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Interfacial encapsulation of bio-based benzoxazines in epoxy shells for temperature triggered healing

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ABSTRACT: Successful application of interfacial engineering for the preparation of cross-linked epoxy microspheres containing thermally polymerizable cardanol-based benzoxazine (Bz-C) monomer in the core is demonstrated. Bz-C is facilely synthesized by Mannich type condensation of cardanol (a by-product of cashew nut industry) and aniline with formaldehyde under solventless conditions. **The encapsulation process relies on the preferential reaction of polydimethylsiloxane immiscible epoxy resin and amine-based hardener to form a cross-linked spherical shell at the interface.** The microcapsule dimensions and core content could be tailored by modulating the operating parameters, particularly stirring speed and Bz-C: epoxy ratio. Spherical microcapsules with a core content of ~37% were obtained when the reaction was carried out at 600 rpm, while maintaining the reaction medium at 70°C with Bz-C: epoxy ratio of 2.3 : 1. The simplicity and versatility of the present methodology are the forte of this technique, which widens the scope for large-scale application of benzoxazines in the field of temperature triggered healing. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42832.

KEYWORDS: differential scanning calorimetry; microscopy; ring-opening polymerization; surfaces and interfaces; thermal properties

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INTRODUCTION

Polybenzoxazines belong to a class of addition cure phenolic systems which possess excellent mechanical, thermal, and flame retardant properties. The flexibility in designing the structure of benzoxazine monomers allows enormous scope in tailoring the properties of polymers for a wide range of applications in the field of polymer technology.[1] In addition, polybenzoxazines exhibit high glass transition temperature (T_g), long shelf life, chemical resistance, low water absorption, release of no by-products which translates to negligible volumetric change upon curing. Most interestingly, benzoxazines do not require any catalyst for their curing, a feature which bestow them interesting candidature as far as healing agents in mendable compositions is concerned,[2] provided they can be encapsulated in fragile microcapsules.

Currently, conventional healing agents are restricted to a class of monomers which undergo catalytic ring opening polymerization, e.g., epoxy, dicyclopentadiene (DCPD), etc., which in turn are encapsulated in the polymeric shells of melamine–formaldehyde, urea–formaldehyde (UF), and gelatin-gum arabic coacervate.[3] Conformist micro-encapsulation procedures involve *in situ* emulsion polymerization of urea or melamine with formaldehyde on the surface of the hydrophobic dispersed phase of the precursor. The condensation process necessitate acidic environment (pH <3),[4,5] conditions which can induce curing in benzoxazines.[6,7] This imposes a restriction on the technique used for the encapsulation of benzoxazines in commonly used shell walls. To circumvent these issues, we have previously reported the encapsulation of benzoxazines in polystyrene shell with a core content of the order of 37%.[8]

In this article, we adopt an interfacial engineering approach to prepare epoxy microcapsules containing core of liquid benzoxazine. The potential of liquid–liquid interface toward the preparation of nanocrystals, thin films[9–11], and microcapsules[12,13] has been well reported. We believe that this concept could very well be extended to prepare microcapsules with interesting morphologies. Our aim is to elaborate this conceptually, and to elucidate this approach, we disperse epoxy–benzoxazine solution in silicone medium followed by addition of a polyamine which reacts selectively with the epoxy. In view of the preferential reaction of oxirane with amine, we engender that the reaction would be

Additional Supporting Information may be found in the online version of this article.

driven to the interface, leading to the formation of cross-linked spherical shell. We adopt a "sustainable" approach for the synthesis of cardanol-based benzoxazine (Bz-C),[14,15] where the role of cardanol is extended as a reactive diluent.[16]

Conventionally, liquid paraffin is used as a dispersing phase; however, the viscosity of liquid paraffin is not high enough to maintain system stability,[17] so rapid polymerization is needed to prevent the coagulation of the polymerization droplets.[18] Polydimethylsiloxane (PDMS) was chosen as the reaction medium in view of its thermal stability and solubility differences with both the resins as well as triethylenetetramine (TETA) hardener.[18] The effect of operating parameters, particularly rate of stirring and Bz-C: epoxy ratio on the microcapsule dimensions, was established to optimize the experimental conditions for the preparation of microcapsules.

EXPERIMENTAL

Materials

Cardanol was procured from Satya Cashew Chemicals Pvt. (India), paraformaldehyde (CDH, "LR"), sodium sulfate (CDH, "AR"), aniline (Merck, "AR"), and chloroform from Rankem. Cardanol used in the current work possess double bonds in the alkylene chain at the m-position, as monoene (25%), diene (40%), and triene (34%), and unidentified product (rest) as determined by high performance liquid chromatography (HPLC). Epoxy resin (Ciba Geigy, Araldite CY 230; epoxy equivalent 200 eq g^{-1}) and hardener (HY 951; amine content 32 eq kg^{-1}) were used as received. Double distilled water was used throughout the course of study. PDMS (CDH, kinematic viscosity 300 cSt) was used without any further purification.

Characterization

Thermo scientific fourier transform infrared (FTIR) (NICOLET 8700) analyzer with an attenuated total reflectance (ATR) crystal accessory was used to perform FTIR spectra of samples in the wavelength range 4000–600 cm^{-1}, recording 32 scans at 4 cm^{-1} resolution for each spectrum. The angle of incidence of the germanium ATR crystal used was characteristically 45°. Bruker AC 300 MHz fourier transform nuclear magnetic resonance (FT-NMR) spectrometer was used to record the ^{1}H-NMR of the samples. The spectrum was recorded in $CDCl_3$ using tetramethylsilane as the internal standard.

Thermal behavior was investigated using Perkin Elmer Diamond STG-DTA under N_2 atmosphere (flow rate = 50 mL min^{-1}) in the temperature range of 50–700°C. A heating rate of 10°C min^{-1} and sample mass of 5.0 ± 0.5 mg were used for each experiment. Calorimetric studies were performed on a differential scanning calorimeter (TA instruments Q 20). For dynamic differential scanning calorimetry (DSC) scans, samples (10 ± 2 mg) were sealed in aluminum pans, and heated from 0°C to 300°C at 10°C min^{-1}. Nitrogen was purged at a rate of 50 mL min^{-1} to minimize the oxidation of the sample during the curing process. Prior to the experiments, the instrument was calibrated for temperature and enthalpy using standard indium and zinc. Thermal equilibrium was regained within 1 min of sample insertion, and the exothermic reaction was considered to be complete when the recorder signal leveled off to the baseline. The total area under the exothermic curve was determined to quantify the heat of curing.

Optical images of suspended micro droplets were captured using an optical microscope Motic, B3-223PL. The surface morphology of samples was studied using a scanning electron microscope (Zeiss EVO MA15) under an acceleration voltage of 1 kV. Samples were mounted on aluminium stubs and sputter-coated with gold and palladium (10 nm) using a sputter coater (Quorum-SC7620) operating at 10–12 mA for 120 s. The microsphere size distribution was determined from the scanning electron microscope (SEM) images. Image J software was used to measure the diameter of 50 spheres per image.

Lap shear strength (LSS) of bonded joints on steel plates of roughness (R_a 0.42–0.51 μm) was measured in accordance with the American standard for testing and materials (ASTM) D1002 using Universal Testing System (International equipments) at a crosshead speed of 1.3 mm min^{-1}.

Preparation of Benzoxazine Monomers from Cardanol

The synthesis of benzoxazine monomer from cardanol has been reported in our previous papers.[16] In brief, a mixture of cardanol (100 g, 0.33 mol), aniline (30.1 mL, 0.33 mol), and paraformaldehyde (19.8 g, 0.66 mol) was slowly heated to 80°C and maintained for a period of 1 h under N_2 atmosphere. The mixture was further heated and maintained at 90°C for additional 2 h, after which it was cooled and 500 mL of water was added to the same. The organic layer was collected after extraction with chloroform. After drying over sodium sulphate and solvent removal under reduced pressure, the residue was dried at 70°C under vacuum to yield Bz-C in quantitative yield as red brown oil.

Microencapsulation of Cardanol Benzoxazine in Epoxy

Benzoxazine was encapsulated in cross-linked epoxy shell by the preferential reaction of epoxy resin with TETA hardener at the silicone–benzoxazine interface, while keeping the mixture suspended in silicone medium by agitation. The immiscibility of the benzoxazine and epoxy resin in PDMS was first verified by capturing the optical images using computer interfaced optical microscope at a magnification of 40 of the suspensions prepared by stirring the resins vigorously (1000 rpm) for a period of 5 min.

Subsequently, epoxy was first homogenized in Bz-C in varying ratio (2.3 : 1–1.0 : 1; 10 g). The reaction was performed in reaction vessel under inert atmosphere. Silicone oil (200 mL) was purged with nitrogen over a period of 15 min. The homogenized benzoxazine–epoxy mixture was introduced into silicone, which was maintained at 70°C under continuous stirring. Stoichiometric quantity of TETA (13% w/w epoxy) was subsequently injected slowly through a hypodermic syringe and the curing reaction was allowed to continue for 8 h under varying stirring speeds (500–700 rpm), after which the reaction mixture was cooled and filtered. Epoxy microspheres were also prepared in the absence of benzoxazines under similar conditions, while maintaining a constant temperature of 70°C and a stirring speed of 600 rpm. The core content of benzoxazine-filled microcapsules was quantified as per the procedure reported previously.[8]

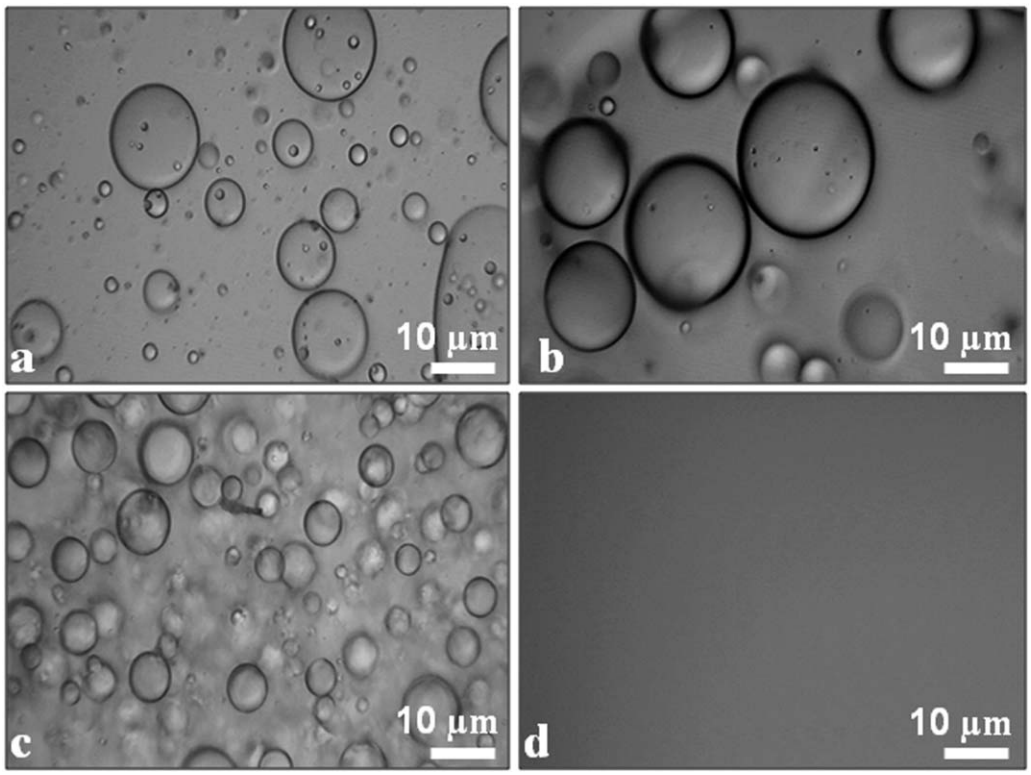

Figure 1. Optical images of (a) epoxy–PDMS, (b) epoxy–benzoxazine–PDMS mixtures, (c) benzoxazine–PDMS, and (d) epoxy–benzoxazine.

$$\text{Core content } (\%) = \frac{\Delta H_{\text{curing, encapsulated Bz-C}}}{\Delta H_{\text{curing, Bz-C}}} \times 100$$

where enthalpy of curing of neat Bz-C ($\Delta H_{\text{curing, Bz-C}}$) is 71.1 ± 1.8 J g^{-1}.

Determination of Adhesive Property of Microcapsules

To demonstrate the potential of the Bz-C encapsulated microcapsules in the context of temperature triggered healing, microcapsules (0.3 ± 0.01 g) with different core content were placed between two steel plates, crushed by manual tapping and placed at 216°C for a period of 1 h. A total of four replicates were tested per sample.

RESULTS AND DISCUSSION

The search for new synthetic methodologies in the context of benzoxazine microencapsulation has led us to explore the potential of interfacial engineering toward the formation of benzoxazine encapsulated epoxy microcapsules. More specifically, we studied the effect of operating parameters on the microcapsule dimensions and core content.

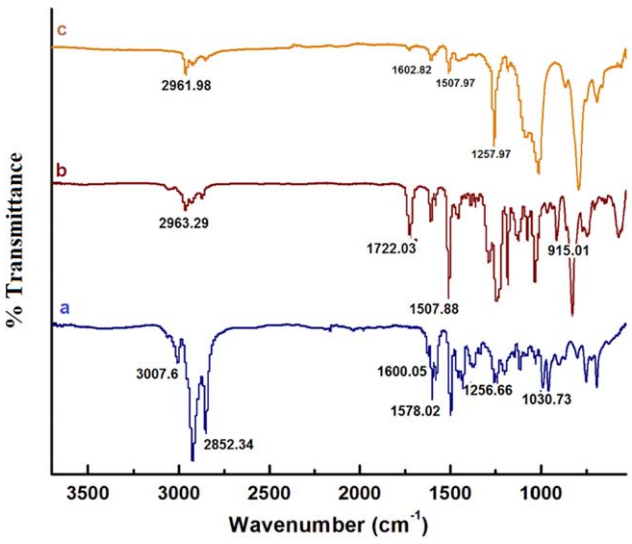

Figure 2. FTIR spectra of (a) Bz-C, (b) epoxy resin, and (c) microcapsules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

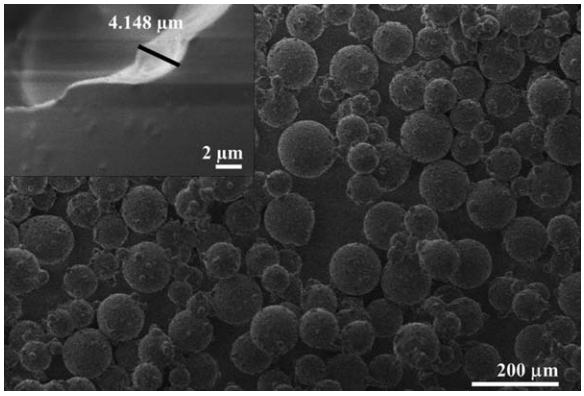

Figure 3. SEM image of Bz-C encapsulated in cross-linked epoxy shell. Inset shows the magnified image of a broken microcapsule indicating thickness of its shell wall.

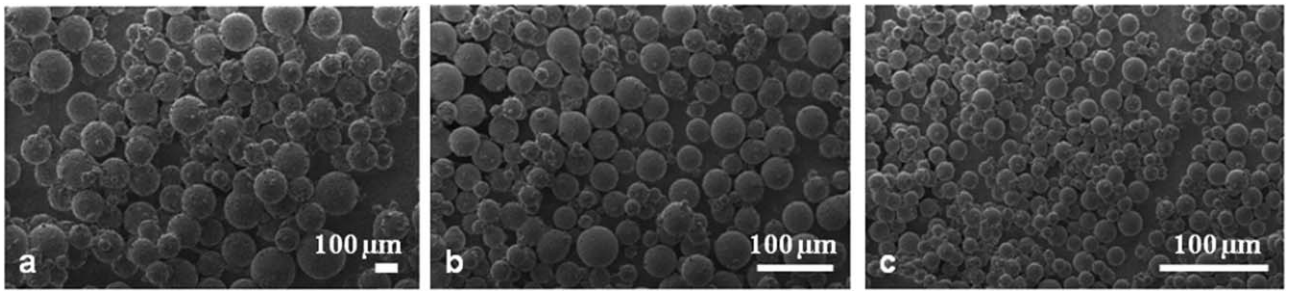

Figure 4. Effect of stirring speed on the surface morphology of microcapsules: (a) 500 rpm, (b) 600 rpm, and (c) 700 rpm.

Preparation of Cardanol-Based Benzoxazine

The synthesis of benzoxazine monomers is usually performed in the presence of polar aprotic solvents, which necessitate elaborate purification steps.[19,20] Solventless synthesis of rigid benzoxazine monomers result in extremely viscous mixtures, especially at higher conversions which in turn result in incomplete conversion of reactants leading to poor yields. A major advantage of using cardanol as the phenolic component is associated with its low viscosity (145 mPa s),[21] which permits its use as a reactive diluent. The reaction of aniline with cardanol and formaldehyde (1 : 1 : 2), post purification led to the formation of a viscous liquid in high yields (>90%). The structure of the monomers was confirmed by ^{1}H-NMR (Figure S1, Supporting Information) and FTIR spectroscopy (Figure S2, Supporting Information).

The formation of oxazine ring was confirmed by the appearance of new absorption bands at ~1250 and ~1030 cm^{-1} due to the Ar–C–O oxazine asymmetric and symmetric stretch, respectively.[22] The absence of absorption bands due to N–H stretching (3360–3442 cm^{-1}) and N–H bending (1619 cm^{-1}) in the spectra of Bz-C further suggests the absence of unreacted aniline in the Bz monomer, thereby indicating completion of the reaction. The formation of oxazines from hydroxyl functionalities was reconfirmed by the presence of characteristic resonances at ~5.3 ppm (s, $ArOCH_2N$) and ~4.6 ppm (s, $ArCH_2N$) in the ^{1}H-NMR spectra.

Microencapsulation of Cardanol-Based Benzoxazine in Cross-Linked Epoxy

The conventional *in situ* polymerization technique involves the formation of the encapsulating shell, essentially in the dispersion medium. For example, in the most commonly reported UF microencapsulation process, the monomers, namely urea and formaldehyde react in the aqueous phase to form a low molecular weight prepolymer. With increasing molecular weight of the prepolymer, deposition occurs at the healant–water interface and the cross-linking process continues to form the microcapsule shell wall.[4] The smooth inner surface of the shell basically results from the deposition of low molecular weight prepolymer at the interface while the prepolymer is still soluble. The roughness observed on the outer shell surface result from the precipitation of higher molecular weight prepolymer formed in the aqueous solution, which subsequently aggregate and deposit on the capsule surface.[23]

On the other hand, in the present study, epoxy microcapsules were prepared by the preferential reaction of the epoxy resin with TETA at the silicone–benzoxazine interface. The Hoy's solubility parameter of epoxy, TETA, and benzoxazine have been calculated based on the group contribution models of Hoy.[24] The structure of the resins and detailed calculations are presented in the Supporting Information. It can be seen that the solubility parameter of cycloaliphatic epoxy, benzoxazine, and TETA are in the same range, i.e., 9.02 $cal^{1/2}$ $cm^{3/2}$ mL^{-1}, 9.01 $cal^{1/2}$ $cm^{3/2}$ mL^{-1} and 10.8 $cal^{1/2}$ $cm^{3/2}$ mL^{-1}, respectively. It was not possible to ascertain the Hoys parameter for PDMS in view of its inorganic–organic hybrid nature; however, the Hansen solubility parameter of TETA (22.7 $MPa^{1/2}$)[22] is markedly higher than that of PDMS (14.9 $MPa^{1/2}$).[7,25] This difference in miscibility results in their existence as phase separated droplets under agitation. To verify the same, the optical images of epoxy–PDMS, benzoxazine–PDMS, and epoxy–benzoxazine–PDMS mixtures were captured, where the presence of droplets in the medium is clearly indicative of its immiscibility (Figure 1).

Preliminary studies were performed to arrive at the optimal reaction conditions, especially reaction time and temperature. For successful encapsulation, the rate of reaction between the epoxy and amine should exceed the rate of molecular diffusion.[26] The reaction condition should be tuned so as to allow the curing process to proceed at the reactive interface till complete exhaustion of the epoxy and amine, thereby leading to the formation of a stable cross-linked shell around the unreacted benzoxazine core. The curing behavior of the cycloaliphatic epoxy resin in the presence of TETA, as established using nonisothermal calorimetry, is presented in the Supporting Information (Figure S3).[27] It can be seen that the exothermic curing process initiates at ~61°C and reaches a peak at ~96°C. On the basis of this curing profile,

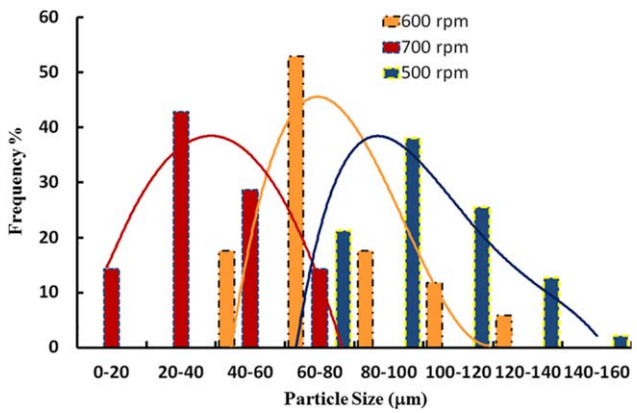

Figure 5. Effect of stirring speed on the average particle size distribution of microcapsules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

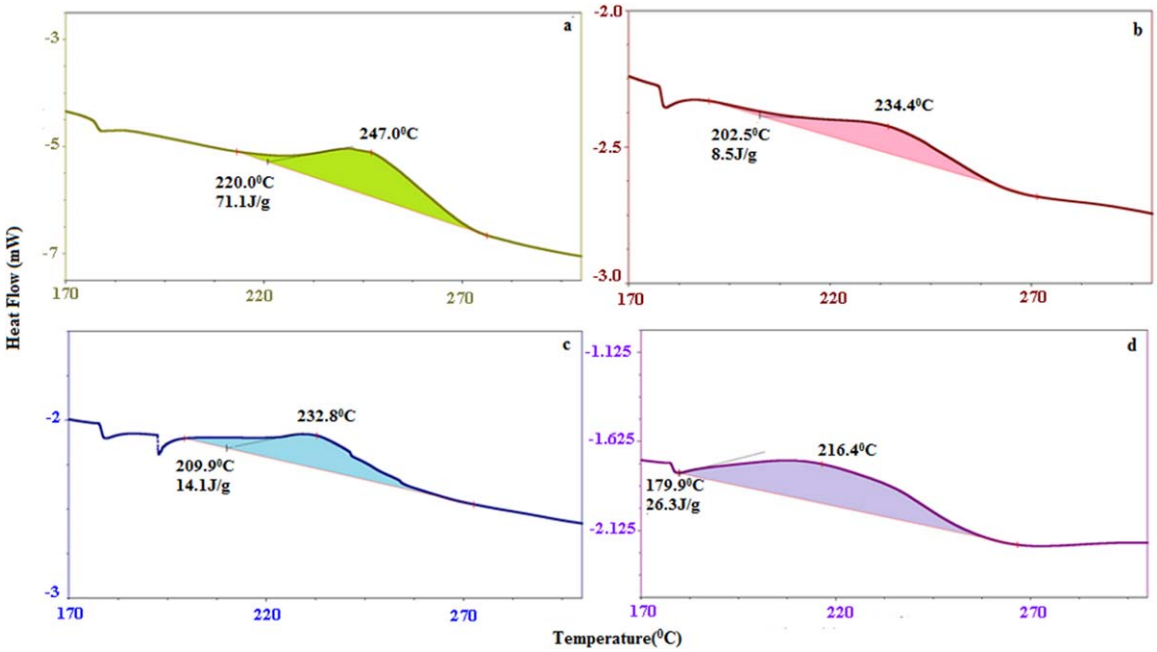

Figure 6. DSC traces of (a) Bz-C and epoxy encapsulated benzoxazine microcapsules prepared using Bz-C: Epoxy ratio of (b) 1 : 1, (c) 1.5 : 1, and (d) 2.3 : 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

studies on encapsulation were performed at temperatures as low as 60°C. However, when the reaction medium was maintained at T <65°C, complete curing necessitated prolonged periods (~36 h), which was too long to be of any practical significance. The rate of the curing reaction increased significantly with increasing temperature and free flowing microcapsules could be obtained within 10 h at 70°C. Further increase in temperature was impractical in view of the strong vapor pressure–temperature dependence of TETA,[28] which led to significant vaporization of the amine, thereby leading to the formation of partially cured and tacky microcapsules. In view of the above, the effects of other operating parameters were performed while maintaining the reaction medium at 70°C.

The FTIR of benzoxazine monomer, epoxy resin, and cured microcapsules is presented in Figure 2. Characteristic band at 915 cm^{-1} associated with the CO deformation due to oxirane ring is visible in the FTIR spectra of liquid epoxy resin.[29] The absence of this absorption and the peaks confirming the structure of benzoxazine in the FTIR spectra of microcapsules indicates successful encapsulation of the benzoxazine monomer in cross-linked epoxy shell.

Effect of Stirring Speed on Particle Size Distribution and Morphology

Bz-C was encapsulated in interfacially engineered cross-linked epoxy shell to form microcapsules, pale yellow in color (Figure S4), the SEM images of a representative batch being presented in Figure 3. The thickness of the shell wall was found to be ~4.1 μm, as can be seen in the SEM images of broken microcapsules (Figure 3, Inset).

The SEM images of the microcapsules prepared under varying stirring speeds are presented in Figure 4 and the related average particle size distribution is presented in Figure 5. It is interesting to note that the high viscosity of the silicone oil employed for the purpose is proficient in stabilizing the suspended epoxy–Bz-C micro-droplets, thereby abating the necessity of a suspending agent.[18] As expected, increasing the rate of stirring led to a shift in the average particle size toward lower dimensions, which could be attributed to the extensive shearing of the large oily droplets into smaller microspheres. Among the experimental parameters: agitation rate, temperature, surfactant type and concentration, hydrodynamics, viscosity, and interfacial tension of the media are primary influential parameters on the microcapsule dimension. Stirring speed, particularly, defines the equilibrium between shear forces and interfacial tension of the discrete oil droplets.[30] It was observed that free flowing microcapsules could not be obtained upon lowering the stirring speeds to <500 rpm (SEM image presented in Supporting Information Figure S5). Increasing the stirring speed to >700 rpm is expected to lead to the formation of microcapsules of significantly lower dimensions to be of any practical value. Under optimal reactions conditions, i.e., stirring speed of 600 rpm, reaction temperature of 70°C and Bz-C: (2.3 : 1), spherical microcapsules were obtained.

Core Content

Core content refers to a quantitative estimate of the polymerizable fraction actually available in the microcapsules, which in

Table I. Effect of Bz-C: Epoxy Ratio on the Core Content of Microcapsules

Bz-C: Epoxy ratio (% w/w)	ΔH_{curing} (J/g)	Core content (%)
1 : 1	8.5	11.9
1.5 : 1	14.1	19.8
2.33 : 1	26.3	37.0

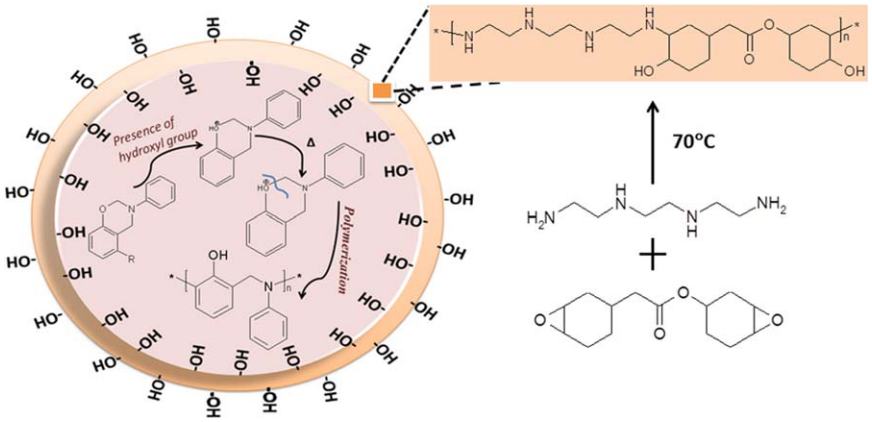

Figure 7. Interaction of hydroxyl groups on the inner surface with the encapsulated benzoxazine. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the present context was quantified as the ratio of heat of curing of encapsulated benzoxazine to that of the neat monomer.[8] In view of the ring strain associated with oxazine ring, Bz-C polymerizes through thermally activated ring opening polymerization and the DSC traces obtained during controlled heating are presented in Figure 6. The DSC trace of cured epoxy microsphere prepared in the absence of benzoxazine has been presented in the Supporting Information (Figure S6). As expected, the exotherm associated with the curing of benzoxazine cannot be observed in the DSC trace. The core content of the benzoxazine-filled microcapsule increased from 12% to 37% as the weight fraction of epoxy in the feed solution was lowered from 50% to 30% w/w while maintaining a constant stirring speed of 600 rpm (Table I).

Although attaining larger core content is a vital target of any encapsulation process, it was not possible to increase the core content further, probably due to high surface energy of microcapsules, which led to their agglomeration on increasing the benzoxazine content in the feed.[25] It was interesting to observe a lowering in the onset of curing behavior as the composition of the feed solution (Epoxy: Bz-C) was varied from 1 : 1 to 2.33 : 1. To gain further insight into this aspect, benzoxazine curing was also studied in the presence of liquid epoxy resin. Interestingly, the curing exotherm was found to shift to higher temperature, as shown in the Supporting Information (Figure S7). These studies confirm that the lowering of curing temperature in the present study could be credited to the interaction of Bz-C monomer with hydroxyl functionalities, which in turn resulted due to the nucleophilic attack of amine on oxirane rings of epoxy resin as per the reaction depicted in Figure 7. Acidic functionalities[31] along with allylic[32] and methylol[33], etc., reportedly play an active role in catalyzing the polymerization of benzoxazines. Our studies indicate that aliphatic alcohols, although less acidic, are also capable of lowering of T_{onset} temperature of Bz-C (T_{onset} = 220°C) substantially to 179°C.

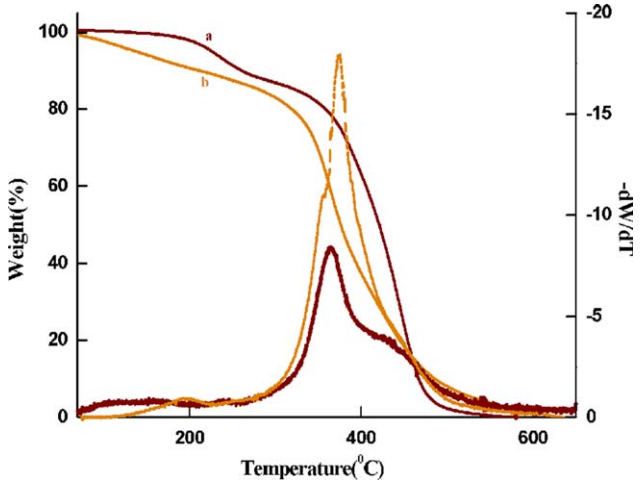

Figure 8. TGA traces of (a) Bz-C encapsulated epoxy microcapsules and (b) Bz-C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TG-DTG traces of Bz-C, both before and after encapsulation in epoxy shells under air atmosphere, are presented in the Figure 8. It can be seen that the polybenzoxazine, formed as a result of temperature-induced curing, undergoes oxidative degradation at 310°C. Encapsulation of benzoxazine in epoxy shell led to a substantial decrease in the curing temperature to 179°C (Figure 6); however, the onset degradation temperature remained practically unaltered.

Adhesive Property of Microcapsules

The adhesive ability of the microcapsules encapsulating benzoxazine was quantified by evaluating the LSS using stainless steel coupons. Cardanol-based benzoxazines have been reported to exhibit LSS of 20–30 kg cm^{-2} at 150°C, which advocate their caliber as healing monomers in mendable compositions.[34] The average values of LSS exhibited by the samples are tabulated in Table II and the representative load–displacement curve is presented in Supplementary Section (Figure S8).

Table II. Lap Shear Strength of Microcapsules with Different Core Content

Bz-C: Epoxy ratio (% w/w)	Core content (%)	LSS (kg cm^{-2})
1 : 1	11.9	13.5 ± 1.9
1.5 : 1	19.8	16.0 ± 2.6
2.33 : 1	37.0	25.3 ± 3.2

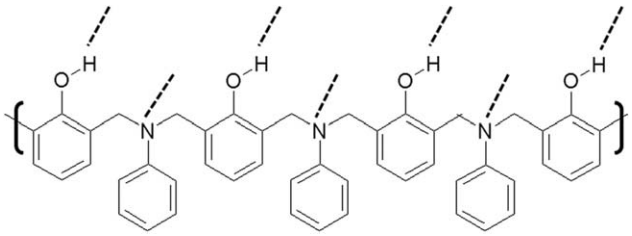

Figure 9. Functional groups in polybenzoxazine involved in H-bonding with the contact surface.

Subsequent to the curing of the Bz-C released from the microcapsules, the plates could not be separated by exposure to solvents like dimethyl formamide (DMF) and toluene, even for extended periods (72 h).The curing of Bz-C by thermally activated ring opening polymerization results in the formation of >N– and –OH functionalities as confirmed by FTIR spectroscopy [Figure S2(c)], which are capable of exhibiting extensive H-bonding with the contact surface as shown in Figure 9, thereby rendering excellent adhesive properties.

Photographs, captured at different stages of the experimentation, are presented in the Supporting Information for clear visualization (Figure S9).

CONCLUSION

The implementation of interfacial engineering for encapsulation of benzoxazine enabled the preparation of cross-linked epoxy microcapsules containing reactive monomer in the core. Reaction parameters, especially benzoxazine: epoxy ratio and stirring speed, were found to have a pronounced effect on the core content and particle size distribution of the microspheres. Under optimal conditions, i.e., stirring speed of 600 rpm, reaction temperature of 70°C, and Bz-C: Epoxyratio of 2.33: 1, spherical microcapsules were obtained with a core content of 37%. The presence of hydroxyl groups formed as a result of epoxy curing was found to reduce the onset of curing temperature from 220°C to 179°C. We believe that in view of the enormous scope in modifying the structure of benzoxazines, low temperature self-healing systems can be devised in the future, which can open up novel opportunities in this field.

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