Original Article

Self-healing epoxy composites: preparation, characterization and healing performance

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Low velocity impact damage is common in fiber reinforced composites, which leads to micro-crack and interfacial debonding, where damage is microscopic and invisible. The concept of self-healing composites can be a way of overcoming this limitation and extending the life expectancy while expanding their usage in structural applications. In the current study, extrinsic self-healing concept was adopted using urea-formaldehyde microcapsules containing room temperature curing epoxy resin system (SC-15) as the healing agent prepared by in situ polymerization. Microcapsules were characterized using Fourier transform infrared spectroscopy (FTIR) for structural analysis. Size and shape of microcapsules were studied using optical microscopy and scanning electron microscopy (SEM). Size of the microcapsules was between 30 and 100 μm. Thermal characterization was carried out using thermogravimetric analysis. Microcapsules were thermally stable till 210 °C without any significant decomposition. Fiber reinforced composite fabrication was carried out in three different steps. In the first step, epoxy resin was encapsulated in urea-formaldehyde shell material, which was confirmed by FTIR analysis. In the next step, encapsulation of amine hardener was achieved by vacuum infiltration method. These two different microcapsules were added with epoxy at 10:3 ratio and composite fabrication was done with hand layup method. Finally, healing performance was measured in terms of low velocity impact test and thermoscopy analysis. Low velocity impact test with 30 J and 45 J impact loads confirmed the delamination and micro-crack in composite materials and subsequent healing recovery observed in terms of damaged area reduction and restoration of mechanical properties.

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1. Introduction

Thermoset polymers are widely used as matrices in most FRP composites used in structural applications due to their ease of processing, low cost and good wettability. They also offer good mechanical properties, as well as good corrosion resistance compared to metals and other engineering materials. They are subjected to different types of stresses during service life, and due to their uniqueness, they have several unique failure mechanisms compared to metals. Crack detection and repair in these types of materials are difficult and therefore self-healing techniques have been explored in a variety of ways to overcome this limitation. Another important issue is concerned with durability of these materials as they are exposed to different service loading due to their viscoelastic properties [1,2].

Dry et al. [3] first introduced capillary glass filled healing agent for self-repairing in cement and then in polymeric composites during fabrication. In a separate work, White et al. [4] used microencapsulation method as self-healing mechanism and showed it to be a better process over capillary glass tube. In their study, they used dicyclopentadiene (DCPD) as healing agent in the presence of urea-formaldehyde microcapsules. Results of the study showed a 60% healing efficiency in polymeric system. Similarly, Blaiszik et al. [5] used PUF microcapsules containing dicyclopentadiene and Grubbs’ catalyst in E-glass fiber and EPON 828/EPIKURE 3274 composites, where they reported an average of 44% bond strength recovery of fiber/matrix interfacial bond for this composite system. Brown et al. [6] did a study on effective healing efficiency of microcapsules based on various diameters for different agitation rate and catalyst concentration.

Epoxy resins are widely used in industrial applications due to their excellent chemical, physical and mechanical properties. Epoxy can be one of the more effective materials as a healing agent over other available healing compounds in respect of cost and healing efficiency for self-healing composites. Damage recovery in large scale composite should be effective and have high restoration efficiency. Several research groups successfully synthesized epoxy contained microcapsules [7,8].

Low velocity impact damage is one of the significant concerns for composite materials. Composite materials show sufficient resistance if the applied load is in the fiber direction, but low resistance to impact loading which is in the transverse direction. Matrix-fiber debonding, delamination, matrix micro-cracking and fiber pull out are the common failure modes in composites under impact loading. Yin et al. [9] studied low velocity impact on the glass fiber reinforced composites with microcapsules. They used epoxy loaded microcapsules with latent hardener CuBr2(2-Melm)4 (the complex of CuBr2 and 2-methylimidazole) as a healing system. They measured compression after impact for the measurement of mechanical performance after matrix recovery by crack repairing. They also used pressure and elevated temperature for the healing of large damaged areas. Patel et al. [10] also performed similar experiments for glass fiber reinforced composite with dicyclopentadiene (DCPD) loaded microcapsules and paraffin wax microspheres containing 10 wt% Grubbs’ catalysts. About 51% of crack length was reduced as healing efficiency after low velocity impact. Williams et al. [11] investigated the healing efficiency for carbon fiber reinforced composite. They used hollow glass fibers as healing agent containers and applied low velocity impact testing for the measurement of healing efficiency by compression after impact. They reported that 90% recovery was possible for this system. Zainuddin et al. [12] studied the effect of the healing recovery for glass fiber reinforced composite. They used SHA in hollow glass tube for the improvement of peak load in low velocity impact testing. The LVI experiment was performed at 56 J for all samples and they showed that 53.6% improvement after second impact for SHA loaded composite in comparison to control sample.

In the current study, microcapsules were synthesized from urea-formaldehyde and characterized. Subsequently, these synthesized microcapsules were encapsulated with a commercially available diglycidyl ether of bisphenol A (DGEBA) epoxy resin; SC-15 part A and part B separately and characterized to study viability of these microcapsules as healing agents for self-healing in fiber reinforced composites. 10% microcapsules contained fiber reinforced composite samples were prepared for the investigation of healing efficiency. After composite fabrication with hand layup, samples were impacted at different energy levels and damaged area investigated with thermography. After 48 h, second impact was introduced at sample position with 10% higher energy compared to first impact for the evaluation of healing performance.

2. Experimental

2.1. Materials

Materials used in the current study for microcapsule synthesis were urea, formaldehyde, styrene, hydrochloric acid (HCl), sodium hydroxide (NaOH), ethylene maleic anhydride (EMA), ammonium chloride (NH4Cl) and resorcinol, which were all purchased from Sigma–Aldrich. DGEBA epoxy resin SC-15 part A was used as healing agent and acquired from Applied Poleramics Inc. Commercially available plain woven E-glass fabric (oriented in two directions, warp at 0° and fill at 90° respectively) was used as the reinforcement in composite and purchased from Fiber Glast Development Corporation. Density of the E-glass fabric was 2.58 g/cm3 with a single fiber diameter of 14–16 μm. Fiber surface was sized with silane agent for a better compatibility and better adhesion between matrix and fiber.

2.2. Synthesis of microcapsules

Custom designed reaction vessel was used in the synthesis of empty and epoxy-filled microcapsules. The reaction vessel consists of two reaction chambers, one contained monomeric solution with 63.5 mm diameter low-shear mixing propeller and the other contained healing agent during synthesis. Fig. 1 shows an image of the reaction vessel. Synthesis of microcapsules used in the study was done by employing the method used in a study by Brown et al. [6] with slight modifications. At room temperature, 2.5% EMA solution was prepared by using
controlled by using HCl and NaOH and maintained between 2.6–3.4. For encapsulation of epoxy, 14 g of SC-15 part A with 2 g of styrene was added to the reaction mixture in the vessel followed by addition of 13 g of formaldehyde (37%, w/w). The mixture in the reaction vessel was placed on a hot plate while mechanical stirring at a rate of 900 rpm.

The mixture was stirred for 4 h at 60 °C. At the end, the set up was allowed to cool and the microcapsules were separated using Busher funnel with acetone and washed with distilled water. The separated microcapsules were dried in a conventional oven at 60 °C for about 24 h. For microcapsules synthesis, identical procedure was used without the addition of epoxy. Fig. 2 shows schematic representation of overall processing of synthesizing epoxy loaded microcapsules used in the current study.

Similar synthesis method was used for the synthesis of empty microcapsules. In room temperature, 200 ml distilled water was added with 2.5% EMA solution into the reaction vessel over hotplate with continuous stirring at 900 rpm. Urea (5 g), NH4Cl (0.5 g) and resorcinol (0.5 g) were added and pH was adjusted at 3.13 by adding NaOH and HCl. 1-Octanol was used to eliminate surface bubbles. Finally, 13 g formaldehyde was added into the solution and reaction was continued for 4 h at 60 °C. Then, synthesized hollow microcapsules were immersed in stainless steel vacuum jar with part B of SC-15 resin system. Vacuum infiltration was done for several hours for amine encapsulation and amine passed through the shell materials. Shell materials acted as permeable membranes. In the beginning, hollow microcapsules floated on top of the amine bath, but after several hours they filled up and were placed at the bottom. Amine contained microcapsules were then filtered without any solvent [7]. Fig. 3 shows schematic diagram for synthesis of empty microcapsules and encapsulation of amine as hardener.

Fig. 1 – Image of custom designed reaction vessel for synthesis of urea-formaldehyde microcapsules.

distilled water in the reaction vessel. EMA solution was mixed with 5.0 g urea and stirred with low shear mixing propeller at 600 rpm. Under agitation, 0.5 g NH4Cl and 0.5 g resorcinol was then added to the mixture and allowed to stir followed by addition of 200 ml distilled water. pH of the solution was
2.3. **Fiber reinforced composite fabrication**

Fiber reinforces composite fabrication was done in three different steps. In the first step, urea-formaldehyde shell materials encapsulated with epoxy were prepared and confirmed by FTIR analysis. In the next step, encapsulation of amine hardener was achieved by vacuum infiltration method. Finally, these two different microcapsules were added with liquid SC-15 at 10:3 ratio and the composite fabrication was done with hand layup method. Fig. 4 represents the schematic process of glass fiber/epoxy composite fabrication. Polarity difference between shell materials and epoxy resin is higher. As a result, dispersion of microcapsules contained part-A and part-B in epoxy is difficult. Moreover, higher mechanical stirring can damage the microcapsules. Magnetic stirring was used for microcapsules protection and the mix was maintained at 40 °C for reduction of viscosity. Now, part A and part B of resin system containing microcapsules were mixed with mechanical at 600 rotations per minute. As 900 rpm was used for microcapsules synthesis, 600 rpm ensured that there was no breakage of microcapsules. After mixing, the resin mixture was degasified for 45 min by placing it in a vacuum oven for removal of bubbles from resin.

Finally, glass fiber-epoxy composites were fabricated by a combination of hand lay-up and vacuum bag molding. For low velocity impact, a total of five layers of glass fiber were manually impregnated with resin using a brush and a hand roller. A plastic bag was placed over mold surface followed by a distribution mesh and a porous Teflon fabric. Impregnated glass fabric layers were placed over the porous Teflon fabric. Finally, another Teflon fabric and a bag was placed over the whole arrangement. Now vacuum was applied for consolidation and removal of excess resin. Room temperature curing was selected for preventing microcapsule's core materials from self-polymerization.

2.4. **Characterization**

2.4.1. Structural

Scanning electron microscopy (SEM) was carried out on unloaded and SC-15 loaded microcapsules to confirm their morphology using JEOL JSM-6400 system. Subsequently, Fourier transform infrared (FTIR) spectroscopy was conducted on synthesized microcapsules using Shimadzu FTIR 8400s equipped with MIRacle™ ATR. Scans were performed from 700–3500 cm⁻¹. FTIR was used for the confirmation of reaction by detecting organo-functional groups present on the microcapsules.

2.4.2. **Thermal analysis**

Thermal stability of microcapsules was studied using conventional thermogravimetric analysis (TGA) using TA instruments’ Q500. The equipment was purged with dry nitrogen flowing at 50 ml/min. Conventional TGA was done at 5, 10 and 15 °C/min from 30 to 500 °C. Polymeric properties of microcapsules were determined by using Q-2000 from TA Instruments Inc. (DE, USA). Hermetic aluminum pans were used for sample analysis with sample sizes approximately 5–10 mg. An identical empty pan was used as a reference. DSC scans were performed at a heating rate of 10 °C/min from 30 to 400 °C under nitrogen atmosphere with a flow rate of 50 ml/min.

2.4.3. **Low velocity impact**

A drop weight impact testing machine (DYNATUP 8210) was used for impact studies. Transient response of the samples was recorded using impulse data acquisition system. Using this system, it is possible to test samples at different energy levels by varying drop mass and height. During the test, specimen was placed at the bottom of the drop tower in a fixture that provides 75 mm of circular clamped support condition. For the tests, square samples of size 80 mm × 80 mm × 4 mm were used. Initial impact was carried out on samples with and without microcapsules at 30 and 45 J. In case of samples with microcapsules, 10% epoxy contained microcapsules were used to determine the healing efficiency. Healing performance was measured by carrying out a second impact after 48 h. During second impact, elevated energy levels of 40 and 55 J, respectively, were used. At least three samples were subjected to impact and data was recorded.

2.4.4. **Thermography NDE**

Thermography is a thermal NDE technique to determine the damage area in composite materials. It is better than other conventional non-destructive evaluation techniques for its quick response. Data reconstruction ability also confirmed its superiority. It consists of a flashlight, which provide IR ray over the surface area of the specimen to heat up the surface. Heat conduction and reflection depends on the quality of the sample. In the presence of damage or defect, heat conduction and reflection gets significantly affected. This physical phenomenon is taken advantage of in the infrared thermography. In this case, reflected heart signature is captured and analyzed. In the current study, an infrared camera was used...
for instantaneous recording of the heat signature. Differential heat profile from the surface is mapped to get profile of the projected image of damaged area. Micro-cracks or damages containing air or vacuum depict lower conductivity resulting in different profile compared to a sound composite material. This difference in signal is reconstructed by using software to get rid of noise. Finally, the color image is converted to black and white image for detection of primary and secondary damage area by using a “MATLAB” code. By counting number of pixels depicting black color and dividing that by total number of pixels and then multiplying with the scanned area, damaged area was computed.

3. Result and discussion

3.1. Morphology of microcapsules

Comparison of hollow urea-formaldehyde microcapsules and epoxy filled microcapsules was made in terms of their structure, size and thermal behavior. Scanning electron microscope (SEM) and optical microscope were used for surface morphology and size distribution of empty and epoxy contained microcapsules. In order to ensure uniform size distribution of synthesized microcapsules, size distributions were analyzed using an optical microscope and an image analysis software. As expected, diameter of synthesized hollow urea-formaldehyde microcapsules and epoxy filled microcapsules were different. The size distribution curve was achieved by at least 100 measurements at different locations and magnifications. SEM micrographs obtained at different locations are also presented in Fig. 5, where variation in diameter and surface roughness of the microcapsules can be seen. Surface roughness of these microcapsules might help for better interaction between matrix and microcapsules during fabrication of self-healing panels. Fig. 6(a) and (b) shows size distribution curves for hollow and epoxy filled microcapsules respectively. Mean diameter of hollow microcapsules was determined to be between 45 and 55 µm, while that of epoxy filled microcapsules was between 45 and 65 µm (Fig. 7). The average diameter of hollow and epoxy filled microcapsules was 75 µm and 79 µm respectively. Brown et al. [6] discussed the effect of agitation rate on microcapsules size and factors that determined the shell thickness of microcapsules. Optimum sizes of microcapsules are required for maximum healing efficiency in terms of healing materials storage with optimum shell thickness. Agitation rate at 900 rpm showed the maximum durability in terms of minimum weight loss in 6 months storage for maximum healing performance [13].

![Fig. 5 – SEM micrograph of hollow microcapsules.](image)

![Fig. 6 – Size distribution of synthesized microcapsules for (a) hollow and (b) epoxy filled.](image)
3.2. Structural analysis of microcapsules

3.2.1. FTIR analysis of epoxy loaded microcapsules

FTIR analysis was used for structural analysis of microcapsules through characteristic absorption band of different functional groups in terms of shell materials and core component. An intense peak appeared at wavelength 1720 cm\(^{-1}\), which is the characteristic peak for carbonyl (\(-\text{C} = \text{O}\)) functional group of shell materials [14]. It is indicated in FTIR curve by a circle (Fig. 8). The presence of core materials in microcapsules was also confirmed by comparing neat epoxy data with encapsulated epoxy microcapsules. The characteristic peak at 1508 cm\(^{-1}\) is due to the presence of \(\text{Ar} = \text{C} = \text{O} - \text{C} - \text{H}\) stretching. Similarly, peaks at 1240 and 1183 cm\(^{-1}\) were for the presence of \(-\text{C} = \text{O} - \text{C} - \text{O}\) str. The \(-\text{C} - \text{N}\) absorption peak appeared at 1101 cm\(^{-1}\). Presence of \(-\text{C} - \text{O} - \text{C}\) str peak are also found at 1033 cm\(^{-1}\). Presence of epoxy group was confirmed by peaks at 913 and 829 cm\(^{-1}\). Thus, it was confirmed from FTIR data that epoxy is encapsulated by Urea-Formaldehyde microcapsules.

3.2.2. FTIR analysis of amine microcapsules

Few milligrams of amine contained microcapsules were taken in a syringe attached with syringe filter and crushed with pressure. Finally, liquid core containing microcapsules were collected in a vial for FTIR analysis. Fig. 9 shows the representative FTIR spectrum for core amine content compared with SC-15 part B. Both FTIR spectra showed similar patterns for different vibration modes of primary amine such as amine N–H stretching, N–H deformation and C–N stretching vibrations. FTIR spectra at 3360 cm\(^{-1}\) and 3290 cm\(^{-1}\) was for asymmetric stretching of the \(\text{–NH}_2\) group. Spectrum at 2913 and 2860 cm\(^{-1}\) might be for cyclic aliphatic groups [14]. Broad scissor vibration appeared at 1600 cm\(^{-1}\) position for saturated primary amine. Out of plane bending vibration appeared at 835 cm\(^{-1}\) for \(\text{–NH}\) groups. Finally, C–N stretching vibrations for primary aliphatic amine appeared at 1111 cm\(^{-1}\) position.

3.3. Thermal analysis of microcapsules

Thermal stability of hollow and epoxy filled microcapsules was studied by thermogravimetric analysis. From TGA data (Fig. 10a) it appeared that microcapsule shell materials are stable till 210°C without significant weight reduction. Approximately 5–8% weight loss was observed at this temperature and was attributed to presence of residual moisture. Beyond 235°C decomposition rate of hollow microcapsules was higher compared to epoxy-filled microcapsules. The same was observed at around 340°C where weight lost constituted approximately 44% and 78% for epoxy-filled and hollow microcapsules respectively. The presence and reaction between epoxy in epoxy-filled microcapsules and shell material (Urea) led to lesser weight loss at this temperature. However, beyond 340°C decomposition rate of epoxy filled microcapsules became higher than that of the hollow. This behavior was due to heat released during polymerization reaction between encapsulated epoxy and the shell material, which accelerated the rate of chemical conversion at that temperature. As a result, residue obtained at the end of TGA scan showed less mass, approximately 16% compared to 21% from hollow microcapsules. A two-step distinct decomposition profile was observed in both empty and epoxy-filled microcapsules. Bulk of the decomposition occurred at 255°C followed by a lesser secondary decomposition at around 382°C. For epoxy filled microcapsules, initial mass decomposition occurred at around 246°C and bulk of decomposition at 366°C as can be seen in
Fig. 9 – Characterization of amine core content of microcapsules and reactive SC-15 part-B by vibration frequency of functional group.

Fig. 10 – (a) Weight loss versus temperature and (b) derivative of weight loss versus temperature of epoxy filled and hollow microcapsules.

Fig. 10b. The relative high decomposition mass was attributed to epoxy polymerization resulting in fewer residue at the end of the scan as mentioned earlier.

DSC analysis of microcapsules reveal the thermally inducted reaction in materials without decomposition. DSC curve (Fig. 11) indicates the presence of water molecules on the surface of epoxy loaded and empty microcapsules. Hydrogen bonds between the hydrogen atoms in water molecules and oxygen atoms in carbonyl groups of urea-formaldehyde shell materials are responsible for the presence of the excess water molecules in the surface of shell materials. Empty microcapsules adsorbed more water molecules compare to epoxy loaded microcapsules. Apolar nature of epoxy molecules might be responsible for the presence of less amount of water adsorption. Peak at 95–105°C temperature, shows the presence of water molecules on the surface of shell materials. Further, there was no characteristic thermally induced reaction in the empty microcapsules except thermal decomposition of the shell materials at 245°C temperature. Endothermic peak confirmed the energy absorption by the urea-formaldehyde shell materials. At the elevated temperature, shell materials may decompose to ammonia, methyl amine and dimethyl amine by self-esterification reaction [15]. Epoxy contained microcapsules showed one endothermic and one exothermic peak where endothermic peak at 125°C temperature was for the water presence on the surface of shell materials.

Fig. 11 – Heat flow as function of temperature of epoxy loaded and hollow microcapsules.
3.4. Low velocity impact characterization of FRP

Load and energy versus time plot revealed the quantitative information about damage due to the impact. 10% microcapsules contained sample and neat sample were impacted at 30 J and 45 J. After 48 h, a second impact was introduced at the same location as of previous impact. When impacted first, samples absorbed energy by undergoing elastic deformation, as well as by creation of damage when the energy exceeded that absorbed by elastic deformation. Sample containing microcapsules released epoxy and hardener by cracking shell materials in the damaged area following which a new covalent bond formation occurred between epoxy molecules and amine based molecules. Thus, there was a healing of sample. As a result, when impacted second time, these samples showed better impact resistance due to repairing. In this test, impact load was applied for the second time to test efficacy of matrix cracking without fiber damage. Healing agent may recover matrix damage as both host matrix and healing agent are made of same materials. Load versus time and energy versus time were plotted for the samples and representative curves of the samples are shown in Figs. 12 and 13 and the average values are listed in Table 1. It is observed that samples without microcapsules represent higher peak loads compared to those with microcapsules for 1st impact 30 J and 45 J. However, after 48 h of first impact, samples containing microcapsules showed better performance compared to neat samples when they were subjected to impact at 40 J and 55 J. At 40 J and 55 J impact, they had an average of 6.16 kN and 7.52 kN peak load respectively compared to 5.36 kN and 6.67 kN for samples without microcapsules. From these results, it can be inferred that epoxy and amine hardener bled from broken materials. Prominent exothermic peak at 225 °C temperature indicated the self-polymerization reaction of core materials. Epoxy core materials not only react by self-polymerization, but also increase the decomposition temperature of the wall materials.

<table>
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<th>Table 1 – Low velocity impact result for 1st and 2nd impact at 30J, 45J and 40J, 55J.</th>
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<td>Maximum load – 1 (kN)</td>
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<tr>
<td>1st impact at 30J (microcapsules contained)</td>
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<td>2nd impact at 55J (neat sample)</td>
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microcapsules, hence react with each other at room temperature and cure as a result of which matrix recovery occurred.

3.4.1. Low velocity impact damage assessment and healing recovery
Damaged area of the impacted laminates were calculated by scanning them with thermoscope followed by a program using MATLAB coding. Fig. 14 shows thermography images of samples immediately after impact and after 48 h. All of the colored images were converted to black and white images, and representative images are shown in Fig. 15. Damage area is increased with increasing impact energy. Higher rate of microcapsules shell rapture may lead to release of extensive amount of healing agents at higher impact resulting in significant matrix recovery. Average damaged area was obtained and tabulated for every type of samples impacted at different energy levels. The images taken after 48 h show less area of damage for samples with microcapsules. Maximum damage recovery was observed for epoxy microcapsules loaded samples impacted at 45 J. Higher load could be responsible for maximum number of capsules rapture. But, 10% microcapsules are insufficient for recovery of central large damage area. Higher content of healing agent can overcome this limitation. We used the following formula for detection of healing performance [12].

\[
\text{\% gain} = \frac{E_{ab} \text{ for healing sample} - E_{ab} \text{ for neat sample}}{E_{ab} \text{ for neat sample}} \times 100
\]

where \( E_{ab} \) is the absorbed energy in J. From calculation it is seen that 29% and 40% healing recovery was observed for 30 J and 45 J impacted microcapsules contained samples compare to neat samples. Average values of damage areas are presented in Table 2.

3.5. Damage area analysis through optical microscopy
Cross sectional analysis of composite materials exposed the damaged area and recovered damage area by healing agent through consolidation of liquid resin. Bleeding of liquid resin from microcapsules in damaged area initiated curing reaction among SC-15 part A and part B as a result of which curing reaction was filled. Fig. 16 represents the virgin microcapsules and damaged microcapsules with bleeding in fiber reinforced composite. Healed area in composite materials showed different color.

Fig. 14 – Thermography images of microcapsules contained samples impacted at 30 J and 45 J.

Fig. 15 – Conversion of color image obtained to black and white image to calculate the damaged area.
Presence of styrene and partial ring opening reaction of epoxy rings with amino groups of shell materials might be responsible for it. After impact, bleeding from microcapsules recovered the damaged area by formation of new bond at the position of micro crack. Hence, mechanical properties were restored from self-healing process by the formation of three-dimensional polymeric networks in damaged area. Complete curing of healing agent showed more contrast in color compare to partial curing of healing agent.

### 4. Conclusion

In this study, urea-formaldehyde microcapsules were successfully synthesized and encapsulated with SC-15 epoxy part A with spherical size and shape. Size of microcapsules ranged between 30 and 100 μm, with average diameter of 75 μm for hollow microcapsules and 78 μm for epoxy-filled microcapsules. Vacuum infiltration method was successfully applied for encapsulation of amine based hardener in hollow microcapsules. FTIR study confirmed the structure of shell and epoxy core materials through detection of the functional groups. TGA study showed decomposition temperatures of hollow and epoxy filled microcapsules around 235°C. DSC study revealed the thermal stability in terms of self-polymerization reaction of core materials.

Composite fabrication was successfully achieved through hand layup followed by vacuum bag molding. Appropriate fabrication technique confirmed the protection of microcapsules in the fiber reinforced composite. Low velocity impact test with 30 J and 45 J impact loads confirmed the delamination and micro-crack in composite materials and subsequent healing recovery observed in terms of damaged area reduction and restoration of mechanical properties. The optical micrograph of fractured samples showed the filling of damaged area by the bleeding of healing agent from the microcapsules cured at room temperature.

### Conflicts of interest

The authors declare no conflicts of interest.

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### References


