_c (1 - \xi) \tag{3}$$



EPON 1163

Scheme 1. Chemical structure of brominated epoxy (Miller–Stephenson) used in this study.

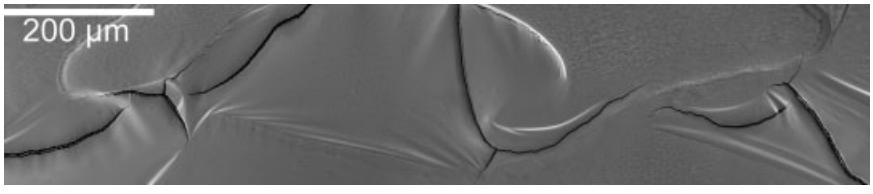


Figure 3. SEM images displaying the healed film on the fracture surface of an EPON 828:DETA specimen containing 5% epoxy-chlorobenzene microcapsules (10 wt% capsule loading).

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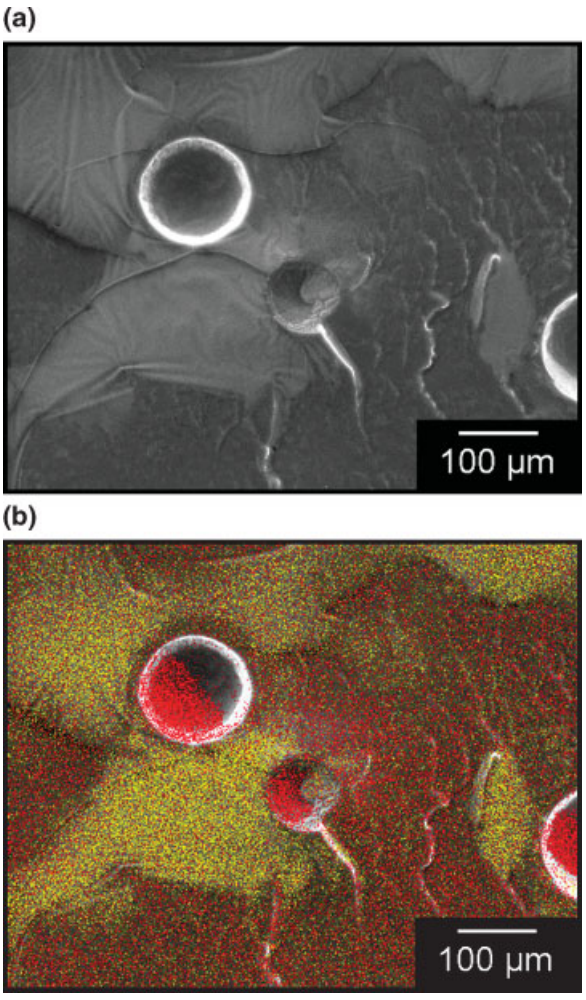

Figure 4. a) SEM image of the fracture surface showing new film formed on the healed crack plane. b) SEM image with an elemental map of the same area (from EDS) showing oxygen in red and bromine in yellow.

where the quantity ξ represents the weight fraction of epoxy resin in the capsules. These equations are used with capsules of varying ξ values to maintain a constant delivery of epoxy or solvent. In our experiments, different amounts of chlorobenzene capsules and epoxy-chlorobenzene capsules were used to make fracture specimens and the results are shown in Figure 5. Twenty-four hours after the initial virgin fracture (first healing event), the samples were tested for restoration of fracture toughness and healing efficiencies were calculated. The healing efficiencies begin to plateau when the epoxy delivered is ca. 0.1 mg cm^{-2}, demonstrating that only a small amount of epoxy is required to react with residual amine functionality in the matrix.

Interestingly, we found that samples could undergo subsequent repair events. After the first healing event, samples were retested after 7 days or longer and reported high peak loads (Fig. 5). Due to the efficacy of rehealing, we chose to wait 7 days after the first healing event for full recovery of fracture

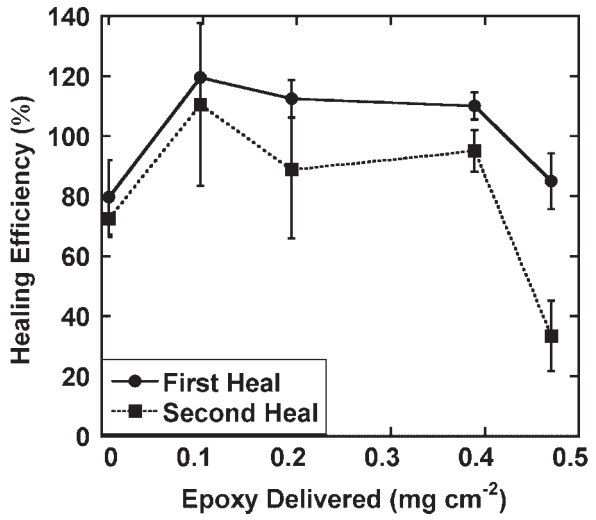

Figure 5. Healing efficiencies reported for in situ short groove TDCB fracture testing with varied amounts of epoxy delivered to the crack plane with the amount of chlorobenzene held constant at 3.15 mg cm^{-2}. Recovery of fracture toughness after the first healing cycle was measured 24 h after the initial fracture. Subsequently, samples were allowed to heal for 7 days for the second healing cycle and then retested for fracture toughness recovery. Error bars represent the standard deviation based on 5 samples.

toughness. Repeated testing of these samples over time showed a decrease in the healed peak load with each healing cycle. A maximum of 3–5 rehealing events were observed over a series of experiments. A possible explanation for this repeated healing is that when re-damaging a specimen, there was evidence of crack branching as shown in Figure 6. Deviated cracks rupture additional microcapsules and release more healing agent into the new crack plane. The release of each solvent was detected during testing by their characteristic smells. However, healing efficiency decreased with increasing number of healing cycles. This reduction in healing efficiencies is a result of local depletion of healing agent and reduction in residual amines available to crosslink with the epoxy.

Given the success of the epoxy-chlorobenzene system, we sought to expand the scope of solvents for self-healing materials, particularly to less-toxic solvents. Aromatic esters emerged as possible, environmentally-friendly solvent alternatives. Microcapsules containing mixtures of esters have been prepared previously for application in the fragrance

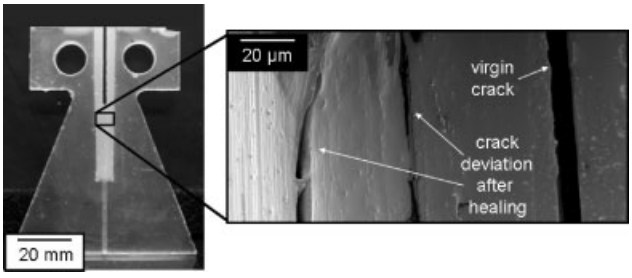

Figure 6. Short groove TDCB specimen with epoxy-solvent capsules and inset shows an SEM image of the virgin crack through the material and subsequent cracking through healed material.

Table 1. Summary of healed fracture peak loads (in Newtons) observed for chlorobenzene and acetate solvents.

Solvent	Long groove TDCB [a] [N]	Solvent In situ [b] [N]	Epoxy-solvent Reference [c] [N]	Epoxy-solvent In situ [d] [N]
Chlorobenzene	66.4 ± 13.9	78.5 ± 12.3	55.7 ± 6.2	99.3 ± 14.9
Phenyl Acetate	66.9 ± 11.7	103.1 ± 10.8	69.5 ± 11.0	83.8 ± 6.6
Ethyl Phenylacetate	70.2 ± 10.4	48.2 ± 5.8	70.3 ± 5.0	83.8 ± 9.2

Average peak loads and one standard deviation based on five EPON 828:DETA (100:12 pph, standard cure cycle) epoxy samples are given for each data set. [a] The solvent reference test shows results for manually injected (30 μL) of solvent using long groove TDCB specimens, while all other tests were done using short groove TDCB specimens. [b] The in situ data shows healing based on 15 wt% capsule loading in the epoxy matrix of pure solvent capsules. [c] The epoxy-solvent reference test point used manually injected (5 μL) solution of 13% epoxy-solvent. [d] In situ tests with 15 wt% capsule loading of 13 wt% EPON 828 in solvent capsules with average diameters of 180 μm.

industry.[29,30] Phenylacetate (PA, dielectric constant $\varepsilon_r = 6.9$) and ethyl phenylacetate (EPA, $\varepsilon_r = 5.4$) were identified as candidates for solvent-based healing in an epoxy material since their polarities are similar to that of chlorobenzene ($\varepsilon_r = 5.6$).[31] Reference tests in which acetate solvents were manually injected into crack plane of TDCB long groove specimens[26] were performed and exhibited healed peak loads similar to that of chlorobenzene (Table 1).

In order to encapsulate these solvents using the UF in situ polymerization method,[4] immiscibility in water is essential. The low dielectric constants for both solvents facilitated the preparation of stable microcapsules with solvent cores. Microcapsules were prepared with PA and EPA cores[27] and embedded in TDCB specimens. Fracture tests on these samples show significant fracture toughness recoveries 24 h after an initial fracture event. Furthermore, epoxy monomer was co-encapsulated with these acetate solvents in the same manner as chlorobenzene and the healed peak loads for reference and in situ tests are reported in Table 1.

EPA was selected as a less toxic solvent to coencapsulate with epoxy monomer for further investigation. As expected, ca. 100% healing efficiencies were observed for this system and a representative load-displacement curve is shown in Figure 7a. In an effort to quantify the healing response of the epoxy-EPA microcapsule system, the mass of epoxy delivered was varied while keeping the amount of solvent constant (Fig. 7b). As observed with chlorobenzene, subsequent repair events are reported for the system containing epoxy-EPA microcapsules. Thus, these results demonstrate that alternative solvents (e.g., EPA, PA) can be used to replace chlorobenzene in future commercialized self-healing products.

Control experiments for the epoxy-solvent microcapsule mixtures were conducted using other solvent combinations. Hexyl acetate ($\varepsilon_r = 4.4$) was identified as a solvent that could be encapsulated using the UF in situ polymerization method but was too nonpolar to demonstrate a solvent healing effect in an epoxy matrix. Hexyl acetate does not demonstrate any degree of healing from reference tests or from in situ testing with prepared UF hexyl acetate capsules ($\eta = 0$). Thus, microcapsules containing 13% epoxy-hexyl acetate were prepared, incorporated into fracture specimens, and displayed a minimal amount of fracture toughness recovery ($\eta = 0.20 \pm 0.14$). At the opposite extreme, microcapsules containing 80% epoxy-hexyl acetate ruptured upon crack damage, but released too much

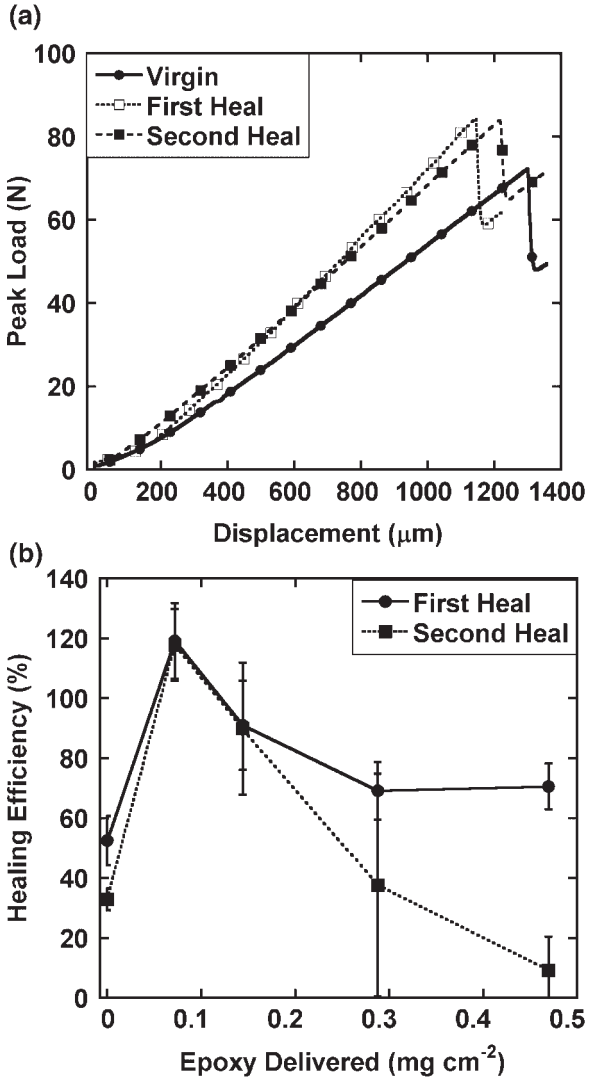

Figure 7. a) Representative load-displacement curves for short groove TDCB specimens containing 15 wt% epoxy-EPA microcapsules showing multiple healing events 24 h and 7 days after initial crack damage. b) Healing efficiencies reported for in situ short groove TDCB fracture testing with varied amounts of epoxy delivered to the crack plane with the amount of EPA held constant at 3.15 mg cm^{-2}. Recovery of fracture toughness after the first healing cycle was measured 24 h after the initial fracture. Subsequently, samples were allowed to heal for 7 days for the second healing cycle and then retested for fracture toughness recovery. Error bars represent the standard deviation based on 5–10 samples.

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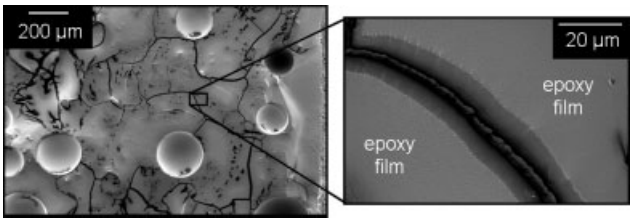

Figure 8. SEM of healed crack plane from an in situ sample with 80% epoxy-hexyl acetate capsules (15 wt% loading). The microcapsules have ruptured to produce an excessively thick epoxy film on the surface (shown in the inset) that prevents the crack faces from joining to heal the epoxy.

epoxy into the crack plane to provide any recovery of fracture toughness ($\eta = 0$) as shown in Figure 8. These control experiments elucidated the contribution of both the solvent and epoxy to the high healing efficiencies.

With the discovery of a system that completely recovers the virgin fracture toughness, we sought to test its stability over time through aging studies. Short groove TDCB specimens were prepared with 15 wt% microcapsules of epoxy-chlorobenzene and epoxy-EPA with no virgin crack and exposed to ambient conditions for varying time periods. After specified time periods, the samples were precracked and fractured. The degree of healing measured 24 h after the initial fracture event is reported in terms of healing efficiencies (Fig. 9). Within experimental scatter, the healing efficiencies decrease only slightly over the time period of a month. Current investigations are underway to determine the projected stability of this system on a longer time scale and its performance under fatigue loading conditions.

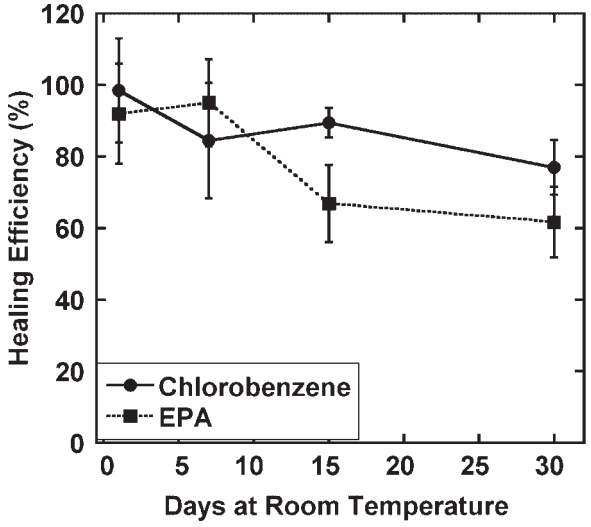

Figure 9. Stability of epoxy-chlorobenzene and epoxy-EPA capsule systems (15 wt% loading) shown over time for samples exposed to ambient conditions before fracturing. Healing data was acquired after 24 h from fracture event and error bars represent standard deviation based on 5 short groove TDCB specimens.

3. Conclusions

The incorporation of an epoxy monomer in solvent-filled microcapsules at various percentages by weight has improved healing efficiencies up to 100% for self-healing epoxy systems. When the amount of solvent delivered to the crack plane is held constant, the amount of epoxy delivered shows a dramatic impact on healing observed. However, too much epoxy in a capsule or none at all result in significantly lower healing efficiencies for the system. These samples exhibit multiple healing events over time as evidenced by the samples' recovery of fracture toughness. The solvent-based self-healing concept has also been successfully expanded to two other less toxic aromatic ester solvents (PA and EPA). Our system is versatile to other solvents yet to be reported and our work is by no means inclusive to show of all the possible solvents that possess healing abilities. Initial aging studies show promising healing ability for a time period up to one month. These advances are significant in designing composites for applications where microcrack damage leads to self-healing and subsequent restoration of the structural integrity.

4. Experimental

Materials: Chlorobenzene, hexyl acetate, phenyl acetate (PA), and ethyl phenylacetate (EPA) were purchased from Sigma–Aldrich and used as received. Urea, ammonium chloride, and formalin (37% formaldehyde) were purchased from Fisher Chemicals. Resorcinol was received from J. T. Baker. Ethylene-maleic anhydride copolymer (EMA, M_w 400 000) was donated by Zeeland Chemicals and used in a 2.5% aqueous solution. EPON® 828 and EPON® 1163 were purchased from Miller–Stephenson. Diethylenetriamine (Ancamine DETA) curing agent was received from Air Products.

Microencapsulations: Microcapsules were synthesized using the UF in situ polymerization procedure with slight modifications [4]. All reactant quantities were decreased by 50%, except the volume of core solution to be encapsulated was held constant at 60 mL [27]. EPON 828 was encapsulated in solutions of chlorobenzene, PA, EPA, and hexyl acetate at various weight percentages. Epoxy resins were dissolved in the respective solvents before adding to the emulsion mixture for encapsulating. The capsules were sieved to include capsules between the range of 125–355 μm and average diameters were determined using optical microscopy.

Fracture Testing: All fracture specimens were prepared by stirring 100:12 pph EPON 828: DETA, degassing the mixture and allowing the samples to undergo a standard cure cycle of 24 h at room temperature (22 °C) and 24 h at 35 °C [26]. Reference tests were conducted with long groove and short groove taped double cantilever beam (TDCB) specimens and manually injecting 30 μL and 5 μL, respectively, of solutions into the grooved-section of the sample [5, 26]. In situ samples were prepared using short groove TDCB specimens and capsules were stirred into the 100:12 pph EPON 828:DETA matrix at various loadings by weight (5–20 wt%) and poured only into the central region of the samples. After curing, samples were precracked with a razor blade and pin-loaded on an Instron load frame under displacement control at a rate of 5 μm s^{-1} until the crack had propagated the length of the groove (25 mm). Healed samples were tested after 24 h from initial fracture event. Healing efficiencies (η) were determined by comparing the healed peak loads to the virgin peak loads, after allowing the sample to autonomically heal for 24 h at room temperature, unless otherwise stated [3]. Environmental scanning

electron microscopy (ESEM) images of the fracture surfaces were taken on a Philips XL30 ESEM-FEG instrument after a sputter-coating treatment with a gold-palladium source. Elemental mapping was conducted on the surface by EDS (attached to the SEM) with a 20 kV electron source and spot size of 2.6 nm.

TOF-SIMS: 2 mm thick samples of the fracture plane were sputter-coated and introduced into the TOF-SIMS (Physical Electronics TRIFT III) sample chamber. The instrument is equipped with a triple-focusing time-of-flight mass spectrometer and a pulsed 22 kV Au metal ion source (average current 2 nA). Static SIMS conditions were employed using a pulsed Au^+ primary ion beam rastered over an area of 500 μm × 500 μm at a bunched mode with the contrast diaphragm in and charge compensation enabled. SIMS spectra were acquired over a mass range of 1 to 2 000 Da in the negative mode for 10 minutes. The mass calibration of negative ions was internally performed by using H^-, O^-, Cl^-, Br^-, Au^-.

Aging Study: Short groove TDCB specimens composed of EPON 828:DETA at 100:12 pph with 15 wt% microcapsules of 13 wt% 828-solvent solution (average diameter = 180 μm) were prepared and underwent a curing cycle of 24 h at room temperature (22 °C) and 24 h at 35 °C. Solvents tested were chlorobenzene and EPA. The samples were left at room temperature (relative humidity ca. 40%) for the following time periods: 7 days, 15 days, and 30 days. Following this time, the samples were precracked and virgin peak loads were recorded. The samples were re-tested 24 h after the initial fracture event and healing efficiencies were measured to compare the virgin peak loads to the healed peak loads.

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