Self-Healing Polymeric Materials Using Epoxy/Mercaptan as the Healant

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ABSTRACT: A self-healing system based on conventional epoxy resin was successfully developed in this work. Epoxy and its hardener mercaptan were microencapsulated as two-component healing agent, and then the microcapsules were embedded in epoxy matrix. Attractive healing effect can be acquired at low capsule content (e.g., 43.5% healing efficiency with 1 wt % capsules and 104.5% healing efficiency with 5 wt % capsules at 20 °C for 24 h). Since only a few healant proves to be sufficient for crack repairing, a better balance between strength and toughness restoration can thus be achieved. As a result of high flowability, fast consolidation, and molecular miscibility of the released healing agent consisting of epoxy and mercaptan, self-healing was allowed to proceed rapidly offering satisfactory repair effectiveness.

Introduction

Structural polymer materials possessing self-healing capability are ideal for long-term operation because the microcracks inevitably generated in service can be repaired without manual intervention. So far, two main strategies of self-healing have been proposed for autonomic crack healing at room temperature. The first one fills fragile pipelines (such as glass capillaries, hollow glass fibers, and three-dimensional microvascular networks) with polymerizable monomers and then embeds them in the target materials.[1–7] The monomers can be bled into damage sites upon fracture and then polymerized to heal cracks. The second one uses liquid resins or solvents that are either microencapsulated or phase-separated when being compounded with the matrix.[8–16] The curable resins would be released into the path of a propagating crack and consolidated due to the catalysis of the neighboring predispersed hardeners that present themselves in the form of solid particles or capsules.[8–15] Besides, healing of polymers with encapsulated solvents is a simple and potentially robust alternative to the recovery of virgin properties of a material after crack damage has occurred.[16]

Considering the feasibility of mass production and broadness of application, the routes based on microcapsulation[8–16] are very promising. Under the framework of this methodology, three self-healing systems, dicyclopentadiene/Grubbs' catalyst, polydimethylsiloxane/tin catalyst pairs, and organic solvents, proved to be able to automatically repair cracks in different polymers. To the authors' knowledge, however, some important universal adhesives like epoxy resins have not yet been successfully applied in this field except that two-part epoxy adhesives had been employed in the aforesaid hollow pipelines strategy.[2–6] It is mainly due to the difficulty in microencapsulation of suitable hardener for epoxy, but not in microencapsulation of epoxy itself. For example, the conventional amine-type curing agents are amphoteric and highly active. They cannot be encapsulated by poly(urea−formaldehyde) under acidic conditions. Without proper protection, the embedded hardener in a self-healing composite might be easily deactivated. Jung et al. used polyoxymethyleneurea-walled microspheres to store an epoxide monomer to be released into cracks and rebond the cracked faces in a polyester matrix.[17] Solidification of the epoxy resin (i.e., the repair action) was triggered by the naturally occurring functional sites or embedded amine in the composites. White et al. indicated that the method was not feasible as the amine groups did not retain sufficient activity.[18] Zako et al. proposed an intelligent material system using 40% volume fraction unmodified epoxy particles to repair microcracks and delamination damage in a glass/epoxy composite laminate.[19] By heating to 120 °C, the embedded epoxy particles (∼50 μm) would melt, flow to the crack faces, and repair the damage with the help of the excessive amine in the composite. In addition to the poor activity of the amine as mentioned above, manual intervention (i.e., heating) was necessary in this case.

Epoxy has good adhesion to many materials and is an ideal candidate for versatile healing agent. Accordingly, a two-component healing agent was developed by the authors, which consists of microencapsulated epoxy and its hardener mercaptan. To meet the criteria of self-healing including high flowability and rapid consolidation, our self-healing system employs low-viscous highly active epoxy as the polymerizable component and mercaptan in conjunction with catalyst tertiary amine as the low-temperature hardener. Considering that mercaptan is very active and not many polymers are suitable for encapsulating it, we choose melamine−formaldehyde which is inert toward mercaptan as the wall material. Naturally, epoxy oligomer is also encapsulated by the same substance. Encapsulation of mercaptan was carried out in an oil-in-water emulsion by an improved in-situ polymerization approach.[20] The resultant capsules have high core content. Here a dilemma has to be solved. That is, miroencapsulation with melamine−formaldehyde should be conducted in acidic medium, while the catalyst for mercaptan (i.e., tertiary amine) is basic. If mercaptan were mixed with tertiary amine first, the subsequent encapsulation reaction could not proceed. To produce microcapsules containing both mercaptan and its amine catalyst, an innovative way was applied by infiltrating the catalyst into the ready-made mercaptan-loaded microcapsules. As the catalyst and

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mercaptan have good solvability and form stable strong base−weak acid pair, no reverse bleeding was observed. The catalyst content can be adjusted by changing infiltration conditions and using assistant solvent.

The objective of this paper is to show crack healing ability of the above two-component healing agent based on epoxy, which was embedded in epoxy matrix. In addition, the influence of the addition of the microcapsules on intrinsic properties of the matrix polymer and stability of the self-healing system were also studied.

Experimental Section

Materials. Two types of epoxy resin were employed. One is diglycidyl ether of bisphenol A (EPON 828, Shell Chemicals Inc.) with epoxide equivalence weight of 0.53 mol (100 g)$^{-1}$, density of 1.17 g mL^{-1} at 20 °C, and viscosity of 12.85 Pa•s at 25 °C acting as the matrix polymer, and the other is diglycidyl tetrahydro-*o*-phthalate (DTHP, Jindong Chemical Plant, Tianjin, China) with epoxide equivalence weight of 0.65 mol (100 g)$^{-1}$, density of 1.24 g mL^{-1} at 20 °C, and viscosity of 0.36 Pa•s at 25 °C as the polymerizable component of the healing agent. Accordingly, two types of curing agent were used. They are diethylenetriamine (DETA) supplied by Shanghai Medical Group Reagent Co. (Shanghai, China) working for EPON 828 and pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) with boiling point of 275 °C at 1 mmHg, density of 1.28 g mL^{-1} at 20 °C, and hydrosulfide group content of 26.55%, purchased from Fluka Chemie AG (Buchs, Switzerland) for DTHP. The catalyst benzyl dimethylamine (BDMA) with boiling point of 183.5 °C was purchased from Shanghai Medical Group Reagent Co. (Shanghai, China).

Preparation of Microcapsules Containing Epoxy and Its Hardener. Diglycidyl tetrahydro-*o*-phthalate (400.0 g) was added into a 2 wt % aqueous solution of sodium styrene−maleate copolymer (1200 mL). The mixture was vigorously stirred at 500 rpm for 30 min, and then 2 drops of 1-octanol were added to eliminate surface bubbles of the epoxy emulsion. The prepolymer of melamine (62.5 g) and 37% formaldehyde (135.5 g) was synthesized at 70 °C for 30 min, and pH value of the solution was kept at about 9−10 by adding triethanolamine. Subsequently, the prepolymer solution was added to the above epoxy emulsion at 50 °C with continuous agitation for 1 h while pH value of the system was kept at about 3 by adding citric acid. Eventually, the reaction mixture was cooled to room temperature, and the deposit of microcapsules was separated through a Buchner funnel, rinsed with deionized water, and vacuum-dried. The core content of the microcapsules (i.e., the weight ratio of core to microcapsule) is 96.9 wt %, as determined by elemental analysis and extraction method (see Supporting Information).

The microcapsules containing the hardener were prepared in two steps. First, pentaerythritol tetrakis(3-mercaptopropionate) was microencapsulated in a similar way as that adopted in making epoxy-loaded microcapsules. Then, the microcapsules were uniformly dispersed into benzyldimethylamine solution at 40 °C for 24 h, filtrated, rinsed with ethyl ether, and dried at room temperature. The ultimate contents of the curing agent and the catalyst inside the microcapsules are 90.7 and 3.9 wt %, respectively (see Supporting Information).

Preparation of Self-Healing Epoxy Composites. The unfilled epoxy specimens were produced through mixing 100 parts EPON 828 with 12.5 parts curing agent DETA, while the self-healing epoxy composites were prepared by mixing different concentrations and weight ratios of the capsules containing epoxy and its hardener with the aforesaid EPON 828/DETA mixture. Either the unfilled epoxy or the filled version was degassed, poured into a closed silicone rubber mold, and cured for 24 h at room temperature, followed by 24 h at 40 °C.

To highlight the role of the healing agent, three types of control specimens were fabricated. They consisted of (i) neat epoxy without microencapsulated healing agent; (ii) epoxy with 5 wt % epoxy-loaded microcapsules, and (iii) epoxy with 5 wt % hardener-loaded microcapsules.

Characterization. To evaluate self-healing ability of the materials, the protocol proposed by White et al. was used, who carried out fracture tests on tapered double cantilever beam (TDCB) specimens.[8,9] Efficiency of healing is defined as the ratio of fracture toughness, K_{IC}, of healed and virgin materials. The specimens were put in an incubator preset at a desired temperature between −10 and 30 °C for 24 h. Afterward, a specimen was taken out, and a natural precrack was created by inserting a fresh razor blade and gently tapping into the molded notch starter. Subsequently, the specimen was pin-loaded and tested under displacement control using a 5 μm s^{-1} displacement rate at 23 ± 0.5 °C and 30 ± 5% humidity. Specimens were tested to failure, while compliance and peak load were determined to estimate the virgin fracture toughness. Load was then removed, allowing the crack faces to come back into contact and to be self-healed at certain temperature in the incubator for different times. Finally, the healed specimens were tested again following the above procedure. Each batch included 10 specimens to yield averaged value.

For healing of the reference specimens by manual injection, 0.03 mL of premixed epoxy and its hardener was injected into the crack planes prior to crack closing.

The time required for the entire process including precracking, TDCB testing, and reassembly was less than 3 min. To check the temperature change of the specimens within this time range, a digital thermometer probe was embedded in the center of a model TDCB specimen prior to the experiment. The results of simulating tests indicated that the temperature change of the specimens that were exposed to room temperature within ∼3 min had nothing to do with the self-healing process (see Supporting Information, Figure S3).

Storage stability of the composites was determined as follows. Over 100 TDCB specimens were produced in one batch and then placed at room temperature. Ten specimens were tested according to the above standard procedure at periodical intervals.

Tensile and flexural properties were measured according to ASTM D 638 and D 790, respectively. Morphological observation and energy dispersive spectroscopy (EDS) analysis were conducted by a Quanta 400 FEG field emission scanning electron microscope (SEM). Prior to the experiment, the sample surface was coated by gold/palladium sputter. Micro-Raman measurements were carried out using a Renishaw inVia (UK) spectrometer equipped with a Leica microscope. The Raman spectra were excited by a 785 nm laser line at a resolution of 1 cm^{-1}, and the laser was focused by a 20× objective to a spot size of ∼10 μm.

Both isothermal and nonisothermal curing kinetics were studied with a TA DSC Q10 calorimeter in N_2. The heating rates for the nonisothermal tests were 1, 2, 3, 4, and 5 °C min^{-1}, respectively.

Results and Discussion

Figure 1 shows SEM photos of epoxy- and hardener-loaded microcapsules as well as their size distribution. Accordingly, it is estimated that volume mean diameters of the microcapsules are 93.9 and 92.8 μm, respectively. Besides, their densities were found to be 1.24 and 1.26 g cm^{-3}, respectively. The similarity in their surface feature, physical properties, and geometry certainly benefits uniform distribution of the microcapsules in the composite (see Supporting Information, Figure S4). As a result, the contact probability between the released epoxy and curing agent would be increased after damage-induced breakage of the capsules. Furthermore, since the two types of core materials possess good intersolubility, their interdiffusion and homogenization in the subsequent polymerization should be favored.

It is worth noting that the microcapsules can form hydrogen bonding with the matrix due to the polar groups (amine and hydroxyl) on their melamine−formaldehyde shells. The strong

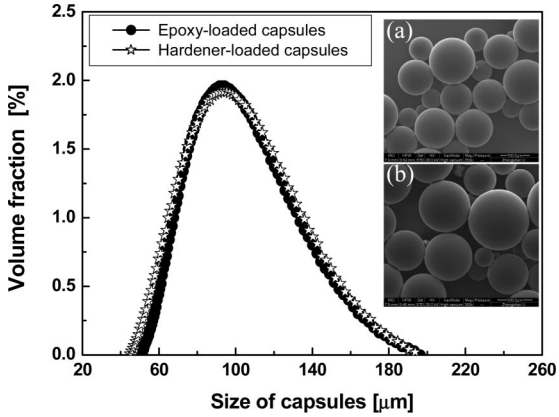

Figure 1. Size distribution and SEM photos of (a) epoxy-loaded capsules and (b) hardener-loaded capsules.

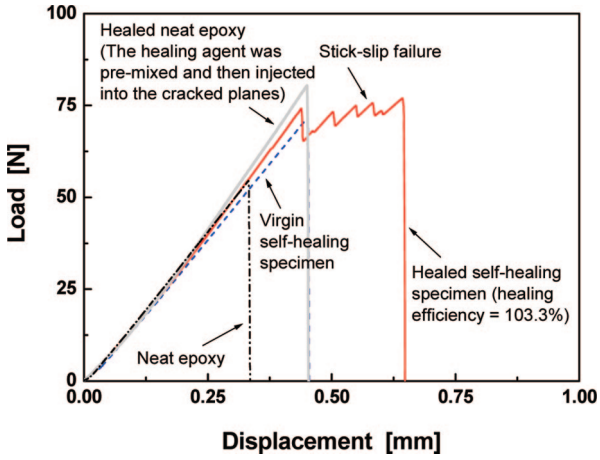

Figure 2. Typical load−displacement curves recorded during TDCB tests. The self-healing composite contains 2.5 wt % epoxy-loaded capsules and 2.5 wt % hardener-loaded capsules. The reference specimen was healed by injecting the premixed epoxy/mercaptan (1.26:1) with a mercaptan/amine catalyst ratio of 100:4.3 to the cracked faces. Healing of the fractured specimens was conducted at 20 °C for 24 h.

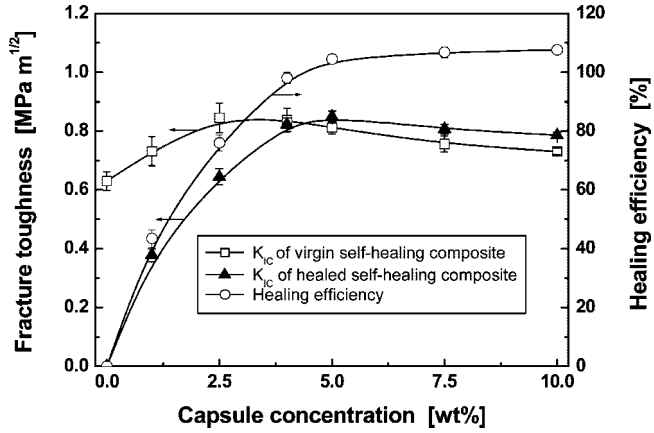

Figure 3. Influence of capsule concentration on fracture toughness and healing efficiency. Weight ratio of the two types of capsules in all the self-healing specimens is 1:1. Healing of the fractured specimens was conducted at 20 °C for 24 h.

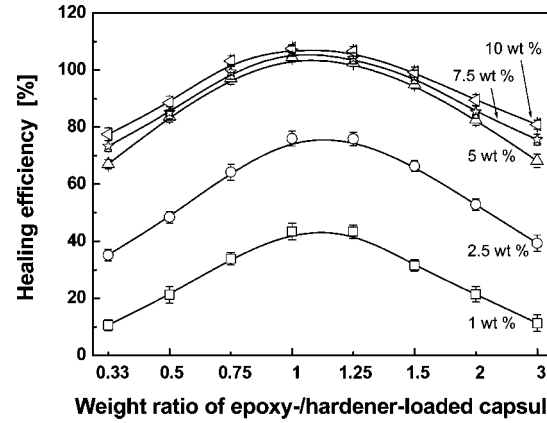

Figure 4. Influence of weight ratio of epoxy-/hardener-loaded capsules on healing efficiency of the self-healing composites with different contents of microencapsulated healing agent. Healing of the fractured specimens was conducted at 20 °C for 24 h.

interaction between the microcapsules and the matrix ensures timely penetration of cracks through the encapsulated healing agent (see Supporting Information, Figure S5).

Figure 2 shows a representative load−displacement curve of a self-healing composite specimen recorded during TDCB test, demonstrating a healing efficiency slightly higher than 100% at rather low microencapsulated healing agent content. Compared to the linear (brittle) fracture behavior of the virgin test, failure of the healed self-healing specimen is characterized by a stick−slip process. Additional energy must have been consumed in the course of fracture. In contrast, all the three types of control specimens (see Experimental Section), which experienced the same healing procedure as the self-healing specimen after the first failure, showed no healing effect and were unable to carry any load upon reloading.

Since Figure 2 has revealed the crack healing ability of the healant, the influence of its concentration on healing efficiency should be known. As exhibited in Figure 3, at a constant weight ratio of epoxy-/hardener-loaded capsules of 1:1, the healing efficiency drastically increases with capsule concentration from 0 to 5 wt % and then gradually levels off within the capsule content range from 5 to 10 wt %. The dependence of fracture toughness of healed self-healing specimens on capsule content also follows similar trend of variation. Clearly, the healing effect is correlative to the healing agent quantity offered by the broken capsules on the fracture planes.[13] Further investigation of the influence of weight ratio of epoxy-/hardener-loaded capsules within the capsule concentration range from 1 to 10 wt % (Figure 4) indicated that the optimal healing effect was obtained at about 1−1.25 (corresponding to weight ratio of epoxy/mercaptan of 1.07−1.33). It means that a total amount of the two types of microcapsules of 5 wt % with almost identical fraction of each type of the capsules is critical for the current system to achieve the highest healing efficiency.

Incorporation of additives into a polymer would inevitably affect its intrinsic properties. It is seen from Figure 3 that the virgin self-healing composites are tougher than the unfilled epoxy. The toughening effect coincides with the observation of Brown et al.[10] The crack pinning mechanism might be operative as characterized by the tails originating from broken capsules on the fracture plane (Figure 5a). As for the static mechanical performance (Figure 6), the reduction in modulus of the specimens with a rise in the capsules content is marginal (e.g., only ∼5% reduction in Young's modulus at 10 wt % of the capsules), while the decrease in strength is relatively obvious (e.g., ∼28% decrease in tensile strength at 10 wt % of the capsules). In general, it follows the law of other microcapsules or rubbery particles filled polymers.[10,21]

To find out the reason for the healing efficiency higher than 100%, simulation healing experiments were done by injecting enough amount of the model healing reagent, i.e., the mixture of epoxy and mercaptan of different proportions with a constant

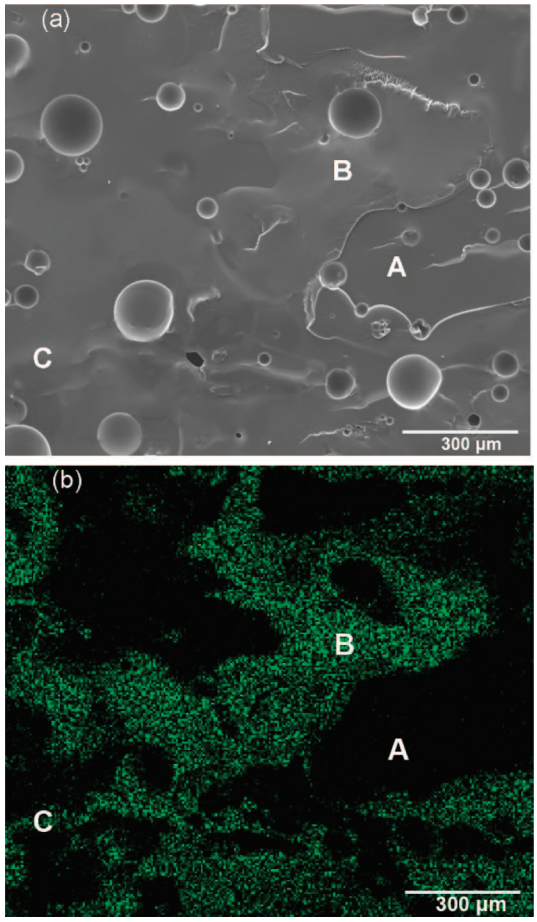

Figure 5. (a) SEM image in conjunction with (b) EDS analysis (with sulfur as the indicator element) of the fracture surface of a healed self-healing composite specimen, which contains 2.5 wt % epoxy-loaded capsules and 2.5 wt % hardener-loaded capsules, respectively. The specimen had been fractured by the first TDCB test, healed at 20 °C for 24 h, and then fractured again by the second TDCB test. Site A: brittle failure of epoxy matrix (sulfur content: undetected); sites B and C: cohesive failure of the membrane from the cured self-healing agent (sulfur content: 37.7 and 25.8 wt %, respectively).

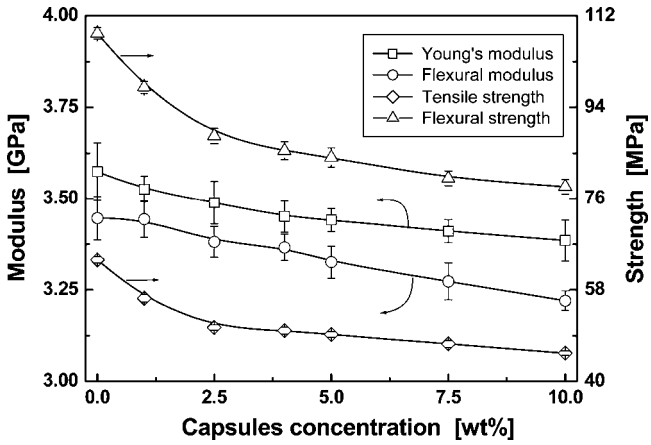

Figure 6. Influence of content of the microencapsulated healing agent on modulus and strength of the self-healing composites. The microcapsules content given in the plot is the sum of the contents of epoxy- and hardener-loaded microcapsules, and their weight ratio is 1:1.

mercaptan/amine catalyst ratio of 100:4.3, to the fracture planes of unfilled epoxy specimen. Both the load−displacement curve of the specimen healed by manual injection (Figure 2) and the healing efficiencies of a group of simulative specimens over a wide range of epoxy/mercaptan ratios (Figure 7) show that the

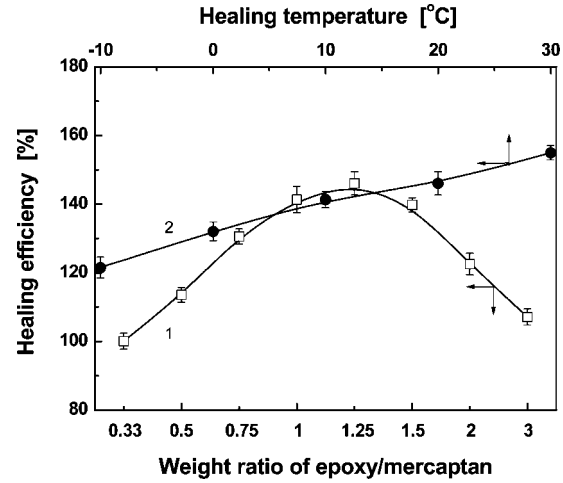

Figure 7. Control tests based on simulation healing showing effects of compositions of the healing agent and healing temperature on healing efficiency of reference specimens. Here the fractured TDCB unfilled epoxy specimens were healed by injecting enough amount of the premixed model healing reagent, i.e., the mixture of epoxy resin and mercaptan of different proportions with a constant mercaptan/amine catalyst ratio of 100:4.3, to the crack planes. Healing of the fractured specimens with different epoxy/mercaptan weight ratios (curve 1) was conducted at 20 °C for 24 h. Besides, the model mixture of epoxy and mercaptan used for evaluating temperature dependence of healing efficiency (curve 2) was prepared at the stoichiometric ratio of epoxy to mercaptan of 1.26 with a mercaptan/amine catalyst ratio of 100:4.3. The healing time was 24 h for different healing temperatures.

recovery of virgin fracture toughness exceeds 100%. In fact, a healing efficiency higher than 100% is meaningless to quantification, but it manifests the healed portions have higher cracking resistance than the matrix. Our independent TDCB fracture measurements of the matrix and the epoxy healing system (produced at epoxy/mercaptan stoichiometric ratio) indicated their fracture toughness, K_{IC}, are 0.63 and 1.18 MPa $m^{1/2}$, respectively. It is known that the bonding material not only heals the cracks but also provides the damaged sites with higher fracture toughness. Under simulative circumstances, uniform spread of the healing agent mixed at optimum epoxy/hardener ratio was guaranteed. Because the inherent miscibility between the polymerizable component of the healing agent (i.e., epoxy) and the matrix epoxy led to good adhesion between them, crack had to deviate from the original fracture plane in reference specimens (see Supporting Information, Figure S6). The effect resulted in high fracture load since the TDCB specimen thickness is larger away from the groove line. A similar phenomenon has been reported by Keller, White, and Sottos,[15] who found deviated tear in healed poly(dimethylsiloxane) elastomer that offered healing efficiencies higher than 100%. In practical applications, because the healed portion has higher fracture toughness than the matrix, subsequent cracking would preferably occur in the rest parts of the composites. Multiple self-healing of the material might thus be available.

The results of simulation healing experiments further indicate that the maximum healing efficiency was obtained near the stoichiometric weight ratio (i.e., 1.26) of epoxy to mercaptan (Figure 7). It is almost the same as the aforesaid optimum weight ratio of epoxy-/hardener-loaded capsules (1−1.25, equivalent to weight ratio of epoxy/mercaptan of 1.07−1.33) that corresponds to the highest healing efficiency of the authentic specimens (Figure 4). It proves that the two types of capsules must have been well distributed in the authentic specimens. So long as the concentrations of the epoxy- and mercaptan-loaded capsules are the same, their breakage allows delivery of the two-part healing agent with composition close to the stoichiometric ratio to the cracked faces. Nevertheless, healing efficiencies of

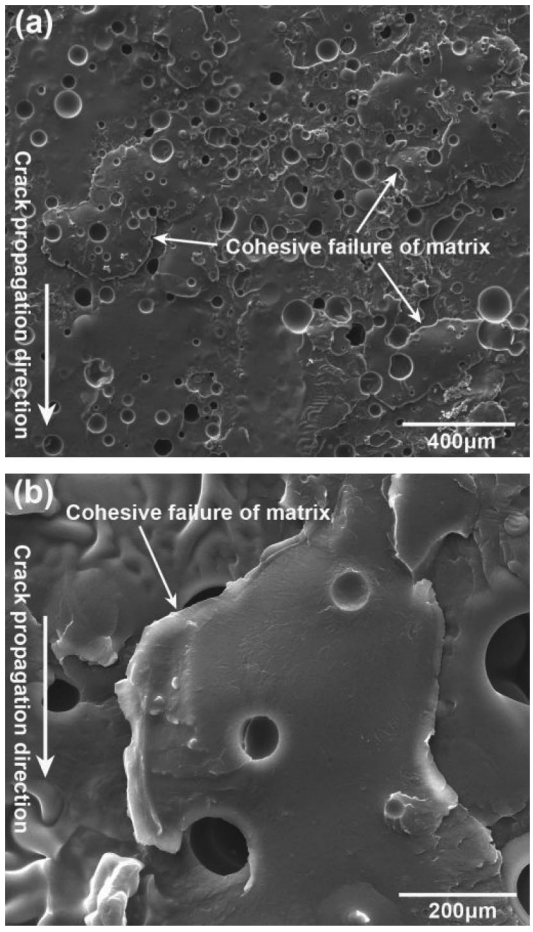

Figure 8. SEM images of the fracture surface of a healed self-healing composite specimen, which contains 10 wt % epoxy-loaded capsules and 10 wt % hardener-loaded capsules. The specimen had been fractured by the first TDCB test, healed at 20 °C for 24 h, and then fractured again by the second TDCB test. The round cavities on the fractured fragments manifest that the latter originated from the matrix.

the authentic specimens are still lower than those of the simulative ones. It means the healing was not as complete as in the control specimens. This is evidenced by the fact that the aforesaid macroscopic crack deviation from the groove line was not perceived in authentic specimens. As seen from energy dispersive spectroscopy (EDS) in Figure 5b, the contents of the "indicator element" (i.e., sulfur) in different regions on the fracture surface of the healed specimen vary greatly. The heterogeneity might result from the mismatched type of the neighbor capsules, uncertainty of the amount and proportion of broken capsules on the rupture planes, and uneven interdiffusion of the reaction agents. As a result, cohesive failures of cured healing membrane (Figure 5 and Supporting Information, Figure S7) and matrix (Figure 8) left their traces on the fracture surfaces of healed specimens. These failures together with opening of a few unbonded surfaces (caused by incomplete coverage of healing membrane) alternatively appeared. Accordingly, crack propagated in a zigzag way on a microscopic scale, as reflected by the stick−slip manner (Figure 2). In principle, such a microscopic zigzag course can be regarded as low-grade crack deviation that also helps to raise fracture load, in spite of the fact the development of cracking looked to be straightaway under visual inspection. Therefore, healing efficiencies of authentic specimens are sometimes slightly higher than 100% but lower than those of reference specimens.

To favor crack healing soon after its formation, fast consolidation of the repair chemicals is required. Epoxy−mercaptan cure is a nucleophilic addition reaction.[22] With the aid of proper

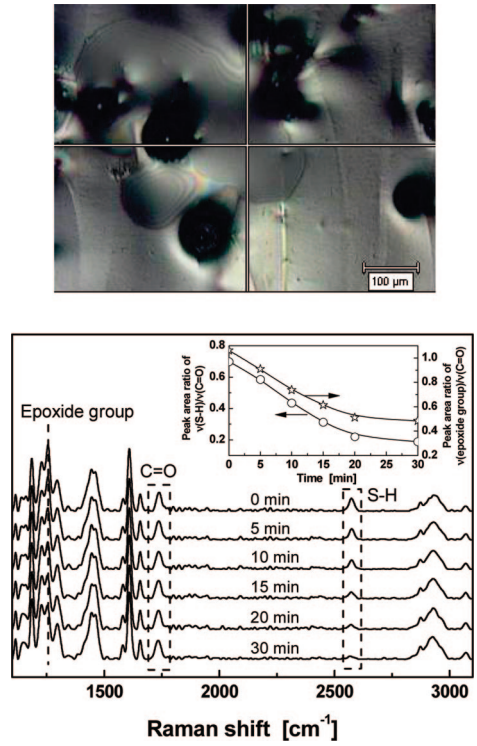

Figure 9. In-situ confocal Raman microscopy observation. The upper photo displays the fractured surface of a self-healing specimen with 2.5 wt % epoxy-loaded capsules and 2.5 wt % hardener-loaded capsules. The typical Raman spectra collected from the center of the very fracture surface at different times counted from the breakage of the specimen are shown in the lower figure. The inset summarizes time dependences of the characteristic Raman peak area ratios. Here three peaks are of interests: stretching modes of epoxide group at 1256 cm^{-1}, carbonyl group at 1738 cm^{-1}, and hydrosulfide group at 2573 cm^{-1}. Since carbonyl originates from epoxy and mercaptan, and the reaction between epoxy and mercaptan cannot produce any carbonyl, the peak area of carbonyl group at 1738 cm^{-1} is able to serve as the reference for showing the variation in the peak areas of epoxide and hydrosulfide groups with time. This figure provides a live record of the curing reaction of the released healing agent in an authentic specimen.

catalyst like tertiary amine, the reaction involving an intermediate mercaptide-ion mechanism is significantly faster than the epoxy−amine reaction, particularly at low temperatures. However, they hardly react with each other without catalysis. In-situ confocal Raman microscopy study of the cracked surface of a self-healing epoxy specimen indicates that epoxide groups quickly react with hydrosulfide groups in the presence of catalyst benzyldimethylamine (Figure 9). About 50% epoxide groups are consumed within 30 min. Isothermal differential scanning calorimetry (DSC) analysis of the model mixture of the healing agent also shows that the curing is an exothermal reaction and the degree of cure increases with increasing temperature (Figure 10). At −10 °C, the exothermic peak becomes nearly inconspicuous as compared to that at 30 °C. It means the curing reaction proceeds very slowly at low temperature, as reflected by the rate constants (see Figure 10 and Supporting Information, Figure S8 and Table S1).

Temperature dependence of healing efficiency of the simulative specimens conforms to reactivity study of the healing agent. Higher healing temperature led to higher healing efficiency (Figure 7). Figure 11 collects the results of crack healing in authentic specimens at different temperatures. The healing is very fast at temperatures from 10 to 30 °C, as expected. The healing efficiency attains 82−88% after 3 h at 20 and 30 °C and exceeds 100% only after 12 h. Although the self-repair process is slowed down with decreasing temperature, an 86% recovery at −10 °C is observed after 36 h. The data are quite

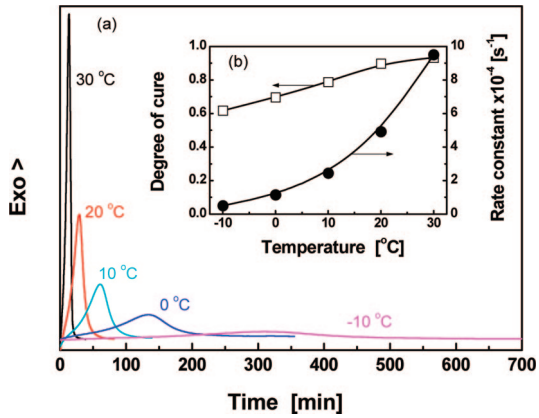

Figure 10. Curing kinetics study of the healing agent. (a) Isothermal DSC scans conducted at different temperatures. (b) Temperature dependences of degree of cure (estimated from isothermal curing kinetics) and rate constant (estimated from nonisothermal curing kinetics, see Supporting Information, Figure S8 and Table S1). The model mixture of the two components of the healing agent used in these tests was prepared at the stoichiometric ratio of epoxy to mercaptan of 1.26 with a mercaptan/amine catalyst ratio of 100:4.3.

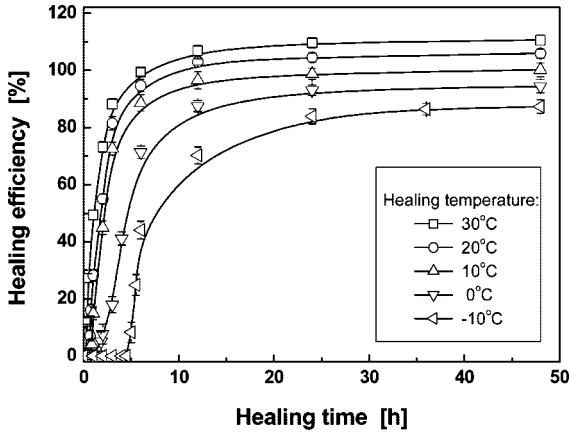

Figure 11. Time dependence of healing efficiency at different temperatures. The self-healing composite contains 2.5 wt % epoxy-loaded capsules and 2.5 wt % hardener-loaded capsules.

satisfactory and demonstrate that our technical route works. It is worth noting that the healing efficiency obtained at subambient conditions might not be accurate enough and can only give a rough estimate of healing ability of the healing system. This is because fracture tests of the specimens were conducted at room temperature, except that they were put in an incubator preset at a desired temperature before and after the TDCB tests. The brief heating that the specimens experienced would more or less enhance fluid transport throughout the damage region and yield an artificially high value of healing efficiency. The detailed mechanisms involved need further investigation.

Stability and durability are important for self-healing materials. Thermogravimetric and DSC tests reveal that no detectable change is found in the components of the healing agent (no matter whether they are encapsulated or not) when temperature is lower than 150 °C (see Supporting Information, Figure S9). This suggests that the microencapsulated healing agent can be handled at a temperature below 150 °C without any variation in its quality. Moreover, the two types of microcapsules possess long-term durability. Having been exposed to room temperature for 1 year, they only exhibit weight loss of about 0.68 and 0.79 wt %, respectively. Visual inspection does not find any leakage from the microcapsules, and their appearances also remain unchanged after long time storage. Since the microcapsules are embedded in composite matrix in practical usage, which would further improve their storage stability. As a result, healing efficiency of the self-healing composite is almost constant within half a year (see Supporting Information, Figure S10). On the other hand, as the freezing points of the components of the healing agent are very low (−51 °C for the epoxy and −68 °C for the hardener), it is expected that the self-healing system might take effect within a relatively wide temperature range.

Conclusions

This preliminary study demonstrates the feasibility of preparing self-healing epoxy composite by embedding the healing agent consisting of two types of microcapsules that contain epoxy and its hardener. High healing efficiency can be acquired at rather low capsules content, so that the basic mechanical properties of the matrix are insignificantly affected. Because the healing agent possesses high flowability and reactivity and belongs to the same family as the matrix polymer, crack healing is automatically conducted at or below room temperature, offering satisfactory repair effectiveness. The microencapsulated healant is quite stable and durable, which broadens process window for fabricating self-healing composites and prevents deterioration of healing capability of the composites during storage.

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Supporting Information Available: Determination of core contents of the microcapsules; structures of the chemicals; temperature change in TDCB specimen during precracking, TDCB testing, and reassembly; photos of TDCB specimen and dispersion status of the microcapsules; thermogravimetric and DSC analysis; and storage stability of the composites. This material is available free of charge via the Internet at http://pubs.acs.org.

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