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Effects of dual component microcapsules of resin and curing agent on the self-healing efficiency of epoxy

Qi Li [a], Siddaramaiah [b], Nam Hoon Kim [c], David Hui [d], Joong Hee Lee [a,c,e,*]

[a] BIN Fusion Research Centre, Department of Polymer and Nano Engineering, Chonbuk National University, Jeonju, Jeonbuk 561-756, Republic of Korea
[b] Department of Polymer Science and Technology, Sri Jayachamarajendra College of Engineering, Mysore 570 006, India
[c] Department of Hydrogen and Fuel Cell Engineering, Chonbuk National University, Jeonju, Jeonbuk 561-756, Republic of Korea
[d] Department of Mechanical Engineering, University of New Orleans, New Orleans, LA 70148, USA
[e] WCU Programme, Department of BIN Fusion Technology, Chonbuk National University, Jeonju, Jeonbuk 561-756, Republic of Korea

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ABSTRACT

Dual component microcapsules of diglycidyl ether of bisphenol A epoxy (DGEBA) (resin) and polyetheramine (hardener) for the self-healing agencies of epoxy were prepared by a water-in-oil-in-water emulsion solvent evaporation technique with the polymethyl methacrylate (PMMA) shell. The chemical structure and morphologies of the microcapsules were confirmed using Fourier-transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM), respectively. The thermal characteristics of the microcapsules were investigated using thermo-analytical techniques such as differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA). Dual components microcapsules of resin and curing agent were embedded into the epoxy matrix and the healing behavior of the system was studied. About 43.5% healing efficiency was achieved with 5 wt.% microcapsules and 84.5% healing efficiency was achieved with 15 wt.% microcapsules at room temperature for 24 h curing. The healing efficiency of the composite with the dual component microcapsules was higher than that of the composite with the single component healing microcapsule due to the easy reaction between the liquid resin and the liquid hardener at the crack surface. The tensile strength of the epoxy with dual component microcapsules increased initially with increasing the content of microcapsules and reached the maximum at 5 wt.%. Above this point, the tensile strength decreased gradually with increasing.

1. Introduction

Self-healing materials represent a new paradigm of active and responsive materials [1–9]. Self-healing has received much interest in intelligent material science because they play a critical role in determining the security, reliability and long-term durability of materials. The self-healing in materials is different from the traditional methods of material repair, including welding and patching. They do not require reliable detection techniques or a special technique for mending materials. Such recovery can occur autonomously or be activated after an application of a specific stimulus (e.g., heat and radiation). One of the most promising and useful approaches to prepare self-healing materials is the incorporation of healing agents into the material, which endows the material with the ability to heal after a damage event.

Structural polymeric 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 strategy 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 polymers [10–14]. In this process, the monomers can flow into the damage sites upon fracture and polymerize to heal the cracks. The second strategy uses either microencapsulated or phase-separated liquid resins or solvents, which are integrated with a matrix [5,15–17].

Dry and Sottos pioneered the concept of polymerizable monomers filling inside hollow fibers and embedding the filled fibers in the target materials [10,18]. White et al. introduced a method of embedding a kind of encapsulated agent (dicyclopentadiene) in polymeric materials [5]. In this process, the microcapsules containing the healing agent are released into the path of a propagating crack, at which point the healing agent polymerizes with the catalyst. Because microcapsules can be mass produced and show

* Corresponding author at: BIN Fusion Research Centre, Department of Polymer and Nano Engineering, Chonbuk National University, Jeonju, Jeonbuk 561-756, Republic of Korea. Tel.: +82 63 270 2342; fax: +82 63 270 2341.
E-mail address: jhl@jbnu.ac.kr (J.H. Lee).

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high applicability, microencapsulation techniques have received much interest [19–24].

The formation of single-component microcapsules embedded self-healing materials is well understood, so these materials have been formed with various types of microcapsules containing different healing agents [5,17,25]. However, the effect of dual-component microcapsules embedded self-healing materials has not been fully investigated. This is mainly due to the problem of finding suitable healing agents. In contrast to the mechanism of single component microencapsulated healing agent, that of a dual-component microencapsulated healing agent are little more complex.

Epoxy resin and its hardener, which adhere well to many materials, are ideal candidates as potential self-healing agents. These materials can flow and can be successfully encapsulated by several methods. Capsulated epoxy and/or its hardener can be cured by controlling the curing temperature and time [17]. Furthermore, their dual component microcapsules are particularly good for healing epoxy systems because these materials possess the same chemistry as the epoxy systems; they can promote self-healing and improve the good interface morphology on the crack plane.

Epoxy resins have been extensively used as high performance materials, adhesives, matrices of composites and electric encapsulating materials due to their high strength and modulus excellent chemical resistance and so on [26]. They can be used as a healing agent. The microencapsulated epoxy resin may be a promising self-healing agent for polymer composites. Microencapsulated epoxy resins have been successfully synthesized in the previous reported works [23,24,27,28]. Polyurea-formaldehyde (PUF) microcapsules containing epoxy resin had been incorporated into epoxy matrixes. With 10 wt.% microcapsules and 2 wt.% $CuBr_2$ (2-MeIm)$_4$ (the complex of $CuBr_2$ and 2-methylimidazole) latent hardener, epoxy matrixes had exhibited 111% recovery of their original fracture toughness. Furthermore, glass fabric reinforced epoxy composites containing microcapsules had achieved 68% healing efficiency [29].

Previously, we reported the effects of processing parameters on the properties of microencapsulated curing agents and on the self-healing behavior of an epoxy system [30]. As a extension of the previous work, this study investigates the crack healing ability of a two-component healing microcapsules of epoxy resin and hardener, which were embedded in epoxy matrix. The influence of the addition of the microcapsules on the properties of the epoxy and on the thermal stability of the self-healing system was also studied.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBPA YD128) epoxy resin (density is 1.20 g/cc and epoxide equivalent weight is 184-190 g/eq) and ployetheramine (D-230) (density: 0.92 g/ml) were purchased from KUKDO Chemicals, South Korea. Poly(methyl methacrylate) (PMMA) (average M_w is 96,000), used as the shell wall material, was supplied by Sigma–Aldrich, USA. Dichloromethane (DCM), sodium dodecyl sulfate (SDS) and polyvinyl alcohol(PVA) were also obtained from Sigma–Aldrich, Germany. All the reagents were of analytical-grade and used without further purification.

2.2. Preparation of microcapsules containing epoxy and hardener

DGEBA epoxy resin microcapsules were prepared by dissolving 4 g of DGEBA and 1 g of PMMA in 30 ml of dichloromethane solvent as the dispersed phase, and then this mixture was added to the continuous phase (50 ml of 1 wt.% aqueous SDS solution) under high-speed agitation, 350 rpm at room temperature for 30 min to get an oil/water emulsion. Subsequently, the resultant oil/water emulsion was poured into a 200 ml aqueous solution with 1 wt.% SDS, and energetic agitation was continued. Dichloromethane was allowed to evaporate completely to obtain PMMA microcapsules containing the epoxy material. The microcapsules were washed several times with distilled water and then dried.

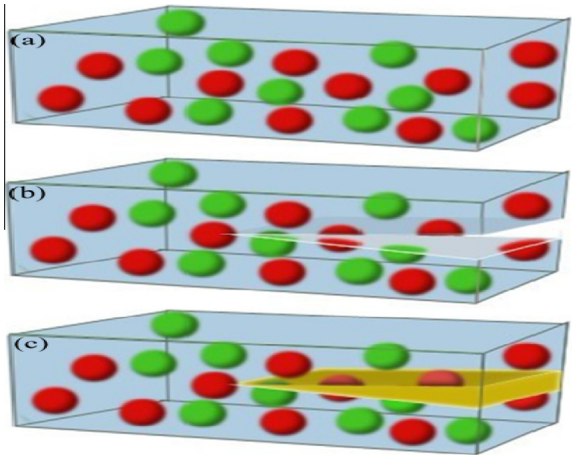
The microcapsules containing the hardener were prepared by dissolving 4 g of polyetheramine hardener and 1 g of PMMA in 30 ml of dichloromethane as the dispersed phase, which was added to the continuous phase (50 ml of 1 wt.% aqueous PVA solution) under high-speed agitation 300 rpm at room temperature for 30 min to get an oil/water emulsion. Subsequently, the resultant oil/water emulsion was poured into a 180 ml of aqueous solution with 1 wt.% PVA, and energetic agitation was continued. PMMA microcapsules with the core hardener were prepared by a procedure similar to the one used to prepare epoxy microcapsules.

2.3. Fabrication of self-healing epoxy specimen

Unfilled epoxy specimens were produced by mixing 90 parts DGEBA epoxy (YD128) with 30 parts hardener polyetheramine, and self-healing epoxy composites were also prepared by mixing various amounts of 5, 10, 15 and 20 wt.%, of dual-components PMMA microcapsules containing epoxy and hardener with the aforesaid epoxy/polyetheramine mixture. Either the unfilled epoxy or the filled version was degassed, poured into a closed silicone rubber mold having the shape of a tapered double cantilever beam (TDCB) and cured at room temperature for 24 h.

To highlight the role of the healing agent, three types of control epoxy specimens were fabricated. They consisted of (i) neat epoxy specimen without a microencapsulated healing agent; (ii) epoxy specimen with 15 wt.% epoxy or hardener contained microcapsules, and (iii) epoxy specimens with varying amounts of both epoxy and hardener-contained microcapsules.

As represented in Scheme 1, the DGEBA epoxy and polyether amine hardener are microencapsulated in a PMMA shell. Both types of microcapsules are dispersed in the epoxy matrix (light blue) to form a dual component microcapsules self-healing epoxy (Scheme 1a). An approaching crack ruptures the embedded microcapsules randomly, releasing epoxy and hardener on the crack surface through capillary flow (Scheme 1b). Curing of the released



Scheme 1. Schematic depiction of the self-healing process of dual-component microcapsules; (a) original composites, (b) crack propagation, (c) self healing of the crack (epoxy contained microcapsule (red) and the hardener contained microcapsule (green)). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

epoxy is triggered by contacting with the released hardener to repair the micro-crack (Scheme 1c).

2.4. Characterization

The morphology of the dual-component microcapsules and the fractured self-healing material surface were analyzed using scanning electron microscopy (SEM, S-3000 N, Hitachi, Japan). The Fourier transform infrared (FTIR) spectroscopy was used in order to probe the functional groups present in the self-healing microcapsules. The FTIR spectra was recorded on a JASCO FTIR 4100, Japan spectrometer using the KBr pellets method in the wave number range 4000–500 cm^{-1} with a resolution of 4 from 36 scan.

The amount of microencapsulated epoxy was determined using thermogravimetric analysis (TGA). TGA was performed using the TA instrument (Q50, USA) under nitrogen atmosphere at a heating rate of 10 °C/min in the temperature range from ambient to 550 °C. Dynamic DSC studies were carried out using the TA Instrument (Q40, USA) to examine the thermal characteristics and curing behaviors of epoxy. The heating rate for the non-isothermal measurements was 10 °C/min from 50 °C to 275 °C under nitrogen gas flow rate of 50 ml/min.

The tensile samples of self-healing agent incorporated epoxy composites were prepared according to the ASTM D638 method. The tensile properties were measured using the MTS Landmark Servohydraulic Test System (USA) at 1 mm/min. Five specimens for each composition were measured and an average value was reported.

2.5. Fracture test

In order to evaluate the self-healing ability of the epoxy materials, fracture tests was carried out on the TDCB specimens following the procedure proposed by White et al. [5,31]. The specimens were cured at room temperature for 24 h. Then, they were taken out of the mold and the pre-crack was created by inserting a fresh razor blade and gently tapping into a molded notch starter. Subsequently, all fracture specimens were tested under a displacement controlled process at a speed of 10 μm/s. The test specimens were mounted on a load frame and loaded to produce a pre-crack that would propagate along the centerline of the specimen until failure. The specimens were then unloaded, allowing the crack faces to come back into contact, and healed in this state for 24 h at room temperature [5,31,32]. Finally, the healed specimens were tested again following the above procedure. For each batch, six specimens were tested and an average value was reported.

Crack healing efficiency, 'η', is defined as the ability of a healed sample to recover fracture toughness and it can be calculated as

$$\eta = K_{healed}/K_{virgin}$$

where K_{virgin} is the fracture toughness of the virgin specimen, and K_{healed} is the fracture toughness of the healed specimen [5].

3. Results and discussion

3.1. Morphology of dual-component microcapsules

The dual-component microcapsules should have similar surface features, physical properties and geometry, which promote the uniform distribution and random rupture of microcapsules in the epoxy composite in the event of a crack.

Typically, the properties and morphology of a microcapsule are influenced by the core/shell ratio, agitation rate, temperature, and surfactant effect. Hence, similar size distribution and surface feature of dual-component microcapsules can be achieved by controlling the processing parameters.

SEM was performed to analyze the surface morphology of the microcapsules. The microcapsules were placed on a conductive carbon tape attached to a mounting piece for imaging. SEM photomicrographs of epoxy- and hardener-contained microcapsules as well as their size distribution are shown in Figs. 1 and 2 respectively. Figs. 1 and 2 show a wide range of size distributions varying from 15 to 100 μm for both types of microcapsules. This range is due to the variation in fluid flow around the propeller and away from the propeller [33,34].

The estimated mean diameters of the epoxy and hardener microcapsules were 52.3 and 50.1 μm, respectively. Their densities were measured to be 1.26 and 1.24 g cm^{-3}, respectively. From Fig. 1a it is noticed that the surface of an epoxy contained microcapsule is rough and scraggly, attached with small microcapsules. Unlike the surfaces of epoxy contained microcapsules, the surfaces of the hardener contained microcapsules (Fig. 1b) are smoother without any agglomeration because of the different chemistry/properties between the epoxy and the hardener. Their similar surface features, physical properties, and geometry certainly promote the uniform distribution of the microcapsules in the epoxy matrix. Because the two kinds of microcapsules have similar surface features and physical properties, they are distributed similarly in the epoxy matrix. This similar distribution leads to the random release of two kinds of healing agents, instead of the release of one kind of healing agent, at the crack plane. As a result, the probability of contact between the released epoxy and the hardener is increased after a damage-induced fracture of the microcapsules. Fur-

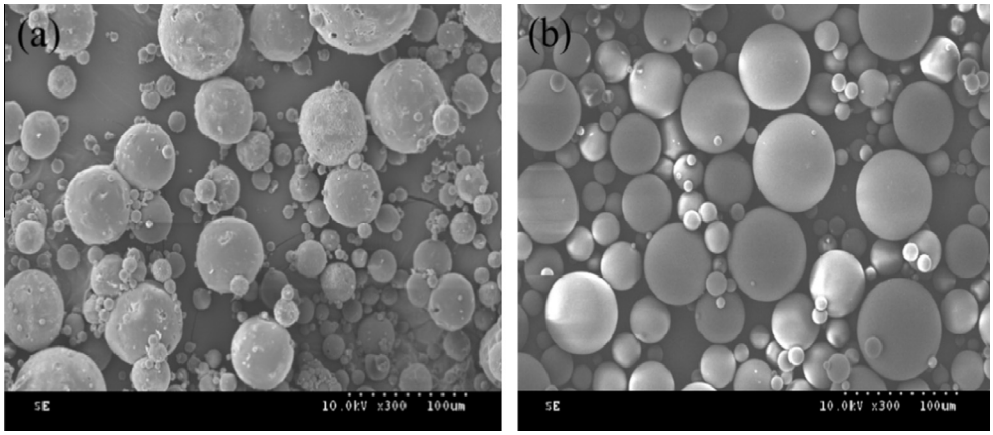


Fig. 1. SEM images of (a) epoxy contained microcapsules and (b) hardener contained microcapsules.

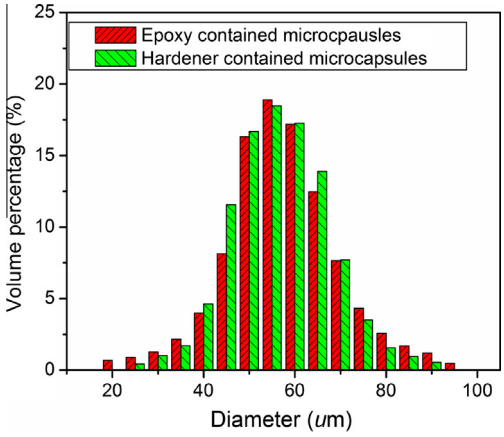


Fig. 2. Size distributions of the microcapsules of epoxy and hardener.

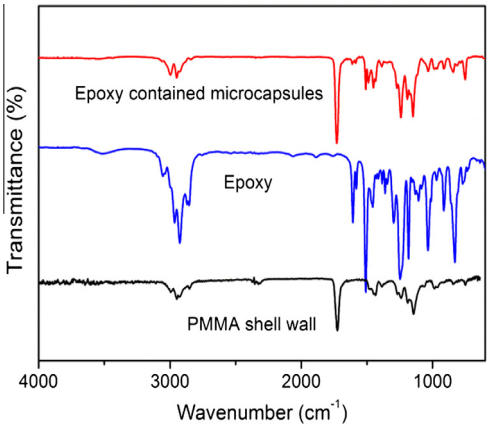


Fig. 4. FT-IR spectra of the epoxy, PMMA and epoxy contained microcapsules.

thermore, since two types of core materials possess good inter-solubility, their inter-diffusion and homogenization in the subsequent polymerization should be favored.

3.2. TGA studies

TGA is a complementary technique that can reveal the composition and thermal stability of the microcapsules. Fig. 3 shows the typical TGA thermograms of the epoxy and PMMA shell system contained microcapsules. In case of the epoxy containing microcapsules (Fig. 3a), the general thermal degradation pattern shows three main stages: in the first stage, the weight loss that occurs at about 260 °C is similar to the degradation of the PMMA; in second stage, weight loss occurs between 365 °C and 430 °C because of the decomposition of PMMA and epoxy; and in the third stage, weight loss occurs above 430 °C because of the degradation of the epoxy. The three stage weight loss degradation pattern of the epoxy contained PMMA microcapsules indicates that the epoxy was indeed encapsulated in the microcapsules. The epoxy content in the microcapsules was approximately 50%. The weight loss above 400 °C was due to the epoxy. From the TGA curve, it was noticed that PMMA completely degraded at around 405 °C. The TGA thermogram of the hardener contained microcapsules was provided in our previous communication [30]. The core content of PMMA (hardener) was approximately 20 wt.%. The core content of epoxy contained PMMA was two times that of PMMA.

3.3. FTIR studies

The chemical structure of epoxy and hardener contained microcapsules was investigated by FTIR spectra. Fig. 4 shows the IR spectra of the epoxy, PMMA shell, and epoxy contained PMMA microcapsules. For the epoxy microcapsules, the absorption peaks at 1249 and 915 cm^{-1} indicate the presence of C—O—C and epoxide groups, respectively. The FTIR spectrum of the PMMA shell microcapsules exhibits a C=O (stretch) absorption band at 1730 cm^{-1}. —CH_2 asymmetric and symmetric stretching absorption peaks appear at 2998 and 2845 cm^{-1}, respectively. Band at 1200 cm^{-1} represent the O—CH_3 stretching vibration. Characteristic peaks of both epoxy and PMMA shell appear in the FTIR spectrum of the microcapsules, which clearly indicates the epoxy encapsulated by the PMMA microcapsules. In our previous work, the characteristic peaks of both PMMA shell and hardener appeared in the FTIR spectrum of the hardener contained microcapsules, indicating the encapsulation of the hardener by the PMMA microcapsules [30].

3.4. Self-healing ability of the composites

The influence of the weight ratios of epoxy-/hardener-contained microcapsules within the microcapsule concentration range from 5 to 20 wt.% (Fig. 5) on the healing efficiencies of epoxy composites was investigated. The healing effect correlated to the quantity of the healing agents offered by the broken microcapsules on the fracture surface. Healing efficiency increased markedly with

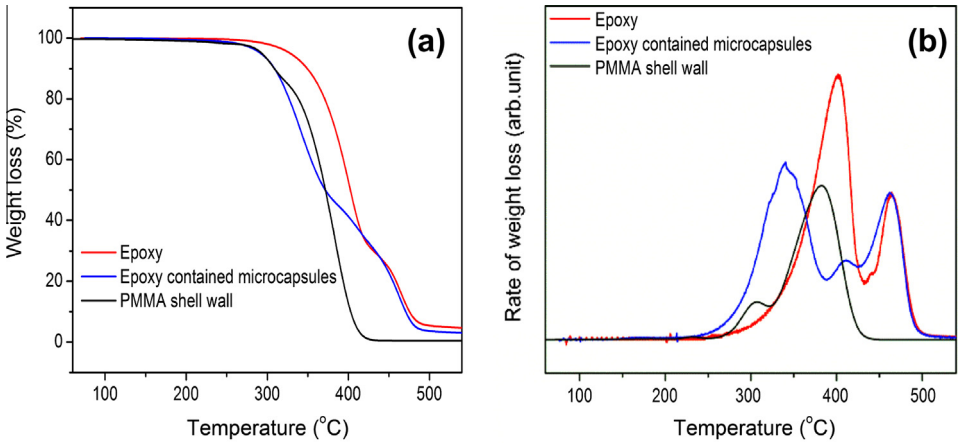


Fig. 3. (a) TGA curves and (b) DTG curves of epoxy, PMMA, and epoxy contained microcapsules.

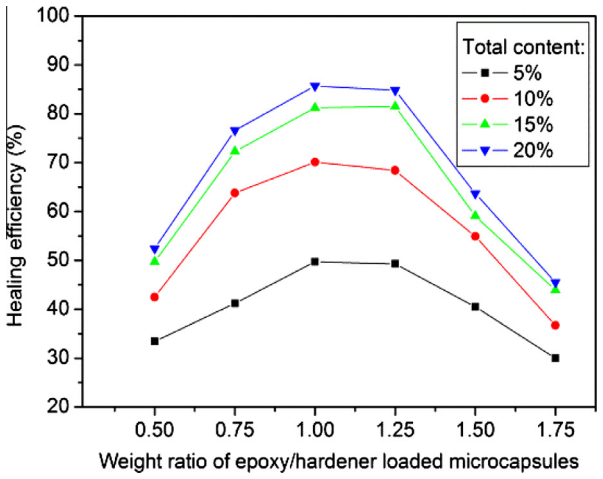


Fig. 5. Effects of weight ratio of microcapsules of epoxy and hardener on healing efficiency of the composites with different loadings of microcapsules healing at 25 °C for 24 h.

an increase in microcapsules content from 5 to 15 wt.%. This rapid increase in the healing efficiency results from the enough released epoxy and hardener to fill the micro-crack space.

The figure also shows that the healing efficiencies of the dual-component healing agents are strongly dependent on the ratio of two types of microcapsules (epoxy and hardener). The optimum healing efficiency was observed when the ratio was in the range of 1:1 and 1.25:1, corresponding to weight ratio of the encapsulated epoxy/hardener of 2.5:1 to 3.1:1 at a fixed total microcapsule content. The maximum healing abilities were obtained from the mixture of released epoxy and its hardener around the stoichiometric ratio of 3:1. This means that a total amount of the dual-component microcapsules with almost identical rupture of each type of the microcapsules is critical for the system to achieve the highest healing efficiency.

Incorporation of additives into a polymer would inevitably affect the intrinsic properties of the polymer. Fig. 6 shows the typical load-displacement plots of pure epoxy and self-healing agent incorporated epoxy specimens, obtained during a TDCB test. A linear (brittle) fracture behavior was observed in the initial test. The pure epoxy loaded specimens does not demonstrate any healing capability after a high load to failure. However, the healed self-healing agent loaded specimens (Fig. 6b–d) exhibit unstable stick-slip cracks propagation. This may be due to the fact that additional energy must have been consumed during fracture. In the figure, the epoxy system embedded with single-component microcapsules such as epoxy contained microcapsules or hardener contained microcapsules showed a low self-healing efficiency of about 39.7% or 50.8%, respectively. This low efficiency is due to the curing of the released epoxy or hardener with the residual functional group on the fractured surface of the epoxy matrix. However, the dual-component microcapsules embedded epoxy system provided enough epoxy and hardener for curing and for promoting the bonding of the new thermoset epoxy to the original matrix interface. The obtained results clearly indicated that the dual component microcapsule system exhibited an excellent self-healing efficiency up to 84.3%.

The SEM image of fracture surfaces of dual-component microcapsules embedded epoxy specimen after healing is shown in Fig. 7. The microcapsules were homogeneously dispersed in the

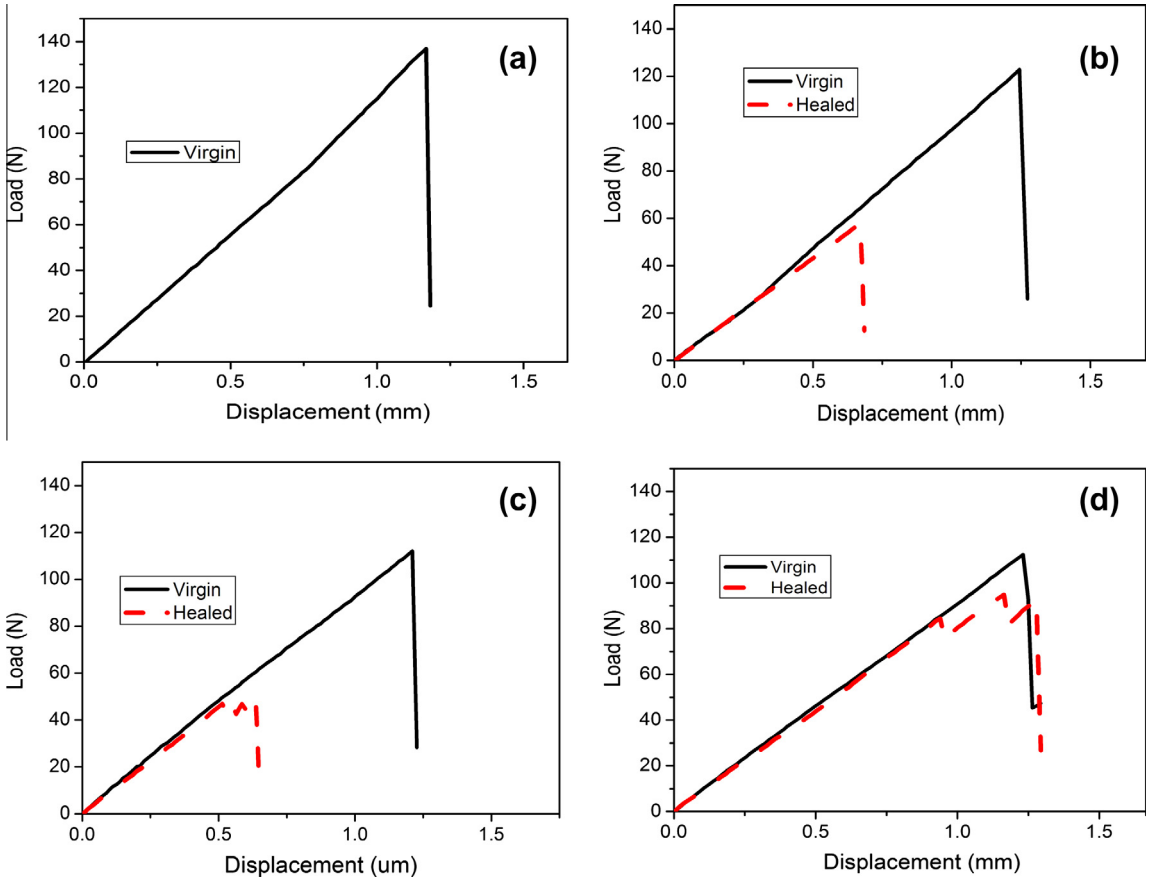


Fig. 6. Typical load-displacement curves recorded through TDCB tests for (a) pure epoxy, (b) epoxy with 15 wt.% hardener contained microcapsules, (c) epoxy with 15 wt.% epoxy contained microcapsules, and (d) epoxy with 7.5 wt.% hardener contained microcapsules and 7.5 wt.% epoxy contained microcapsules.

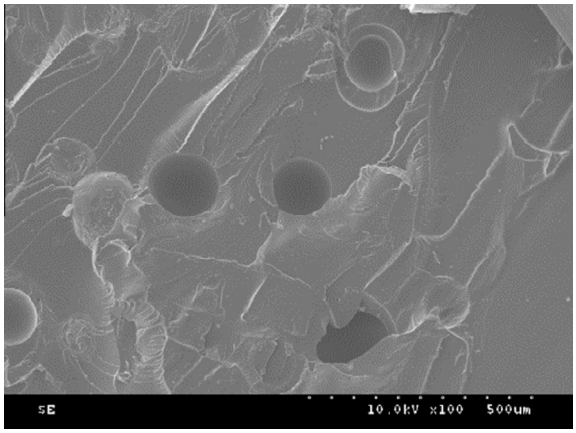
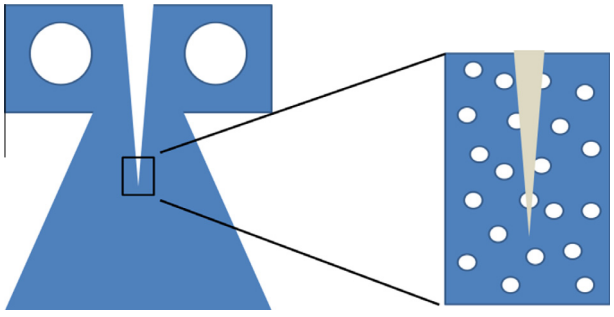


Fig. 7. SEM micrographs of the fractured surface of epoxy specimen with dual-component microcapsules after healing.



Scheme 2. The indication of DSC specimen took from TDCB specimen.

epoxy, forming an unclear interface between microcapsules and the epoxy to suggest good compatibility with the epoxy matrix. The fracture surface shows cleavage of the microcapsules and changes from a normally smooth surface to a more textured appearance with the addition of the microcapsules.

3.5. DSC studies

The reaction between the epoxy and the hardener is exothermic in nature [35]. Hence, the self-healing process of the dual-component microcapsules in an epoxy matrix can be well explained by monitoring the changes in thermal behavior of the samples by DSC. Materials from the same locations of different specimens were analyzed using DSC thermograms. The locations from where samples were taken from TDCB specimens for DSC measurements are shown in Scheme 2. The samples for DSC studies were taken out from the crack planes immediately when the specimens were loaded and tested to failure the first time.

The DSC thermograms of the specimens with different contents of dual-component microcapsules at 1:1 (epoxy/hardener) weight ratios are presented in Fig. 8. The flat and nearly smooth curve with increasing temperature of the specimen without self-healing agent microcapsules, 'a' indicates that the cure behavior of the epoxy matrix remained almost unchanged. However, all the dual-component microcapsules embedded specimens exhibited the obvious broad exothermic peaks centered at about 129 °C due to the exothermic curing reaction. Moreover, with increasing dual-component microcapsules content in the epoxy matrix, the peak intensity increased. This increase is mainly due to the fact that a higher content of dual-component microcapsules increases the amount of mixture of re-

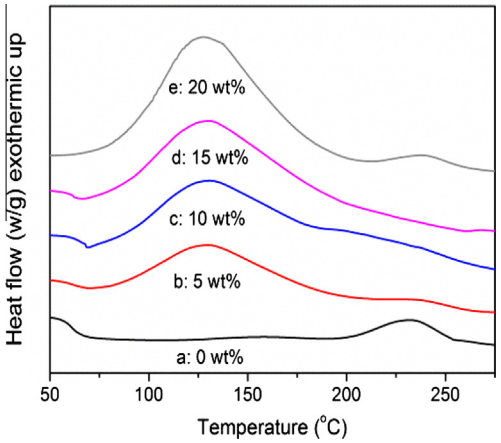


Fig. 8. DSC curves for the microcapsules embedded epoxies with different loadings of microcapsules.

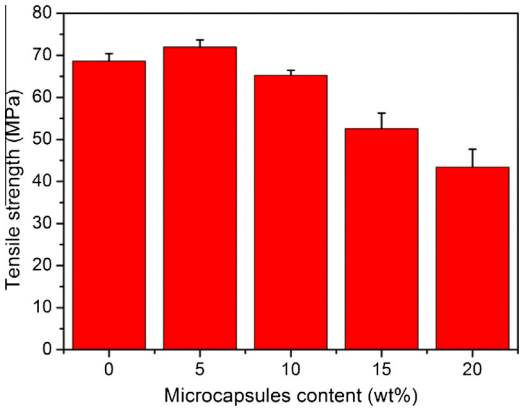


Fig. 9. Tensile strength of the epoxies with various dual-component microcapsule contents.

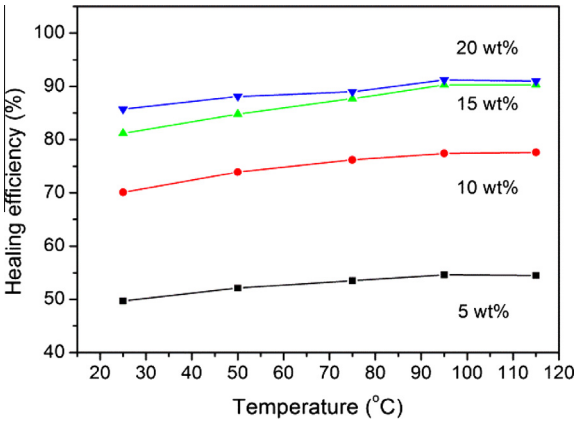


Fig. 10. Self healing efficiency of the epoxy with different contents of dual component microcapsules at various healing temperatures.

leased epoxy and hardener from the ruptured microcapsules into the cracked pristine epoxy laminates.

An optimal combination of microcapsules and matrix is necessary to ensure good mechanical property of a material, which significantly determines the applications of the material. The tensile strengths of the dual-component microcapsules embedded epoxy composites were measured to understand the effects of microcap-

sule content on the tensile strength of a material. Fig. 9 shows the tensile strengths of the dual-component microcapsules embedded epoxy systems according to microcapsules content. Tensile strength of the epoxy increases initially with increasing microcapsule content and shows the maximum value at 5 wt.%. After this point, it deceases with further increasing the content of microcapsules. The enhanced tensile strengths of the specimens may be attributed to the increased toughness by incorporating thermoplastic PMMA shell.

Healing temperature may have an important effect on the self-healing behavior and self-healing efficiency of the epoxy. Fig. 10 shows the temperature dependence of the healing efficiency of microcapsules incorporated epoxy. The healing efficiency of the epoxy increases slightly with increasing the healing temperature. This is due to the fact that a higher temperature can improve the curing reaction between the epoxy and hardener and the healing agents is easy to flow on the crack surfaces due to lower viscosity at higher temperature.

4. Conclusions

This study demonstrates the feasibility of fabricating a self-healing epoxy composite by embedding a healing agent consisting of dual-component microcapsules that contain epoxy and its hardener. Spherical microcapsules with average diameter in the range 50–62 μm were prepared at 350 rpm. Once the microcapsules were filtered and dried, free-flowing powder was obtained at high yields. Like a matrix polymer, microencapsulated epoxy and hardener have an excellent compatibility with the matrix. The healing efficiency of epoxy was affected by the content and ratio of the dual-component microcapsules. 15 wt.% dual-component microcapsules offered satisfactory repair effectiveness (84.3%) without significantly affecting the mechanical performance of the epoxy composite. As a result of high flowability, fast consolidation, and molecular miscibility of the released healing agents consisting of epoxy and hardener, self-healing was carried out successfully at room temperature and high healing efficiency was achieved. Furthermore, increasing the temperature can increase the self-healing efficiency of epoxy slightly. The feasibility of the dual-component microcapsules embedded self-healing epoxy was proven and dual-component system can broaden the process window for fabricating self-healing composites and prevent from the deterioration of healing capability of the composites during storage.

Acknowledgments

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