



Development of self-healing coatings based on urea-formaldehyde/polyurethane microcapsules containing epoxy resin

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Abstract

In this study, the synthesis of urea-formaldehyde/polyurethane (UF/PU) microcapsules containing epoxy resin for self-healing and anti-corrosion coatings with good stability has been reported. Spherical microcapsules were prepared with a diameter of about 50–720 μm and a shell thickness of 0.6–0.7 μm via in situ polymerization in an oil-in-water emulsion using 2,4-toluene diisocyanate-based pre-polymer along with the urea-formaldehyde. Scanning electron microscopy (SEM) and optical microscopy (OM) were employed to evaluate the shape and morphology of the microcapsules. Fourier transform infrared (FTIR) spectroscopy showed the absence of free isocyanate groups within the microcapsule shell confirming the completion of shell formation reactions. OM illustrated that the microcapsules were stable over a period of 30-days in toluene and xylene. Increasing microcapsule loading improved crack repairing and anti-corrosion performance of the coating layer. Low-carbon steel coupons coated with an epoxy resin containing 10 wt% microcapsules and scribed using a scalpel blade showed no visible sign of corrosion after up to 5 weeks of exposure in a standard salt spray test chamber.

KEYWORDS

applications, coatings, microscopy, spectroscopy, thermogravimetric analysis (TGA)

1 | INTRODUCTION

In the last decade, various autonomous self-repairing systems have been developed and used in a wide range of applications in aerospace, automobile, nutraceutical, pharmaceutical, food packaging, and biomedical industries.^{1–10} Self-healing materials are a group of intelligent compounds that are structurally capable of spontaneously repairing damaged areas during their service life¹¹ or production.^{4,12} Self-healing systems may be classified into intrinsic and extrinsic. An intrinsic self-repairing system requires no external healing agent while

in an extrinsic system a healing agent is loaded inside a micro-carrier, such as a vascular network, a hollow fiber or a microcapsule.¹³

Numerous microcapsule-embedded self-healing materials have been reported in the literature including those containing DCPD/Grubbs catalyst,^{14,15} epoxy/mercaptan,¹⁶ oil-soluble solvents and reactive epoxy resins in polymeric, polyaniline hollow microspheres,¹⁷ urea-formaldehyde (UF) shell,^{18,19} one-component isocyanate-based system.^{13,20,21} For instance, in the study reported by Cho et al.,²³ polydimethylsiloxane (HOPDMS) was utilized as a repairing agent dispersed in

vinyl ester system and, di-*n*-butyl-tin dilaurate (DBTL), as the catalyst was microencapsulated in polyurethane shell. In 2019, Jin et al.²⁴ reported the preparation of functional microcapsules with the thermally expandable shell of acrylonitrile (AN) with methyl methacrylate copolymer or AN-methacrylate copolymer containing a mixture of *N,N*-dimethylbenzylamine, and liquid hydrocarbons. The microcapsules were implemented into an epoxy resin and the catalyst was released from the ruptured microcapsule shells at the elevated temperature. By changing the amount of catalyst and liquid hydrocarbons, authors were able to control the curing time and temperature of the resin. Wang et al.,²⁵ studied the effect of synthesis conditions including core:shell ratio, mixing rate, reaction time, and the type of emulsifier on physical properties of poly(urea-formaldehyde) microcapsules (PUF) containing epoxy.

In self-healing systems that use microcapsule-embedded epoxy resin, hardener could be either encapsulated or dispersed in the polymer matrix.²⁶ However, it should be noted that one of the most significant concerns in the application of microencapsulated materials is the stiffness of the microcapsule shell and its durability to withstand against the rupturing due to the internal and external stresses during the microcapsule preparation process and throughout the dispersion into the polymeric matrix.^{5,11} Yuan et al.²⁷ reported the synthesis of epoxy resin-filled PUF microcapsules by evaluation of various process parameters such as type and concentration of surfactant, pH, heating rate and microencapsulation time. However, the PUF microcapsule shell was usually porous that caused the reduced stability of microcapsules both during the storage and after dispersion in the polymeric matrix. Li et al.²⁸ reported the preparation of polymethyl methacrylate (PMMA)-based microcapsules via solvent evaporation route using a dual epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) and polyether amine (hardener) via water-oil-water emulsion. A nanoencapsulated amine-based corrosion inhibitor prepared via a multi-stage emulsion polymerization has been also reported in the literature.²⁹ Others³⁰ reported the preparation of a self-repairing epoxy-based system using microencapsulation of a modified aliphatic polyamine (Epikure 3274) via vacuum infiltration into hollow PUF capsules. Diluted epoxy resin (Epon 815C) was also microencapsulated in PUF microcapsules via in situ polymerization. A self-healing epoxy coating containing polyurea (PU) microcapsules comprising ethylenediamine (EDA) core material has been also reported.³¹ Authors claimed that coated samples containing 5 wt% EDA/PU microcapsules exhibited corrosion resistance efficiencies up to 90%.

Recently, Tzavidi et al.,²⁶ reported the preparation of self-healing coatings containing epoxy resin filled PUF-based microcapsules. The group argued that the process

variables affected the size and morphology of microcapsules and did not significantly influence the efficiency of the microencapsulation process. Wang et al.,³² reported the preparation of ethyl cellulose (EC)-based microcapsules comprising epoxy resin via the solvent evaporation method. It was revealed that due to the evaporation of dichloromethane solvent, the holes were formed on the EC's shell. The size and amount of holes on the microcapsules' shell were influenced by the viscosity grade of EC.

Although PUF microcapsules can be prepared using a robust well-established synthesis procedure from the relatively low cost of raw materials,^{13,20} they have found limited utility in self-healing applications due to the high porosity of the microcapsule shell that leads to the release of the core material and hence reduces the stability and shelf life of microcapsules particularly in the solvent-based systems. A strategy to address this issue is the preparation of two-component microcapsule shells.^{1,33}

In this study, for the first time the synthesis of urea-formaldehyde/polyurethane microcapsules containing epoxy resin for self-healing and anti-corrosion coatings with good stability is reported. Epoxy resins are among the most important core materials in self-healing coatings due to their ability to react with a wide range of hardeners at different temperatures.³⁴ As a principle, better miscibility between the healing agents and the epoxy-based coating is expected. Therefore, in this study, reactive epoxy resin was used as a core material for microencapsulation. Epoxy resin with the minimum level of BA solvent (either 10 or 30 wt%) was initially microencapsulated with urea-formaldehyde and then the shell was reinforced using TDI-based pre-polymer in a non-toxicity solvent. These microcapsules exhibited extended durability while dispersed in the coating formulation. Several techniques such as optical microscopy, SEM, Fourier transform infrared (FTIR) spectroscopy, particle size analysis (PSA), thermogravimetric analysis (TGA) were utilized to characterize the synthesized microcapsules. The effect of microcapsule addition on the repair mechanism and anti-corrosion performance of an epoxy-based coating was also evaluated using SEM study and standard salt spray test.

2 | EXPERIMENTAL

2.1 | Materials

Epoxy resin based on diglycidyl ether of bisphenol A (DGEBA), KER 828, with epoxy group content of 5,260–5,420 mmol/kg and molar mass of 184–190 g, and its amide-based hardener, Crayamid 140C, with an amine

value of 370–410 mg KOH g⁻¹ were supplied by KUMHO P&B Chemicals Inc. and Cray Valley, respectively. Gum Arabic (GA) as an emulsifier, 1,4-butanediol (BD), *n*-butyl acetate solvent (BA), urea, resorcinol, ammonium chloride, and formaldehyde were analytical grade and obtained from Merck Industrial Group. 2,4-toluene diisocyanate (TDI) was provided by Sigma Aldrich. Hydroxy-terminated polyester resin, Tacryl 352N, and its isocyanate-based crosslinking agent, Desmodur N 75 MPA/X were provided by TAAK Resin Co, (Iran) and Covestro AG, (Germany), respectively. Low carbon steel coupons (Q-panel size) were supplied from supplied by local producers.

2.2 | Synthesis and characterization of PU-based pre-polymer

26.3 g TDI was dissolved in 141.7 g BA under magnetic agitation and N₂ gas purging for 5 min at 50°C in a 2-necked glass vessel. The solution container was immersed in a temperature-controlled oil bath and the temperature was raised to 50°C by a controllable heater device. Then, BD (3.2 g) was slowly added to the solution under magnetic stirring and N₂ purging for removing air moisture.²⁰ After 20 min, the vessel was sealed with parafilm (BemisNA Co.) and the mixture was continuously agitated for further 36 h. The NCO content of the reaction product was measured frequently until achieving the desired theoretical value of ≈20%.²⁰

Synthesized pre-polymer (PPU) was characterized by measuring free NCO groups according to ASTM D2572-10 test practice. The initial NCO content of TDI was determined as 48.2% according to³⁵:

$$\text{NCO}_i\% = \frac{2(M_{W_{\text{NCO}}})}{M_{W_{\text{TDI}}}} \times 100 \quad (1)$$

where NCO_i, M_{W_{NCO}}, and M_{W_{TDI}} are initial NCO content, the molecular weight of NCO, and molecular weight of TDI, respectively.

NCO value represents the abundance of isocyanate groups in the pre-polymer structure and hence the reactivity of the pre-polymer compound that could be obtained from:

$$\text{NCO}\% = \frac{0.042N(B-V)}{W} \times 100 \quad (2)$$

where *B* (ml) and *V* (ml) stand for consumed hydrochloric acid volume for titration of the blank and the PPU samples, respectively. *N* is the normality of hydrochloric acid, *W* (g) shows the sample weight and

the conversion factor (0.0420) represents the milliequivalent weight of the isocyanate group.²¹

2.3 | Preparation and characterization of UF/PU microcapsules

The interfacial polymerization method was used to synthesize UF/PU-based microcapsules.^{1,27} For this purpose, in the first step, 13.5 g GA was dissolved in 120 ml deionized water for about 3 h. Then 0.25 g resorcinol, 2.5 g urea, and 0.25 g ammonium chloride were added to the reaction vessel under mechanical mixing (Heidolph RZR 2120) at a mixing rate of 300 rpm. The pH of the mixture was adjusted at 3.5 by adding a few drops of HCl solution (0.1 N). To prepare microcapsules with low BA content, in the second step, 10 g of PPU diluted with 60 wt% of BA (6.67 g) was added to 27 g epoxy resin and 3 g BA and mechanically stirred to obtain a homogeneous solution. The resultant solution was then added drop wise to the abovementioned GA solution under either 500 or 700 rpm mixing speeds. About 10 min later, 6.32 g formaldehyde solution (37%) was added drop-by-drop to the suspension to stabilize the emulsion. The reaction temperature was elevated up to 55 ± 1°C at 1°C/min and the reaction was continued for further 3 h.^{1,34} After cooling the solution to the ambient temperature, microcapsule suspension was rinsed several times with plenty of distilled water. In the end, synthesized capsules were dried using a freeze dryer instrument (Dena Vacuum Industry Co. Iran) at -45 ± 5°C and 10 ± 2 m Pa. To examine the effect of the solvent content of the core material, additional microcapsules were prepared following a similar procedure, however; using epoxy with 30 wt% BA content. For simplicity, microcapsules prepared using epoxy with 10 and 30 wt% BA are denoted by M10 and M30, respectively, in this manuscript. Initial core:shell ratio (mass balance) was considered as 79.2:20.8 weight ratio for both microcapsules synthesized at mixing speeds of 500 and 700 rpm.

The microencapsulation yield was determined by dividing the weight of resultant capsules to the weight of initially used materials.^{1,13,36} The average yield of synthesized microcapsules was calculated as 63 ± 2.5%. The core:shell ratio of the microcapsules prepared at mixing speed of 700 rpm was determined using solvent extraction method.⁴ For this purpose, about 0.2 g of microcapsules were dispersed into 20 ml BA and sonicated using an ultrasonic bath (Model HD3200, KE-76 probe, Bandelin) for 2 × 10 min. The shell material was then filtered using a filter paper, rinsed several times with BA, and dried in an oven at 50°C for 2 h. The weight of the

core material was obtained by subtracting the weight of the shell, and thus the core:shell ratio was calculated.

2.4 | Determining epoxy equivalent weight of encapsulated epoxy resin

The epoxy equivalent weight (EEW) for the neat and extracted resin from the microcapsules was determined according to GOST 12497-78 (equal to ASTM D1652-11 test practice). For this purpose, 2 g prepared microcapsule was poured into 4 ml BA and sonicated for 15 min using a sonication probe (Bandelin, HD3200, KF-76 probe, 70 W). The microcapsule shell was separated from the dispersion using a filter paper.

Blank solutions were prepared by adding 2.8 ml HCl 37% to 140 ml acetone. Four drops of methylene red as indicator were added to 25 ml of a mixture of HCl and acetone. Titration was carried out using NaOH (0.1 N) solution until obtaining a yellowish solution. The consumed volume of NaOH was recorded. The process was repeated for the neat epoxy sample (0.3 g). The EEW was calculated using³⁷:

$$EEW = \frac{1000W}{N(V_{\text{Blank}} - V_{\text{Sample}})} \quad (3)$$

where N stands for NaOH normality, W is the weight of the epoxy resin (g), V_{Blank} and V_{Sample} represent the volume of used NaOH for titration for blank and sample, respectively. EEW measurements were carried out in triplicate and the mean value was quoted.

2.5 | Evaluation of microcapsule stability

The stability of microcapsules was evaluated during a period of 30 days immersion in toluene and xylene solvents. For this purpose, 1 g of microcapsules synthesized at mixing speed of 700 rpm was dispersed in 5 ml solvent and the stability of the microcapsules in the solvent was investigated using an optical microscope.

2.6 | Healing property and anti-corrosion performance of the samples

The repairing property and corrosion resistance of epoxy coating samples containing various levels of microcapsules (0, 1, 3, 5, 10, and 20 wt%) were studied. Various wt % of capsules were slowly loaded into the epoxy resin under magnetically mixing at a speed of 150 rpm for 15 min. The samples were placed in a vacuum oven for

about 10 min to remove trapped air bubbles. The hardener was loaded to the coating samples with a resin:hardener weight ratio of 100:58, stirred for further 5 min. The samples were applied on the degreased low-carbon steel plates (75 mm × 150 mm) using a film applicator (Model 352, ERICHSEN Co.) with a wet coating thickness of $500 \pm 20 \mu\text{m}$. The samples were then left to cure in ambient temperature for about 48 h.

The healing properties of coatings were investigated by creating a scribe line with a 2 cm length on the coated specimen using a No. 11 scalpel blade. The scratched area was then evaluated 48 h later using SEM microscopy.

For evaluation of corrosion resistance of the samples, an X shape scratch lines with about 4 cm length each was created on the coated samples using a scalpel blade (No. 11) and kept at room temperature for 1 day. The edges and back of the sample were coated with hot-melt mixture of beeswax and colophony resin. The coated low-carbon steel samples were exposed to salt spray for 7 weeks in a standard salt spray test chamber (S75-V109, Pars Horm Co.) according to ASTM B117 standard method using a 5 wt% NaCl solution at $35 \pm 1^\circ\text{C}$.⁵ The scribed regions were evaluated for any sign of rust and corrosion product every week time interval.

In order to evaluate the influence of polymeric matrix type on the curing behavior of the released core materials, 5 wt% microcapsules were separately dispersed into the epoxy and polyurethane resins under magnetically stirring. After removing trapped air bubbles, the required hardener was added to the mixtures, mixed for an additional 5 min. The coating samples were then applied on a PVDF substrate using the ERICHSEN doctor blade film applicator with a wet film thickness of $500 \pm 20 \mu\text{m}$. After 48 h at ambient temperature, the samples were separated from the PVDF substrate and immersed in liquid nitrogen. The films were broken and then left in ambient temperature to cure for about 48 h. The cross-section of the samples was evaluated by means of SEM micrographic.

2.7 | Analytical methods and microscopy

FTIR spectroscopy of PPU was carried out using an FTIR spectrophotometer (Bruker EQUINOX IFS48, Ettlingen, Germany), in KBr pellet, collecting 16 scans in the range of $400\text{--}4,000 \text{ cm}^{-1}$ with 4 cm^{-1} resolution. FTIR spectroscopy was also employed to study the structure of microcapsule (shell and core).

The molecular weight of PPU was determined by means of gel permeation chromatography (GPC) technique according to ASTM 6579-11 test practice by means of an Agilent GPC 1100 equipped with IR-detector.

The microcapsule size and size distribution were determined using PSA device, AZM 110 CILAS, in wet mode. For this purpose, 1 g microcapsule was dispersed in 200 ml distilled water under magnetic agitation for about 10 min and then the dispersion was located in the sample holder for the PSA measurement. The test was carried out in triplicates and the mean values were quoted.

Thermal behavior of synthesized capsules prepared at mixing speed of 700 rpm was evaluated by means of the TGA (PL-1500, from Polymer Labs). TGA was carried out from the room temperature to 600°C at a heating rate of 10°C/min under N₂ atmosphere. The thermal behavior of the microcapsules was evaluated every month, up to 6 months after synthesis. Since the changes in the thermal behavior of the monthly tested samples were not significant, therefore; merely the TGA thermographs of the fresh and 5 months aged microcapsules are presented. The core:shell ratio of the fresh and 5 months aged (at ambient conditions) microcapsules were calculated from TGA thermographs.

The reactivity of microencapsulated epoxy resin was evaluated using Differential Scanning Calorimetry (DSC) technique (Netzsch, model 200-F3 Maia, Germany, temperature variety of -25 to 350°C).

Formation, shape, morphology, and stability of microcapsules were evaluated with an optical microscope (ZEISS Stemi 305) equipped with an Axiocam ERc 5s digital camera and, with scanning electron microscopy (SEM), Vega-TESCAN, operated in the secondary electron mode at 20 kV. In addition, SEM micrographs were used to determine the shell thickness of the capsules and to assess the reactivity of epoxy filled microcapsules embedded in a coating comprising pre-dispersed amine hardener. Crack filling property of microcapsule-embedded epoxy-based coating samples was also studied utilizing SEM micrographs by examining the scratched area was after evaluated 48 h.

3 | RESULTS AND DISCUSSION

3.1 | Pre-polymer characterization

Using Equation (2), the NCO content of PPU was estimated to be $21.7 \pm 3.2\%$ after 36 h reaction in BA. Furthermore, based on GPC analysis, the arithmetic and weighted average M_w for PPU were 1,034.4 and 1,201.3 g/mol, respectively, and the number of repeated units (n) was determined as 1.16. These values are significantly higher than our previous report,²⁰ where the arithmetic and weighted average M_w were 697.6 and 816.3 g/mol for the synthesized PPU.

In comparison, using cyclohexane (CH) as the core solvent, Yang et al.³⁸ reported an NCO content of 20.1 ± 0.6 wt% after 24 h, with the arithmetic M_w , weighted average M_w , and the number of repeated units for the synthesized PPU being 1,270 g/mole, 1,690 g/mole, and 3.152, respectively.³⁸ The lower reaction time and higher M_w of PPU in this case could be explained based on the differences in the solubility of TDI and BD in BA versus CH.²⁰ The lower NCO content of PPU in the presence of CH further corroborates these results, indicating the improved reaction between diol groups of BD and diisocyanate of TDI which leads to an increase in the M_w of synthesized PPU. Higher M_w of the pre-polymer is desirable since it results in a higher M_w and hence enhanced mechanical properties of the microcapsule shell material.¹⁸ This is an important consideration as the microcapsules shell should be strong enough to protect core materials from premature release.^{20,21,38} However, the effect of higher M_w on the viscosity of pre-polymer, the rate of polymerization (upon formaldehyde addition), and crosslinking density of the final product should also be considered.

It should be noted that although using BA as solvent resulted in a lower M_w and a higher NCO% for the synthesized PPU compared to CH, CH is suspected human carcinogenesis.³⁹ In comparison, BA has low systemic toxicity and can be irritating only after prolonged skin contact.

3.2 | Shape, morphology, size, and size distribution of synthesized capsules

The shape and morphology of the synthesized capsules were evaluated utilizing optical microscopy and SEM micrographs. Figure 1 shows optical microscopic images of microcapsules prepared at mixing speeds of 500 and 700 rpm, containing epoxy resin diluted with 10 wt% BA solvent (M10). These images reveal that the capsules were poly-dispersed and spherical with no inter-capsule bonding. No noticeable air voids within the capsules were detected, indicating that the epoxy resin was well-encapsulated by the shell compounds.²⁰ As the mixing speed increases, the shear force applied by the mixing increases, resulting in a reduction in the size of the droplets (core material). Therefore, in the microencapsulation process, the microcapsule shell is formed around the smaller droplets and subsequently the size of the final microcapsules is reduced. Viscosity, core:shell ratio, miscibility with shell compound, surface tension, and the microencapsulating method are the main parameters that are expected to affect the size and surface morphology of microcapsules.²⁰

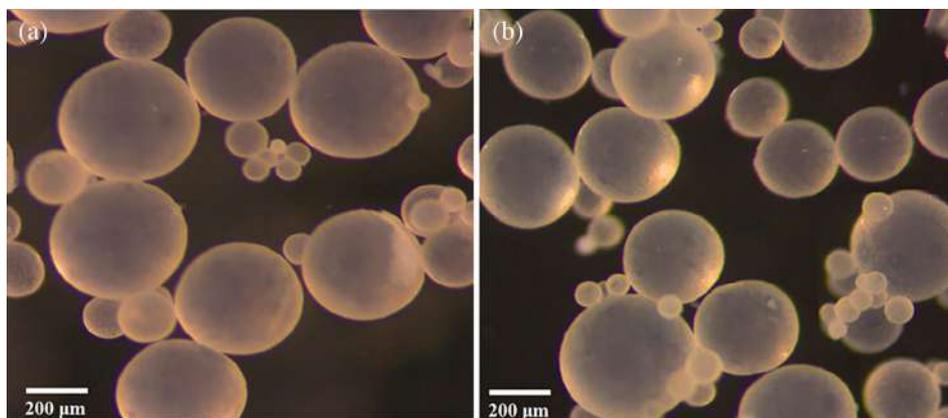


FIGURE 1 Optical images of M10 microcapsules prepared at (a) 500 rpm and (b) 700 rpm [Color figure can be viewed at wileyonlinelibrary.com]

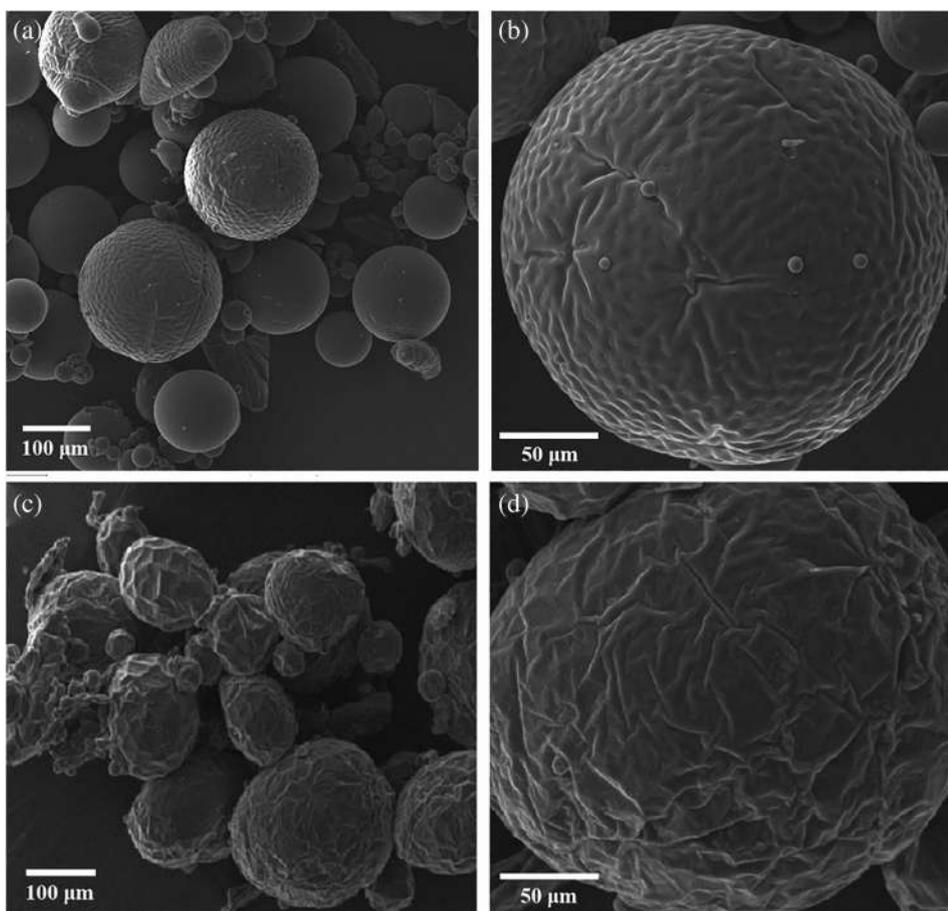


FIGURE 2 SEM micrographs of M10 (a and b) and M30 (c and d) microcapsules

Figure 2 shows SEM micrographs of UF/PU-based microcapsules filled with epoxy resin diluted with 10 and 30 wt% BA solvent (since PPU also contained 60 wt% BA, the final BA wt% in the core material was more than these values). According to SEM micrographs, with increasing the BA wt% (which is used for decreasing viscosity of the core materials), the extent to which microcapsule's shell was wrinkled also increased. The wrinkling of the microcapsule shell occurred likely due to the leakage of solvent from the core of the microcapsules (M10 and M30) during the microcapsule drying

process that increased surface-to-volume ratio of microcapsules.⁴⁰ This effect is pronounced at higher solvent contents since as wt% of BA increased, the concentration gradient and hence the driving force for BA transfer across the microcapsule shell also increased, resulting in a greater loss of BA and hence a greater degree of wrinkling of microcapsule shell. This phenomenon can improve the mechanical interlocking between microcapsules and the polymeric coating and enhance the mechanical properties of the self-repairing material.^{13,20} Also, wrinkled microcapsules could enhance the release rate in applications such as self-repairing materials,

drug-delivery, and chemicals scavenging. Furthermore, Figure 2 shows that microcapsules prepared using epoxy resin with 30 wt% BA appeared to be slightly smaller than those prepared using epoxy with 10 wt% BA, likely due to the lower viscosity of the core material at higher solvent concentrations.

The size distribution of M10 microcapsules prepared at mixing rates of 500 and 700 rpm is shown in Figure 3. With increasing mixing speed, the average diameter (d_A) and the volumetric mean diameters (d_m) of microcapsules reduced from $313 \pm 17 \mu\text{m}$ and $355 \pm 12 \mu\text{m}$ for 500 rpm to $262 \pm 21 \mu\text{m}$ and $282 \pm 27 \mu\text{m}$ at 700 rpm, respectively. d_A was considered as the diameter with the highest volumetric fraction and d_m as the average of weight component multiplied by the corresponding diameter. Microcapsule size significantly influences its self-healing performance since the quantity of repairing material available for release depends on the size of microcapsules.^{40–42} Earlier studies have shown that a balance of self-healing and mechanical properties can be achieved by optimizing microcapsule size and wt% in the coating formulation.^{41,42} It is recommended that the size of the microcapsule should be preferably smaller than the coating thickness.⁴² However, smaller microcapsules were found to be less effective in terms of self-healing properties.⁴³

3.3 | Chemical characterization of synthesized microcapsules

FTIR spectroscopy was carried out to study the functional groups of PPU, to evaluate the structure of synthesized microcapsules, and to examine the microencapsulation of

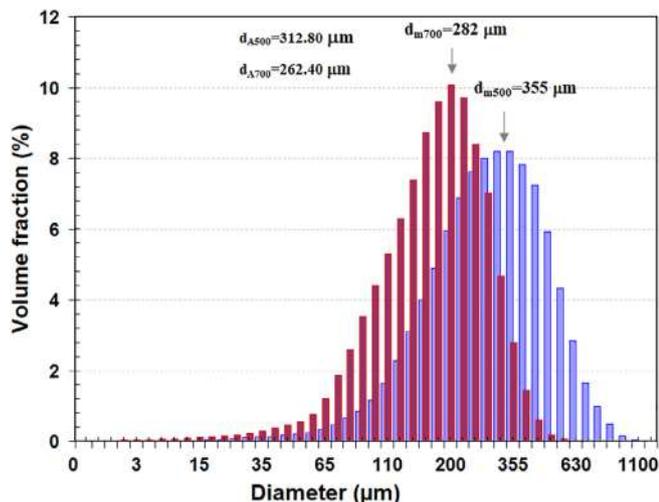


FIGURE 3 The PSA plots for M10 microcapsules prepared at mixing speeds of 500 and 700 rpm [Color figure can be viewed at wileyonlinelibrary.com]

healing agents. Figure 4 shows FTIR spectra of PPU, core, shell, and synthesized UF/PU capsules. For PPU, the most prominent absorption peak appeared at $2,272 \text{ cm}^{-1}$ which is related to the stretching vibration of NCO groups.^{20,22} This peak was largely suppressed in the FTIR spectrum of the microcapsule shell, indicating the presence of only a relatively small amount of free NCO groups.¹³ The low amount of free NCO groups in shell material signified near-complete crosslinking reaction was achieved in these samples. The absorption peaks at $3,308$, $2,964$, $1,605$, and $1,507 \text{ cm}^{-1}$ are, respectively, related to stretching vibrations of N—H, C—H, and double bonds in the benzene ring. The presence of the absorption peak related to C—H bond indicates the formation of polyurea shell in synthesized microcapsules.^{1,21,44} The absorption peak at $1,120 \text{ cm}^{-1}$ is indicative of C—N stretching vibration.^{13,20,45} In the FTIR spectra of core materials and microcapsule, two intense peaks at areas of 898 and 912 cm^{-1} correspond to C—O—C bonds in the epoxy resin backbone structure.¹ The absorption peaks at the region below $3,000 \text{ cm}^{-1}$ illustrated symmetric and asymmetric of C—H bond of *n*-butyl acetate solvent of core content.^{13,20} As conclusion, FTIR spectroscopy results confirm the encapsulation of epoxy resin with a shell with the polyurea structure which is in agreement with the literature.^{1,46} The possible reactions for the preparation of two-component shell (UF/PU) are shown in Figure 5.^{1,34}

The EEW of epoxy resins is an important characteristic property for their reactivity and the performance of the final coating product. The EEW of neat and encapsulated epoxy resin was calculated in the range of 183 – 188 g/eq that are in agreement with information provided by the supplier (184 – 190 g/eq). This result indicates that the structure of epoxy resin was unchanged before and after the microencapsulation process.

3.4 | Stability and thermal behavior of the synthesized capsules

TGA was utilized to study the thermal behavior of the two-component polyurea capsules synthesized at a mixing speed of 700 rpm. TGA and DTG thermographs of neat epoxy resin, BA microcapsule, and microcapsule shell are shown in Figure 6a,b. Weight loss in the TGA thermographs for different samples was apparent between one to three different temperature zones (Table 1). The first weight loss occurred at temperature region about 100 – 255°C , which is mainly due to the evaporation of *n*-butyl acetate solvent either neat or encapsulated along with the epoxy resin. Below 255°C , the

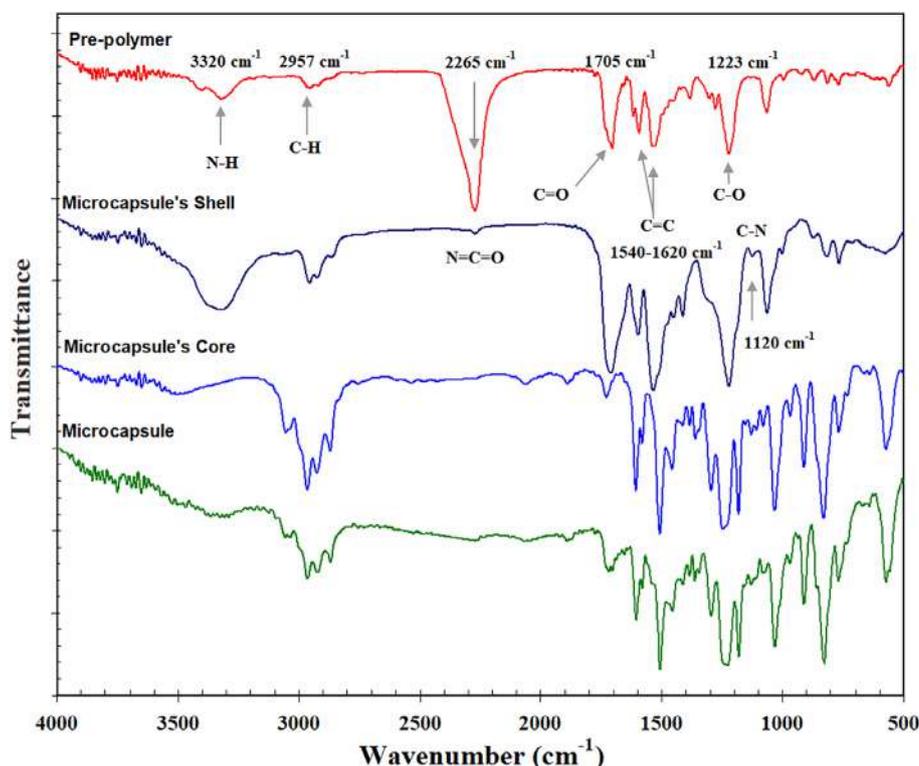


FIGURE 4 FTIR spectra of pre-polymer, core, shell, and synthesized PU/PUF microcapsules [Color figure can be viewed at wileyonlinelibrary.com]

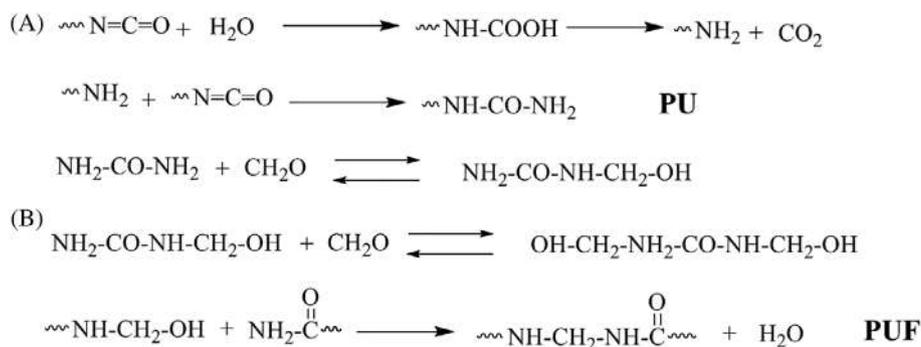


FIGURE 5 Possible reactions during two-component shell (PUF/PU) formation^{1,22}

weight loss for neat epoxy resin and microcapsule sample was calculated as 9.90 and 4.85 wt%, respectively.

The next temperature zone for weight loss appeared at 255–350°C, which may be associated with the decomposition of the epoxy resin, either neat or microencapsulated and/or due to the partial degradation of pre-polymer shell molecules.¹³ At this temperature zone, the weight loss was calculated as 73.05, 33.45, and 23.25 wt% for neat epoxy, microcapsule and microcapsule shell, respectively.

Finally, the last region of weight loss was detected at 345–600°C, which is attributed to the final oxidative decomposition of epoxy resin and shell of polyurea-based microcapsule.¹ However, due to the overlapping of the degradation temperatures of the shell of the microcapsules and epoxy resin, it is not possible to find out

precisely the core to shell weight ratio from the thermogravimetry technique.⁴⁷

The thermal decomposition of the neat epoxy resin can be divided into mainly two stages: the initial oxidative degradation process is in the temperature range of 255–350°C with a weight loss of 73.05 wt%. The weight loss at this temperature zone is most likely due to some complex reactions including; the crosslinking and branching interactions of molecular chains provoked by oxygen, and free radical chain scission of the isopropylidene linkage and, in addition to the removal of the hydration water.⁴⁸ The next stage is occurred in the temperature variations of 345–600°C among the weight loss of 9.94 wt%, as a result of macromolecular chains oxidative decomposition of the epoxy resin to the small depredated molecular products.⁴⁸

FIGURE 6 (a) TGA, (b) DTG thermographs for BA, epoxy, fresh microcapsule, PU/UF shell and 5 months aged [Color figure can be viewed at wileyonlinelibrary.com]

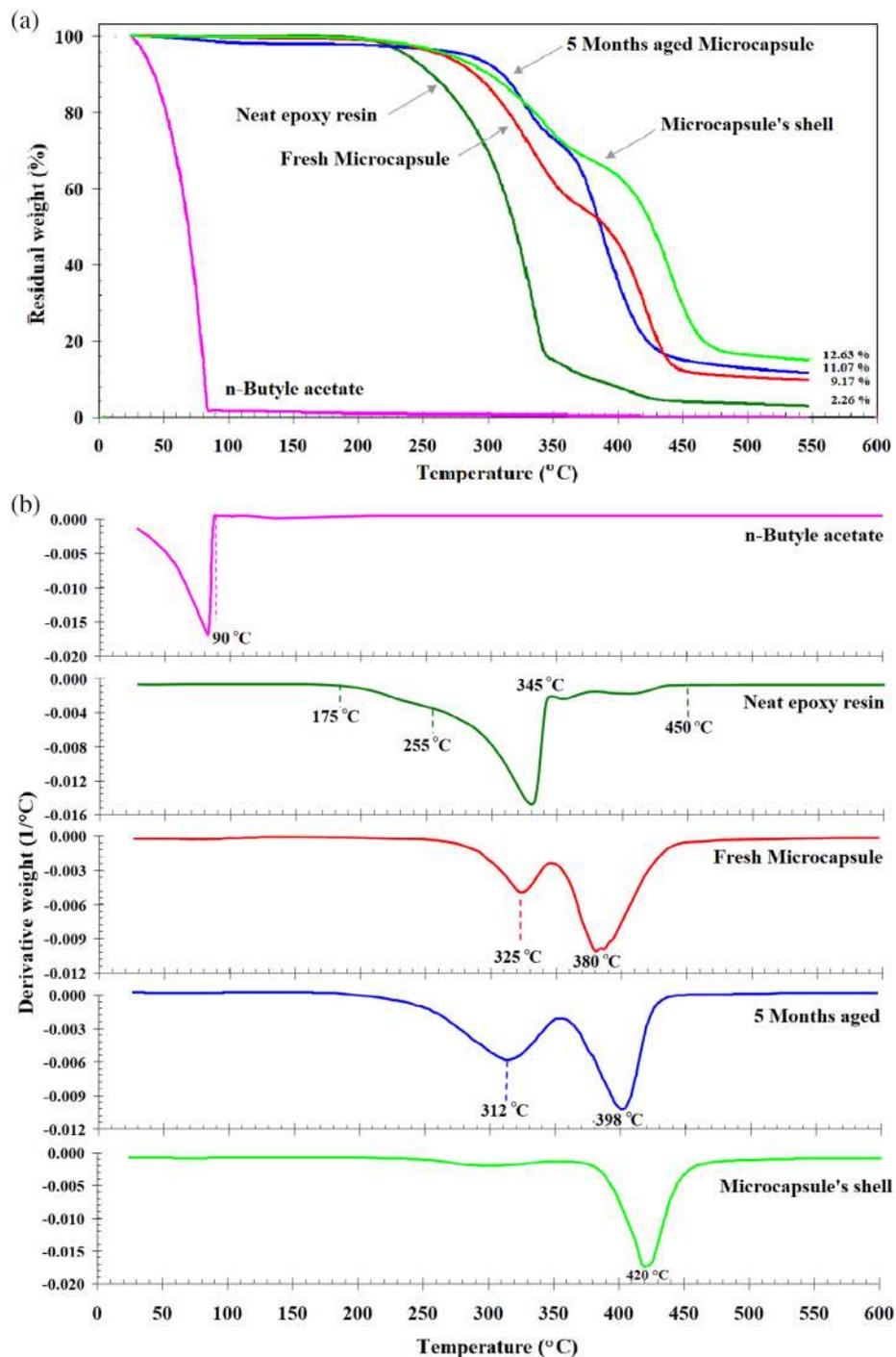


TABLE 1 TGA data of BA, epoxy resin, microcapsule's shell, fresh and 5 months aged microcapsules

Sample	Temperature ranges (°C)			Total residual weight (%)
	≤255	255–345	350–600	
<i>n</i> -Butyl acetate	99.25	0.75	0.0	0.0
Epoxy resin	9.90	73.05	9.94	2.26
Fresh microcapsule	4.85	33.45	50.38	9.17
Microcapsule's shell	1.85	23.25	45.57	12.63
5 months aged microcapsule	3.50	28.55	56.83	11.07

The maximum degradation temperature (T_{\max}) of neat epoxy, microcapsule's shell, fresh and 5 months aged microcapsules are shown in DTG curves in Figure 6b. It is a notable fact that the maximum of the derivative weight of the microcapsules (shell, fresh, and 5 months aged) is higher than neat epoxy resin. The results also revealed that the T_{\max} of aged microcapsules is relatively higher than its counterpart for fresh microcapsules. This

TABLE 2 Estimated core:shell ratios for microcapsules obtained using different measurement methods

Method	Core:Shell (wt%)
Mass balance	79.2:20.8
Extraction	70.5:29.5
TGA—fresh	75.5:24.5
TGA—5 months aged	65.5:34.5

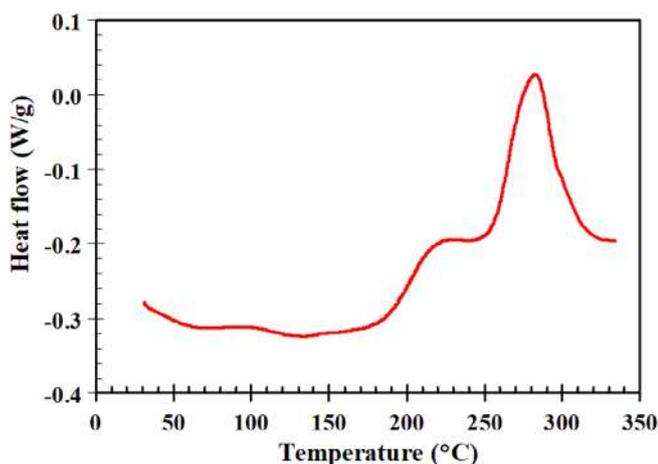


FIGURE 7 DSC thermograph of epoxy filled capsules prepared at mixing speed of 700 rpm [Color figure can be viewed at wileyonlinelibrary.com]

is mainly attributed to the starting of curing reactions of epoxy resin inside the capsules with the progressing time.

Table 2 shows the initial of core:shell ratio estimated from mass balance and the calculated ratios by TGA and extraction methods.⁴ The initial core to shell ratio was determined as 79.2 to 20.8, however; this ratio was calculated as 75.5 to 24.5 and 70.5 to 29.5 from the TGA data and the extraction method, respectively. These results are in general agreement however the lower core amount in the extraction method could be attributed to inefficiencies in the extraction process.

The storage stability of microcapsules after 5 months aging at ambient conditions was also evaluated by the TGA technique. With progressing microcapsules aging, the preliminary drop in corresponds TGA curve was due to slow evaporation of BA. A reduction in the core content (BA + epoxy resin) with aging from 75.5 to 65.5% was detected. This is probably owing to the removal of BA solvent and/or partially crosslinking of core materials.^{13,43} The results suggest that the BA content of the core decreased from 4.85 to 3.50 wt% after 5 months of aging.

The thermal behavior of microcapsules was also evaluated by the DSC test. Figure 7 shows DSC thermographs of capsules synthesized at a mixing speed of 700 rpm. The results revealed an exothermic heat flow peak at around 250–335°C, representing solvent evaporation and decomposition of epoxy and/or microcapsule shell.^{13,49} These results are in agreement with the TGA analysis and confirm the presence of epoxy resin inside the microcapsules. This finding also indicates that the microencapsulation process did not affect the epoxy resin.³⁴

Toluene and xylene are the most frequent solvents that are used for the industrial-based resins. Accordingly, the stability of prepared microcapsules in these solvents was evaluated following their dispersing in toluene and xylene and storage for 30 days. Figure 8 shows optical images of the microcapsules prepared at 700 rpm, before (282 ± 27 μm) and after 30 days storage in toluene and

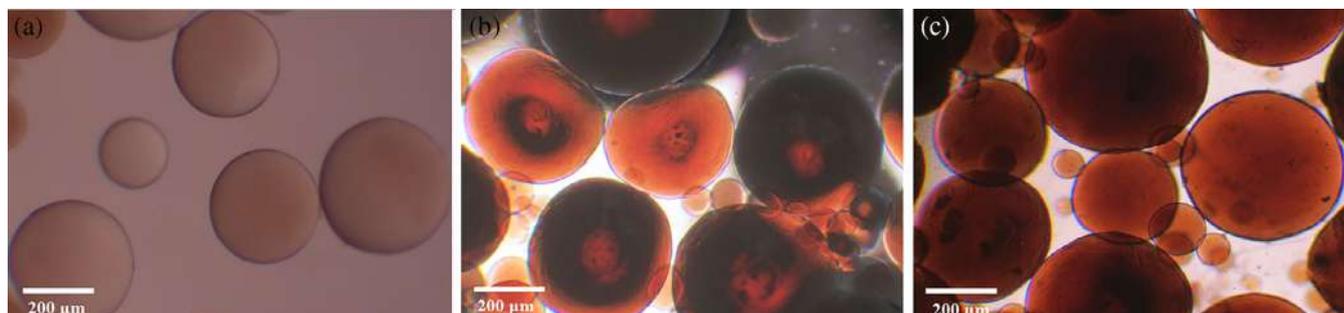


FIGURE 8 Optical microscopic images of M10 microcapsules prepared at mixing speed of 700 rpm, (a) before, (b) dispersed in toluene, and (c) xylene after 30 days of immersion [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 9 SEM micrograph of M10 microcapsule shell (scale bar is 1 μm) [Color figure can be viewed at wileyonlinelibrary.com]

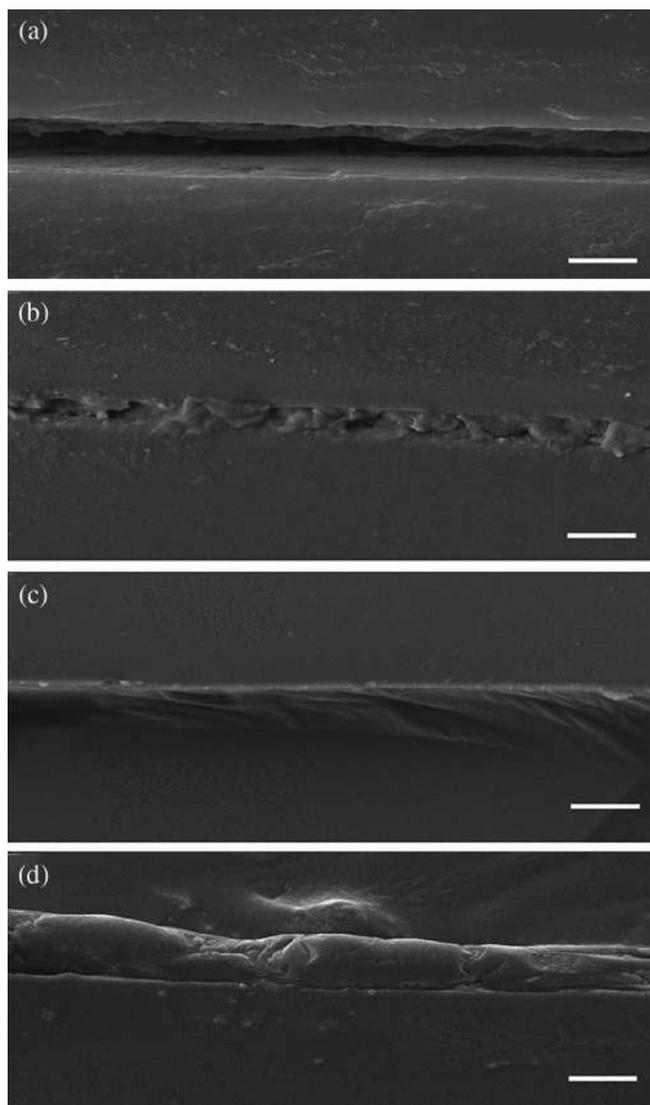
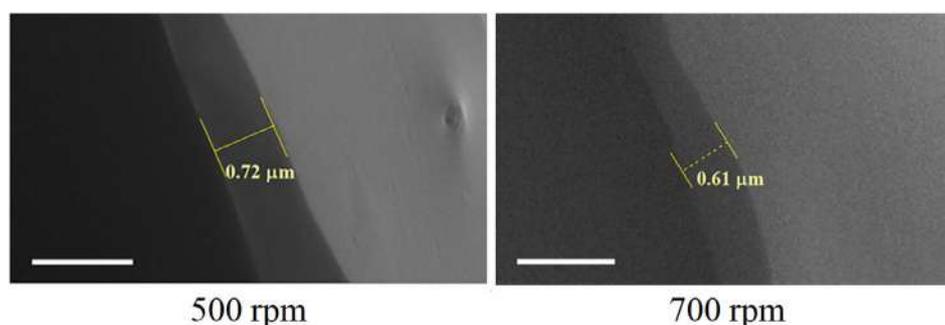


FIGURE 10 SEM micrographs of the scratched area of epoxy coating samples containing various amounts of M10 microcapsules. (a) neat epoxy coating, (b) 5 wt% microcapsules, (c) 10 wt% microcapsules, and (d) 20 wt% microcapsules (scale bar is 25 μm)

xylene ($287 \pm 18 \mu\text{m}$). A slight increase in the diameter of the microcapsules, after being immersed in the solvents for 30 days, can be due to a measurement error (the

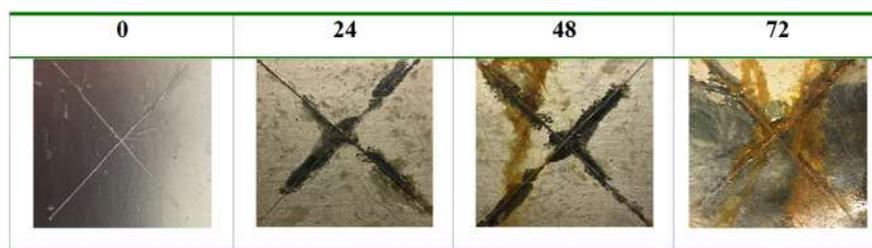
difference is within the standard deviation of the result) or as a result of slight swelling of the microcapsules. As it is apparent, microcapsules successfully retained their spherical form and dispersed following this procedure.

Generally, shell thickness determines microcapsule stability in various environments. The SEM photographs of M10 microcapsule shells prepared at agitation rates of 500 and 700 rpm are illustrated in Figure 9. These images show that increasing mixing speed led to a decrease in shell thickness. This is expected since a higher mixing rate resulted in smaller particle size, and hence at a given core:shell ratio, the total surface area of microcapsules increased and therefore shell thickness reduced. From Figure 9, the shell thickness of 500 and 700 rpm prepared microcapsules reduced from $0.7 \pm 0.03 \mu\text{m}$ to $0.6 \pm 0.03 \mu\text{m}$, respectively.

SEM micrographs of the healed area in the epoxy films containing various amounts of epoxy resin-filled microcapsules are shown in Figure 10. These micrographs show enhancing scratched filling area was achieved for the coating samples with a higher microcapsule content. According to these results, coatings containing 20 wt% microcapsules showed the optimum filling efficiency. The healing efficiency has been reported to depend on factors such as the size of the microcapsules, the amount of healing agent, and the percentage of loaded microcapsules in the coating.^{13,36,50}

Natural salt spray test was performed to study the effect of microcapsule wt% on the self-repairing property of the epoxy-based coated specimens. Visual observations of the scratched epoxy coated containing various wt% of M10 microcapsules synthesized at mixing speed of 700 rpm during 7 weeks exposure to the salt spray fog are shown in Figure 11.

For the neat epoxy sample, corrosion products and rusting were apparent along the scratched area 24 h after the salt spray test. With further increasing exposure time up to 72 h, the rusting developed to all underneath of the coating layer and spread to the all surface area of the sample. However, microcapsule embedded coating samples reveal appropriate corrosion resistance compared



(a) Neat epoxy sample

Exposure time (week)	1	3	5	10	20
1					
2					
3					
4	-				
5	-				
6	-	-			
7	-	-	-		

(b) Epoxy samples containing various wt% microcapsules

FIGURE 11 Visual appearance of different coated samples during various exposure times in natural salt spray chamber (the size of each image is 5 cm × 5 cm) [Color figure can be viewed at wileyonlinelibrary.com]

with blank epoxy coating samples. The corrosion resistance degree of coating directly depends on the microcapsule loading. Increasing the microcapsules content leads to a better corrosion resistance delay in rusting of the scratched area. At a higher microcapsules content, more

microcapsules are ruptured and hence more healing agent is released in the scratch area, increasing the thickness of the repaired layer. For the sample, in coatings having 1 wt% microcapsules, the rusting development was evident 1–2 weeks after the salt spray exposure test.

FIGURE 12 SEM micrographs of showing the compatibility of microcapsule with (a) epoxy, and (b) polyurethane coatings (scale bar is 50 μm)

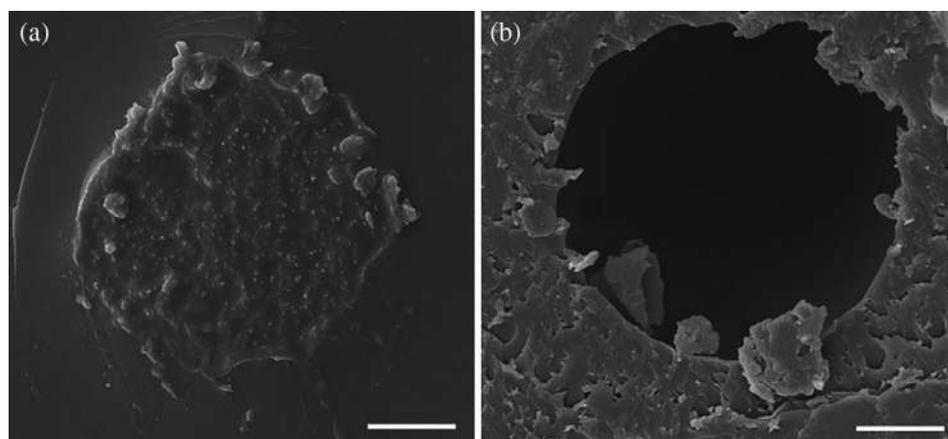


TABLE 3 Comparison of the results of this study with other published articles on the subject of preparation of microencapsulation of epoxy resin

Authors	Shell type	Shell component	Core material	Solvent (core diluent)	Coating matrix	Microcapsule properties: (I) Storage stability, (II) stability in solvent, (III) thermal stability, (IV) mechanical properties	Coating properties: (V) Self-healing, (VI) corrosion resistance, (VII) mechanical properties
Current study	PU/UF	Dual	Epoxy	BA	Epoxy	I, II, and III	V and VI
Wang et al. ²⁵	PUF	Single	Epoxy	TMPEG	Epoxy	Not reported	Not reported
Tzavidi et al. ²⁶	PUF	Single	Epoxy	BGE	Not reported	I and III	Not reported
Yuan et al. ²⁷	PUF	Single	Epoxy	BGE	Not reported	II and IV	Not reported
Li et al. ²⁸	PMMA	Single	Epoxy-amine	DCM	Epoxy	III	V and VII
Jin et al. ³⁰	PUF	Single	Epoxy-amine	CGE	Epoxy	I and III	V
Wang et al. ³²	EC	Single	Epoxy	DCM	Not reported	III	Not reported

Abbreviations: BA, butyl acetate; BGE, butyl glycidyl ether; CGE, o-cresyl glycidyl ether; DCM, dichloromethane; ethyl acetate; TMPEG, trimethylolpropane triglycidyl ether.

These results show that, even with the addition of a relatively small amount of microcapsules into the coating formulation, the corrosion resistance of the coating significantly improved. Also, in comparison to our previous work using monomeric²⁰ or bulky¹³ polyurethane and drying linseed oil,⁵ improvement in terms of corrosion resistance was notably superior. The results also reveal that even after 4 and 5 weeks of exposure time to the salt spray, no significant corrosion products and rust were observed along the scratched area of the samples comprising 5 and 10 wt% capsules.

SEM micrographs of cross-section of epoxy and polyurethane-based coating samples containing 5 wt% microcapsules synthesized at mixing speed of 700 rpm are shown in Figure 12. This test was performed to study the curing status of released core content after rupturing microcapsule shell. The coating samples were broken in liquid nitrogen, 24 h left in ambient conditions, and SEM micrographs were prepared from their cross-section area. The micrograph (Figure 12a) shows that epoxy core material discharged from the microcapsule, and cured with the dispersed amine composition within its

surrounding polymeric matrix. It is apparent that the core material entirely cured with the free amine component and filled the room inside the broken microcapsule. This test apparently shows the possibility of using epoxy resin-filled capsules in an epoxy system comprising a slightly extra amount of curing agent.

However, for microcapsule embedded polyurethane-based sample, no healing was observed in the SEM micrograph (Figure 12b), as a result of un-curing status of released epoxy core content. The micrograph shows that the core material was completely discharged from the microcapsule and the microcapsule was left "empty". Hence, given the incompatibility of amine compounds with the urethane matrix, this type of microcapsule did not provide any self-healing properties. It is also important to note that the use of excess amounts of curing agent in the epoxy coatings should also be carefully balanced since the excess amine may reduce the molecular weight of the final cured system, and decrease the mechanical properties and hence the durability of the system.

3.5 | Comparison with previous work

A summary of the specifications and tests for determining the characterization properties of the epoxy-filled microcapsules and the polymer coatings containing them prepared in the current study and in the published articles^{25-30,32} is depicted in Table 3. As can be seen, in addition to the use of non-toxic BA solvent in core dilution and microencapsulation process, the stability of microcapsules, significantly increased due to the synthesis of two-compound shell microcapsules.

4 | CONCLUSIONS

The synthesis of two-component urea-formaldehyde/polyurethane-based microcapsules containing epoxy resin has been achieved utilizing successive in situ and interfacial polymerization methods. Prepared microcapsules with the mean diameter of about 282 μm and shell thickness of 0.6 μm at a mixing rate of 700 rpm were selected as appropriate microcapsules via proper core content (>70%). Spherical shaped and morphologically wrinkled microcapsules were observed in SEM studies. There was an inverse relationship between the rate of mixing and microcapsule size, so that with increasing agitation speed, the size of the microcapsules was reduced. The results revealed that the core:shell ratio was about 75:25, and the microcapsule yield was 65% on

average. The healing property of epoxy coating with three different contents of 5, 10, and 20 wt% of microcapsules was assessed by SEM micrographs. It was found that coatings containing 20 wt% microcapsules had maximum healing efficiency. The corrosion resistance of coatings containing these microcapsules showed an increase in barrier properties compared with the neat epoxy coating. This is in agreement with the results obtained from scratch repairing property. The epoxy-filled microcapsules prepared in this way offer attractive prospects for a wide range of applications including thread-locking, adhesives, anti-corrosion coatings, and automobile industry.

CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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