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Effect of TETA microcapsules on self-healing ability of dual component epoxy system

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ABSTRACT

To deliver epoxy composites with enhanced self-healing ability, this study investigates healing efficiency of dual component epoxy system consisting of microcapsules containing epoxy (DGEBA) and different variants of hardener (TETA) microcapsules. Morphological investigation under FESEM confirms formation of spherical shaped intact TETA microcapsules at high agitation speed with average size of the ~65.32 µm and reduced wall thickness of ~1.823 µm. Reaction temperature is found to play significant role to tune the roughness of the microcapsule surfaces. The single edge notched bending (SENB) test was performed to evaluate the healing ability. It was found that with incorporation of microcapsules, the fracture toughness decreases but the healing efficiency increases with increase in content of microcapsules. The maximum healing efficiency observed was 65.61%. High concentration of TETA microcapsule (prepared at high agitation speed) in epoxy network gives the essence for their applicability as a potential ingredient to elevate the healing efficiency. To enhance the healing ability further of the composites as well as fibre reinforced composites with unaltered mechanical properties we believe synthesis nanocapsules and their incorporation could have significant impact. Copyright © 2016 VBRI Press.

Keywords: Smart polymers; self-healing composites; solvent evaporation technique; microcapsule; single edge notched bending test.

Introduction

Epoxy-based thermosets are used as structural composites in numerous application including aerospace, automotive, energy, etc [**1**]. These components are usually subject to fatigue loading in day-to-day use and eventually fail under stress [**2**]. Failure usually starts in the form of a micro/nano crack located deep within the structural component. However, it is practically very difficult to identify such cracks and almost impossible to fix them. Self-healing materials could be a possible solution to enhance the life-time of such materials. The motivation for synthesizing self-healing materials has been derived from biological organisms, where the damage event itself triggers the healing mechanism autonomously without any external intervention. Apparently there have been many attempts to design and develop smart materials with the ability to autonomously repair internal and external damage. [**3-9**].

Our research is primarily focused on developing self-healing materials that have a plurality of embedded microcapsules containing liquid healing agent. During the propagation of a crack, the microcapsules get ruptured and the healing agent flows into the crack plane by capillary action and then polymerizes. This mechanism ensures that the crack has been bridged completely and as a result inhibits its further propagation. At the heart of this technology are the microcapsules containing liquid healing agent and it is of paramount importance to improve their yield and quality in order to improve the self-healing efficiency of the system. Recent works carried out in both academia as well as industries highlights the healing of small crack using reinforced capsules containing single healing agent and catalyst in polymeric matrix [**9-13**]. Joseph *et al.* demonstrates encapsulation of diclyclopentadiene (DCPD) and embedding in polymeric matrix to find the healing behavior [**14**]. The processing sensitiveness to prepare uniform sized DCPD microcapsules hinders their application as self-healing agent. In other works, use of different core materials such as 5-ethylidene-2-norbornene (ENB) [**15**], dibutylphthalate-(DBP-) filled urea-formaldehyde (UF) [**16**] DCPD/ENB blend [**17**], styrene [**18**], polydimethylsiloxane [**19**], and epoxy [**20-22**] is also investigated. These capsules get ruptured as the crack intervenes and releases the healing agent into the crack plane through capillary action and polymerizes in presence of catalyst, thus heals the crack. These reports postulate efficient healing of composites provided, the capsules and the catalyst are in close proximity to each other and uniformly dispersed in the matrix. To overcome such limitations, use of dual microcapsules has been suggested by many [**21-23**]. However, there are very few literatures on dual encapsulation of amine hardener and epoxy resin [**24-26**]. In general, one part of the microcapsules contains epoxy resin and other contains curing agent. When both the microcapsules are fractured, the individual healing agents mingle and get cured according to their epoxy-hardener curing stoichiometry and thus healing occurs. The highly active nature of the amine-based hardeners limits their encapsulation in water or organic solvents. In situ emulsion polymerization [**5-13**, **28**, **29**] technique has been employed in some cases but the difficulty in controlling pH-value and

incomplete polymerization rendered the technique incompatible for processing amine based healing agents. Also, the need for an additional catalyst to cure the healing agent when it comes out into the crack plane makes the process of synthesis complex and expensive.

In view of the above technical deficiency, researchers studied the encapsulation of epoxy and amine-based resins using solvent evaporation technique [**24**, **27**] and test their technical feasibility to render their applicability as self-healing materials. However, drawing a broad conclusion out of these works is restricted due to lack of reliable results. Li Qi *et al.* [**27**] reported on the feasibility of dual encapsulation of epoxy and hardener containing microcapsules and showed the effects of variation of epoxy-hardener stoichiometric weight ratio, variation of microcapsule content and healing temperature on the healing efficiency of the resulted composite. But, they did not investigate the effect of variation in size and core content of microcapsules on self-healing ability. The effect of variation of size, core content and surface morphology of TETA microcapsules on healing performance of dual component self-healing composites was not reported in any literature. Therefore, the aim of the present study is to investigate the effect of processing parameters on the physical properties and surface morphology of microcapsules containing amine-based hardener triethylenetetramine (TETA) and epoxy resin diglycidyl ether of bisphenol A (DGEBA) prepared using solvent evaporation induced phased separation technique. Furthermore, we evaluated the self-healing efficiency of epoxy composite containing these dual encapsulated microcapsules by Single-edge-notch bending (SENB) test. [**21**,**22**]. The schematic drawing of expected self-healing mechanism in SENB sample containing TETA microcapsule and DGEBA microcapsule has been shown in **Fig. 1**. The process parameter for DGEBA microcapsules was kept constant while, the processing parameters for TETA microcapsules is varied to determine the effect of TETA microcapsules on healing performance of the composites.

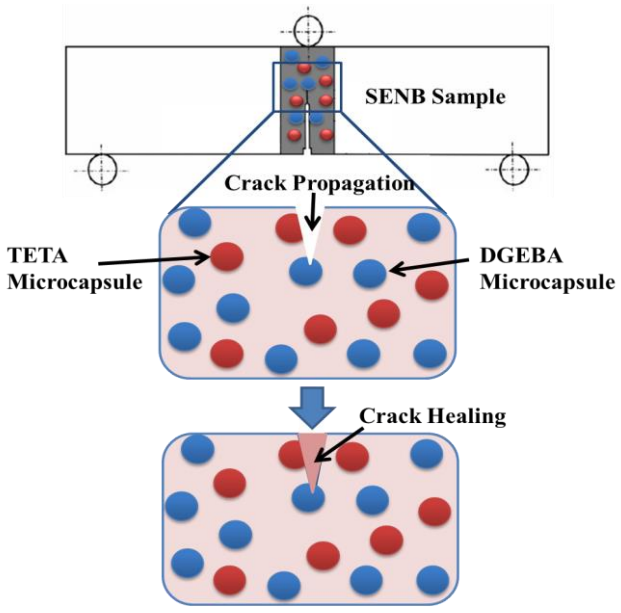

Fig. 1. Schematic drawing of self-healing mechanism in SENB sample.

Experimental

Materials

Diglycidylether of bisphenol-A (DGEBA) based epoxy resin (Araldite, GY 250) with density 1.17 g/cc and Triethylenetetramine, (TETA, K6) hardener with density 0.95 g/cc were used as the healing materials (Atul India Ltd). Poly (methylmethacrylate) (PMMA, Avg. $M_w$is 96,000) used as shell material was purchased from Alfa-Aesar. Sodium Dodecyl Sulfate (SDS) and Polyvinylalchohol (PVA) used as emulsifier were obtained from Sisco Research Laboratories Pvt. Ltd. (Mumbai) and Lobachemie (Mumbai) respectively. The organic solvent, DCM, was purchased from Merck specialties Private Ltd. (Mumbai). All the reagents used in this work were of analytical-grade and used without further purification.

Preparation of TETA microcapsules

The capsules were prepared by a solvent evaporation induced phase separation process. A solution was prepared by dissolving 4 g of TETA and 1 g of PMMA in 30 ml of DCM. This solution is then slowly poured into 60 ml aqueous solution of 1 wt.% PVA drop wise under high agitation speed of 400 rpm and at room temperature (about 35 ^{o}C). The resulting solution is stirred continuously for 45 minutes. It is then diluted with 180 ml aqueous solution of 1 wt.% PVA and kept under continuous agitation for two hours. The capsules are washed with deionized water several times and air dried. The same process was repeated for capsules prepared with 600 rpm agitation speed. To investigate the surface morphology of the microcapsules, the processing temperature was varied as 45 ^{o}C, 65 ^{o}C and 75 ^{o}C with fixed agitation speed (450 rpm). The various processing parameters for TETA microcapsules are tabulated in **Table 1**.

Table. 1. Processing parameters of hardener and DGEBA microcapsules.

Capsule Type	Shell material	Core material	Agitation speed (rpm)	Processing Temperature	Mean Dia.	Core content	Shell wall thickness
Hardener Containing microcapsule	PMMA	TETA	450	35 ^{o}C, 45 ^{o}C, 65 ^{o}C and 75 ^{o}C	74.21554	14.35	2.29 µm
			600		65.32525	16.50	1.823 µm
Epoxy Containing microcapsule	PMMA	DGEBA	300	35 ^{o}C	134.484	48.354	4.949 µm

Preparation of DGEBA microcapsule

For the case of DGEBA microcapsules prepared with PVA, agglomeration occurred during washing of microcapsules with deionized water due to presence of unreacted core materials on the surface. So, SDS was used as emulsifier as it is a stronger stabilizing agent as compared to PVA. Moreover, SDS prevents the micro-droplets from combining together and growing in size. 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. Later the mixture was added to the continuous phase (50 ml of 5wt.% aqueous SDS solution, looking into the fact of favorable reaction at high concentration for the synthesis of de-agglomerated microcapsules) under high-speed agitation of 350 rpm at room temperature (35 ^{o}C) for 30 min to get an oil/water

emulsion. Subsequently, the resultant oil/water emulsion was poured into a 200 ml aqueous solution with 5wt.% SDS with continuous energetic agitation. Dichloromethane was allowed to evaporate completely to obtain PMMA microcapsules containing the epoxy material and finally washed with deionized water and then air dried.

Preparation of epoxy self-healing composites

A neat sample was prepared by blending DGEBA and TETA in the ratio of 12:1. The self-healing composite samples were prepared by dispersing 5 wt.% and 7 wt.% of epoxy and TETA microcapsules in the ratio of 1:1 by weight. The blending of epoxy system and dispersion of microcapsules were done using overhead stirrer. The process is followed by degassing under high vacuum of 1.33×10^{-3} to 1.33×10^{-4} bars of the uncured epoxy systems to eliminate entrapped air bubbles. It is then casted into silicon rubber mould having the shape of specimen as per ASTM D638 (tensile specimen) and ASTM D5045 (SENB specimen). The samples are then cured at 80 ^{o}C for 24 hours. The sample preparation with their respective codes for both types of specimens is shown in **Table. 2**.

Table. 2. Sample codes with variation of microcapsule content and process parameter.

Sample Code	Process Parameter of hardener containing capsule	Process Parameter of epoxy containing capsule	Dual Capsules Content (1:1)
Neat epoxy (NE)	--	--	--
DEC-A	450 rpm	350 rpm	5 wt.%
DEC-B	450 rpm		7 wt.%
DEC-C	600 rpm		5 wt.%
DEC-D	600 rpm		7 wt.%

Characterization

The morphology of the microcapsules and the fractographic investigation of the test specimens were endorsed from field emission scanning electron microscopy (FESEM) (Zeiss, Supra55) at an acceleration voltage of 5 kV. Crack length of the SENB samples was identified under optical microscope at 200X. The Fourier Transform Infrared (FTIR) spectroscopy of samples was recorded with PerkinElmer Spectrum 100 series to examine the functional groups present in the microcapsules. The capsules was ground to fine powder and mixed to potassium bromide to form thin palettes for FTIR measurements. The core content is a major factor which determines the healing performance of the resulted self-healing composite. The core content of microcapsules was determined by extracting the core material by Soxhlet extraction. Initially, the weight (W_i) of the sample was taken very precisely. The microcapsules were grounded and crushed using mortar and pestle at 130 ^{o}C and then Soxhlet extraction was performed using xylene as the extracting solvent for two days and then dried in hot air oven at 80 ^{0}C for two hours. The sample was dried in hot air oven and finally the weight of the residue (W_f) was taken again. The core content (W_{core}) was evaluated using the following Equation (1) and the data obtained are tabulated in **Table 1**. The same process was repeated for at least 5 samples and the final value was taken as the average of the number of samples.

$$W_{core} = \left(1 - \frac{Ws}{Wi}\right) \times 100\% \quad (1)$$

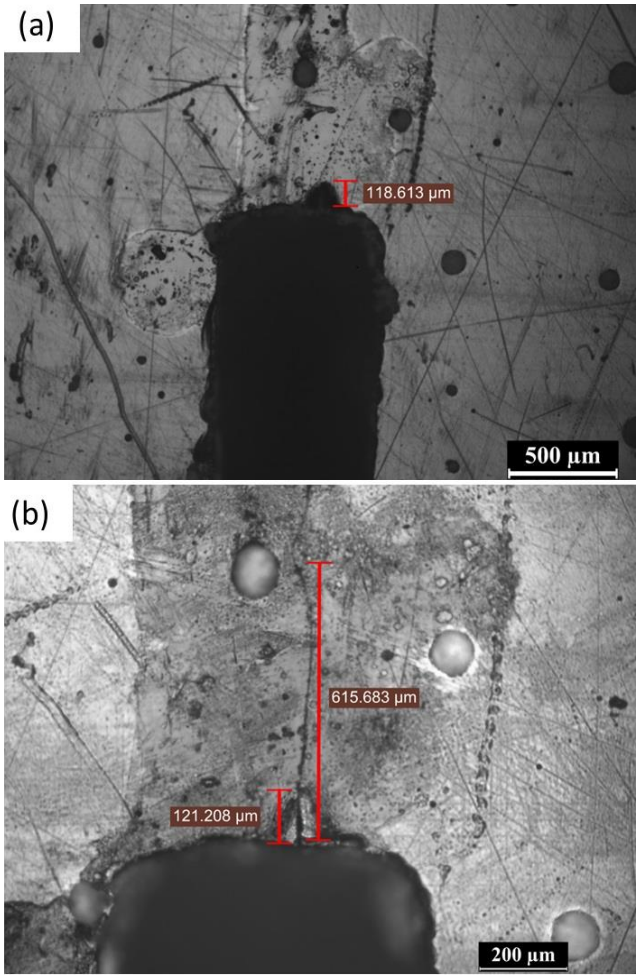

Fig. 2. Optical microscopic image of SENB samples (a) before loading and (b) after loading and healed sample.

The tensile test samples of both neat and self-healing composite were prepared according to ASTM D638 method. The tensile properties were measured with the help of a computerized universal tensile machine (INSTRON, Model 8801) at a crosshead speed of 1mm/min. In order to evaluate the self-healing ability of the composite, fracture test was conducted on virgin and healed SENB specimens as per ASTM D5045. The SENB specimen containing 5 wt% of dual microcapsule with initial crack is shown in **Fig 2 (a)**. This crack in the SENB specimens was initiated further at controlled displacement at speed of 5µm/s as illustrated in **Fig. 2(b)**. Later the specimens were subjected to room temperature healing for 24 hours. Finally, the healed specimens were tested again to determine the healing efficiency. The healing efficiency 'η' is defined as the ability of a healed sample to recover fracture toughness and it is calculated as,

$$\eta = K_{IC\ healed} / K_{IC\ neat} \quad (2)$$

where, $K_{IC\ healed}$ is the mode I fracture toughness of the healed specimen and K_{ICneat} is the mode I fracture toughness of the neat specimen [**22**].

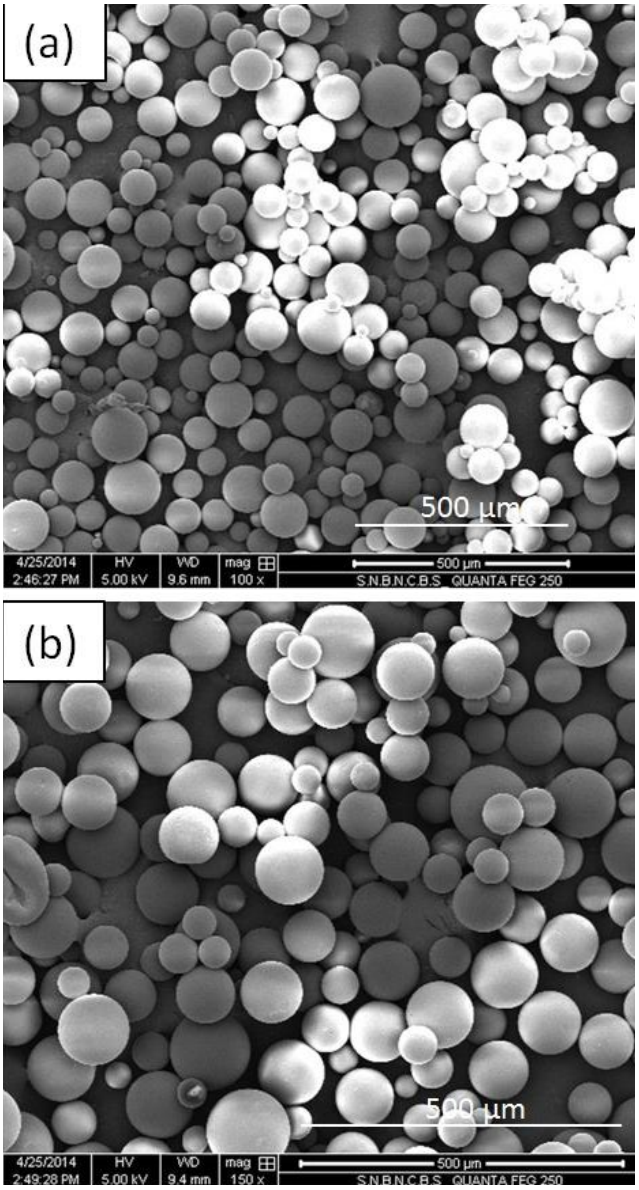

Fig. 3. Morphology of (a) TETA and (b) DGEBA microcapsules.

Results and discussion

Morphology of microcapsules

The morphological structure and size of hardener and DGEBA microcapsulesis investigated under FESEM as can be seen in **Fig. 3**. By keeping the concentration of emulsifier constant (1 wt.% PVA), in case of TETA microcapsule, increase in agitation speed from 450 to 600 rpm resulted in reduced microcapsule size as depicted in **Table. 1**. **Fig. 3(a)** confirms formation of spherical shaped intact TETA microcapsules at agitation speed of 600 rpm. The average size of the microcapsule is determined as ~65.32 µm. In general, the role of emulsifier is to stabilize the TETA-DCM-PMMA micro-droplets in the oil water emulsion and prevent them from coalescing. Here, 1 wt.% of PVA provides the necessary structural stability for the synthesis of de-agglomerated TETA microcapsules. The core content (wt.%) is found enhanced from 14.35 to 16.5 hence, resulting in approximately 14.5% increase in core material. In case of DGEBA microcapsules processed at agitation speed of 350 rpm and in presence of 5 wt.% of emulsifier concentration (SDS), stable de-aggregated spherical morphological structure is observed (**Fig. 3**(**b**)). However, the size of DGEBA microcapsules (~134.5 µm) is found greater than that of TETA microcapsules as illustrated in **Table. 1**. The core content is determined as 48.35 wt.%. This is suggestive towards alleviation of microcapsule size due to the potential impact of agitation speed.

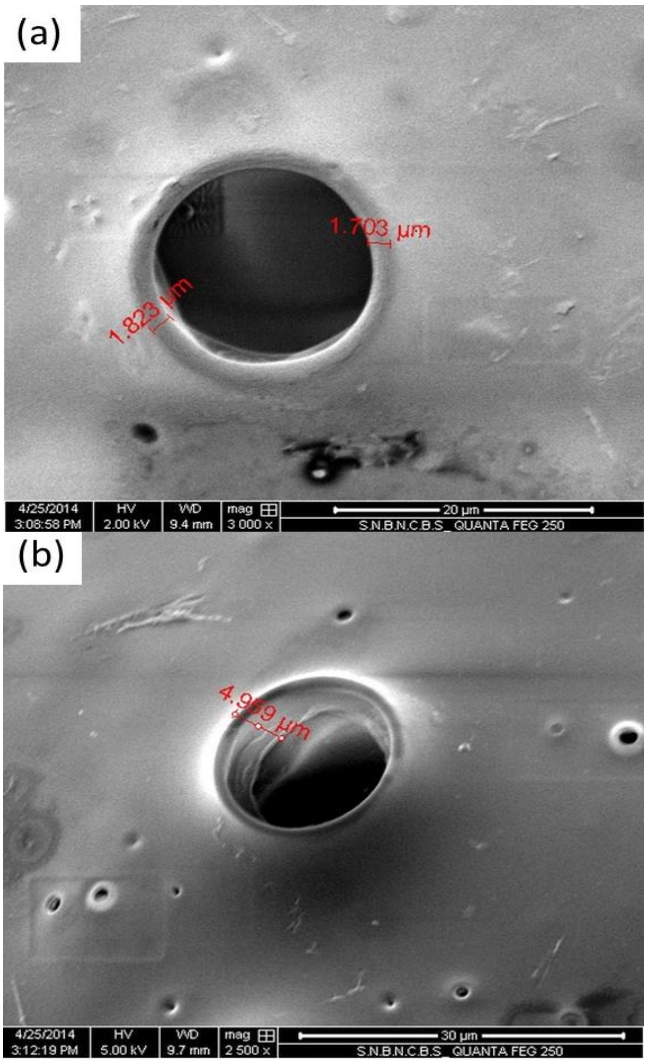

Fig. 4. Variation of shell wall thickness of (a) TETA microcapsules prepared at 600 RPM and (b) DGEBA microcapsules at 300 RPM with 5 wt. % SDS.

However, the core content is largely dominated by the significant role of emulsifier concentration during processing. This effect of emulsifier concentration on core content is also showed in other refs. [**20**, **30**]. Moreover, stronger emulsifier (SDS) has potential to provide a symptomatic enhancement in core content. The shell wall thickness of both TETA and DGEBA microcapsules are examined under FESEM as shown in **Fig. 4**. It has been found that, in case TETA microcapsules, increase in agitation speed has reduced the shell wall thickness. The wall thickness is observed as ~1.823 µm **(Fig. 4(a)),** when processed at agitation speed of 600 rpm also depicted in **Table. 1**. The wall thickness for DGEBA microcapsules is

largely enhanced as can be seen in **Fig. 4(b)**. The size is found as ~4.949 µm. This enhancement in wall thickness is owing to the shear and interfacial tensile forces during processing in oil-water emulsion. Low shear forces have negligible effect for hindering the polymerization reaction to form thick shell material around the core. At high mechanical forces, the shell wall polymerization by evaporating the DCM has resulted in reduced wall thickness [**27**].

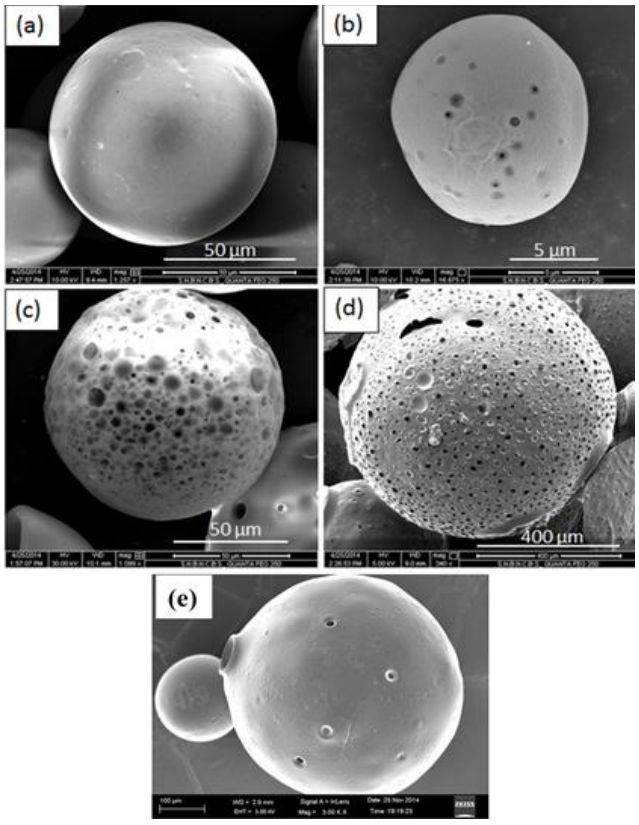

Fig. 5. Surface morphology of the TETA microcapsules prepared at (a) room temperature (b)45 °C (c) 65 °C and (d) 75 °C and (e) DGEBA microcapsules prepared at room temperature.

Investigation under FESEM of the microcapsule surfaces processed at reaction temperatures (35, 45, 65 and 75 °C) elucidate variation in surface morphology as can be seen in **Fig. 5**. In general, quick evaporation of reaction solvent (DCM) significantly affects the surface morphology of microcapsules [**27**]. Hence, an optimum reaction temperature is desirable. Reaction at 35 °C showed hardly any features on microcapsule surfaces **(Fig. 5(a))**. Uniform evaporation of DCM possibly led to such featureless surfaces. Increase in reaction temperature to 45 °C generates small spherical dimples on the surfaces of TETA microcapsules, which has been significantly enhanced at further higher reaction temperature of 65 °C (as shown in **Fig. 5(b) and (c))**. These dimples are found busted leaving behind visible porosity throughout the surfaces of microcapsules when processed at reaction temperature of 75 °C, can be seen in **Fig. 5(d)**. This behavior evidences the effect of DCM evaporation rate on surface morphology of microcapsules. Formation of pores is undesirable to restrict diffusion of the healing agent from the microcapsules. In brief, reaction temperature plays significant role to tune the roughness of the microcapsule surfaces. By considering this fact DGEBA microcapsules were subsequently processed at 35 °C by keeping other parameters same. The obtained surface of the DGEBA microcapsule **(Fig. 5(e))** evidences presence of dimples, which are supposed to enhance the adhesion behavior when incorporated in composites.

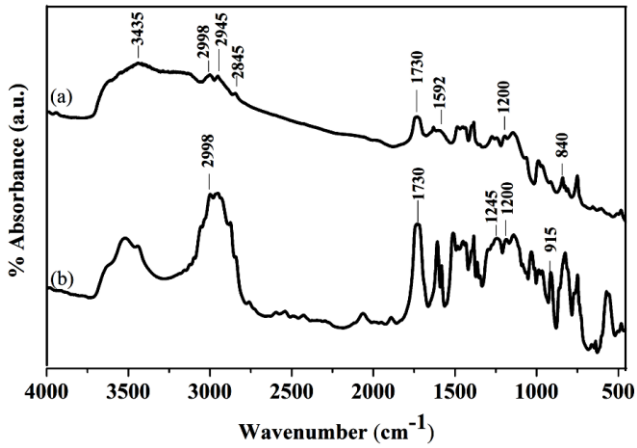

Fig.6. FTIR spectra of (a) TETA and (b) DGEBA microcapsules.

Chemical structure of microcapsules

The chemical structure of TETA and DGEBA microcapsules is harvested from FTIR spectroscopic analysis which is shown in **Fig. 6**. In the case of TETA microcapsules, the appearance of the FTIR band at 1592 cm^{-1} and 840 cm^{-1} represent N-H bending vibrations. Presence of broad peak at 3453 cm^{-1} in the FTIR spectra of TETA microcapsules confirms secondary N-H stretching [**27**]. These peaks are mainly due to the presence of TETA in microcapsules. Appearance of peak at 1730 cm^{-1} is corresponding to C═O stretching, whereas, ─CH_2 asymmetric and symmetric stretching peaks appears at 2998 and 2845 cm^{-1}, respectively. These peaks endorse formation of PMMA shell material on TETA core, illustrating successful encapsulation. In case of DGEBA microcapsules, absorption peaks at 915 cm^{-1} strongly confirms C─O stretch vibration in oxirane ring of epoxyas can be seen in **Fig. 6**. Also, peak at 1245 cm^{-1} confirms presence of epoxy group. Encapsulation of DGEBA is confirmed C═O (stretching), asymmetric and symmetric stretching of methylene group [**24**].

Mechanical response and healing ability

Tensile behaviour and SENB fracture behavior were investigated in order to isolate various effect of microcapsule on mechanical performance of dual microcapsule embedded self-healing epoxy composites. The tensile stress strain behavior as can be seen in **Fig. 7** exposes the tensile property variation arising due to varied microcapsule concentration and size. A clear picture depicting degradation in tensile properties is observed for all the variants. The tensile strength of NE is found as 81.12 MPa. A dramatic decrease in tensile strength is observed for all the variants of dual microencapsulated composites, as can be seen in **Fig. 8**. For DEC-A (5 wt.%)

and DEC-B (7wt.%) the tensile strength is observed as 40.20 MPa and 34.46 MPa. Hence, two fold and three-fold decrease in tensile strength is demonstrated. On the other hand, in case of DEC-C (5 wt.%) and DEC-D (7wt.%) the tensile strength is found reduced in comparison to NE, giving ~69% and ~64% reduction. Qi Li *et al.* incorporated dual capsules in epoxy and observed similarbehaviour [**24**]. The elastic modulus of NE is observed as 1.1629 GPa.

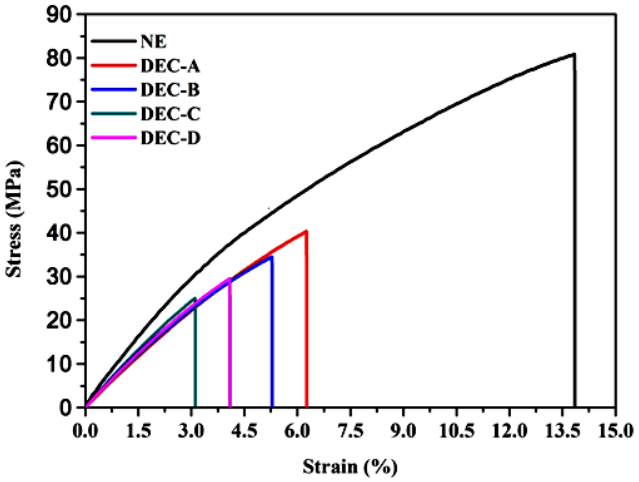

Fig. 7. Stress Strain curves of dual microcapsule embedded self-healing epoxy composites.

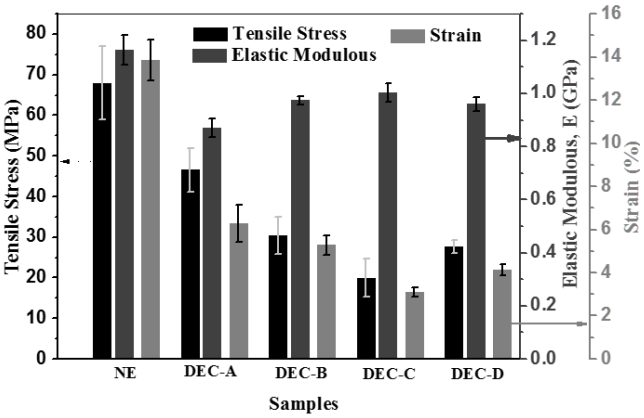

Fig. 8. Variation of tensile strength, elastic modulus and strain % of dual microcapsule embedded self-healing epoxy composites having different microcapsule content.

Incorporation of microcapsule reduces the elastic behaviour of composites as shown **Fig. 6**. In case of DEC-A, DEC-B, DEC-C and DEC-D the stiffness is observed as 0.871, 0.954, 1.004 and 0.960 GPa. Hence, a reduction of ~25.10, 17.96, 13.66, and 17.45% with respect to NE is found. In general, stiffness in composites is largely dominated by the concentration effect of the high modulus fillers [**27**]. Here, the reduction in elastic modulus with increase in concentration of the microcapsules confirms the detrimental effect of low modulus shell walls of hardener and epoxy. In case of DEC-A as well as DEC-B composites, significant reduction in elastic modulus gives an essence of hardener microcapsule dominance on the stiffness of the composites. Incorporation of hardener containing microcapsules with thin shell wall for DEC-C composite is found to uplift the stiffness to a modest value comparable with that of NE. But, enhancement in concentration marginally decreases the stiffness thereof as seen in case of DEC-D composite. **Fig. 8** demonstrates reduction in tensile strain due to incorporation of all microcapsule variants in epoxy. The tensile strain for NE is observed as 13.84%. In case of DEC-A, DEC-B, DEC-C and DEC-D the tensile strain is observed as 6.27, 5.28, 3.0934 and 4.1117%. Hence, a reduction of ~54.69, 61.85, 77.65, and 70.29% with respect to NE is observed. In case of DEC-A and DEC-B, size as well as concentration effect of hardener containing microcapsule mainly governs the tensile strain. For DEC-C and DEC-D, reduced hardener containing microcapsule size is possibly restricting the chain mobility of the epoxy network under stress resulting in decreased strain.

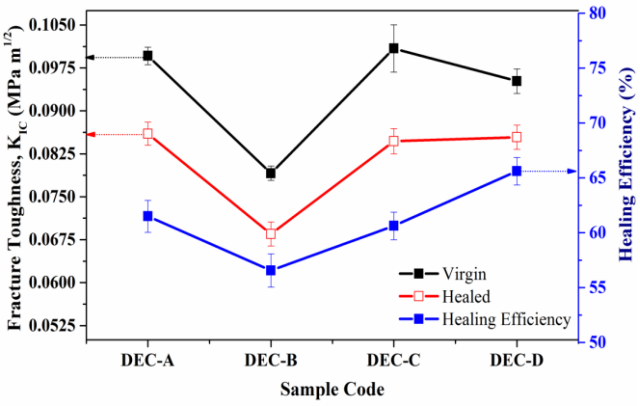

Fig. 9. Fracture toughness and healing efficiency of the SENB sample with variation of microcapsules.

This effect is further verified by understanding the fracture toughening behaviour in NE as well as dual microcapsule embedded self-healing epoxy composites in presence of crack. The variation fracture toughness of virgin and healed samples elucidates the vital change in intrinsic properties of epoxy network due to incorporation of hardener and epoxy containing microcapsules as can be seen **Fig. 9**. For NE, the fracture toughness is found as 0.1398±0.0025 MPa $m^{1/2}$. The fracture toughness is reduced significantly to a value of 0.0996±0.00152MPa $m^{1/2}$ and 0.0791±0.00125MPa $m^{1/2}$ for DEC-A and DEC-B composites. An effective enhancement in fracture toughness for DEC-C composites is observed but increase in microcapsule content reduces the fracture toughness thereof. Similar behaviour is demonstrated by the respective healed SENB specimens, but, the fracture toughness is reduced further. The healing efficiency determined is also shown in **Fig. 9**. In case of DEC-A and DEC-B, healing efficiency is found as 61.5 and 56.56%. The decrease in healing efficiency for DEC-B is mainly ascribed to the increase in weight ratio of dual microcapsules and their poor dispersion in composites. Further, low core content (14.35 wt.%) of hardener containing microcapsule additionally deteriorates the healing efficiency. For DEC-C, the healing efficiency is found as 60.63%, which was remarkably uplifted to 65.61% with increase in concentration of lower sized, enhanced core content (16.5 wt.%) of the hardener containing microcapsule for DEC-D composites. The maximum

efficiency hence is found with the samples prepared at 600 rpm and 7 wt.% of dual microcapsule content. The obtained results clearly indicate the dominating effect of lower sized and enhanced core content of hardener containing microcapsule for exhibiting excellent self-healing efficiency.

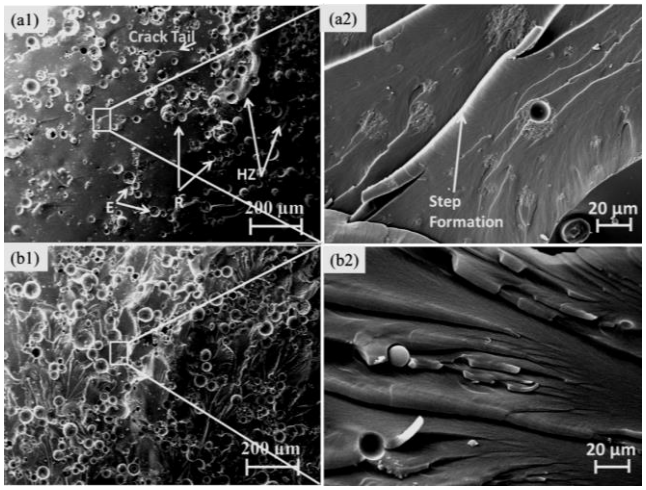

Fig. 10. Fracture behaviours of the SENB specimens at (a) 5 wt.% of microcapsule content and (b) 7 wt.% microcapsule content at (1) relatively low magnification and (2) high magnification.

Evidence of such behaviour is investigated further by analysing the fracture surface of healed SENB specimens under FESEM. The FESEM photomicrograph demonstrating the fracture surface of the SENB samples of DEC-C and DEC-D composites containing dual microcapsules is shown in **Fig. 10**. In the photomicrograph shown, hardener containing microcapsule is indicated by 'H' whereas; resin containing microcapsule is indicated by 'R'. For both DEC-C and DEC-D composites, homogeneous dispersion of microcapsules is observed. Fracture surface of DEC-C shows presence of few hardener containing microcapsules. However, most of the resin containing microcapsules is found broken as can be seen in **Fig. 10(a1)**. On the other hand both 'H' and 'R' is found broken, giving rise to textured appearance as shown in **Fig. 10(b1)**. For both DEC-C and DEC-D tail like structure nearby the vicinity of the hardener containing microcapsules is found. The tail like structure demonstrates crack blunting process around the microcapsules. On further magnification of this zone **(Fig. 10(a2))**, step like behaviour is observed highlighting the enhanced compatibility with epoxy network [**28**-**30**]. This may have formed due to discontinuity of the microcapsules in the crack path and out of plane divergence of the crack path in the interfacial zone. In case of DEC-D composites, enhanced step like featured as demonstrated in **Fig. 10(b2)** endorses complete equatorial fracture due to better compatibility of microcapsules present in epoxy network. This behaviour is suggestive for enhanced healing ability. Moreover, presence of healing zones (indicated by HZ) for DEC-D composite predicts high amount of epoxy and hardener release during fracture resulting in promotion of interfacial bonding in presence of crack. In brief, healing ability is found to be dominated by the behaviour of hardener containing microcapsule in dual encapsulated epoxy composites.

Conclusion

This study demonstrates the effectiveness of the TETA microcapsules to elevate healing performance of dual component self-healing composites. The size of the TETA microcapsules was found to decrease with increase in emulsifier concentration and agitation speed. The minimum size of the microcapsule was found as ~65.32 µm at 600 rpm and 1 wt.% of emulsifier concentration. The core content of the microcapsule was found increased with processing at high agitation speed. The maximum core content of hardener containing microcapsule was 16.5 wt. % at 600 rpm. The FTIR analysis revealed the successful encapsulation of both types of microcapsules. The variation in processing temperature showed significant impact on surface morphology of the TETA capsules. It was observed that, at higher processing temperature dimples are found and are busted leaving behind visible porosity throughout the surfaces of microcapsules. Tensile strength as well as fracture toughness behaviour reveals detrimental effect of microcapsule content on properties. The tensile stiffness of NE is observed as 1.16GPa which was decreased with incorporation of microcapsules. Low modulus shell material of hardener and epoxy microcapsules might have reduced the stiffness. Moreover, for DEC-C and DEC-D, reduced size of hardener containing microcapsule possibly restricts the epoxy chain mobility within the network under stress resulting in decreased strain. Maximum healing efficiency for DEC-D (7 wt. % microcapsule content) SENB specimen was found as 65.59%. The enhancement is largely attributed from the mechanistic study endorsing complete equatorial fracture due to better compatibility of microcapsules present in the epoxy network. In brief, we believe that optimal TETA microcapsule with respect to its size, core content and surface morphology significantly alters the healing efficiency of the dual component epoxy systems.

As an essential outcome, this study enables the identification of the important process parameters and their individual influence on the yield and quality of polymeric microcapsules carrying liquid healing agents for use in self-healing composites. The future scope of work would be to work on the synthesis and characterization of stable nanocapsules. The reason being unlike microcapsules, nanocapsules will not reduce the mechanical strength of the composites. Other scope would be to incorporate the microcapsules in fibre reinforced thermosetting or thermoplastic composites.

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Author's contributions

All the authors have made substantial contribution in conception and development of the composite, performing tests, interpretation of data and drafting the article. The Authors have no competing financial interests.

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