Chapter

Applications of Microcapsules in Self-Healing Polymeric Materials

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Abstract

Self-healing polymeric materials have a great potential to be explored and utilized in many applications such as engineering and surface coating. Various smart materials with self-healing ability and unique self-healing mechanisms have been reported in recent publications. Currently, the most widely employed technique is by embedding microcapsules that contain a healing agent into the bulk polymer matrix. When cracks develop in the polymer matrix, the curing agent is released from the microcapsules to cross-link and repair the cracks. Microencapsulation of the healing agent in the core can be achieved by *in situ* polymerizing of shell material. This chapter presents a general review on self-healing materials, and particularly, self-healing of epoxy matrices that includes epoxy composite and epoxy coating by microencapsulation technique. Microencapsulation processes, including types of resin used, processing parameters such as core/shell ratio, concentration of emulsifiers, viscosities of aqueous and organic phases and stirring rate are discussed.

Keywords: self-healing, epoxy, microencapsulation, microcapsule

1. Microcapsule-based self-healing epoxy composite and epoxy coating

The use of microcapsule-based systems has attracted much attention during the last decade. The advantages include the esthetic recovery combined with the fast release of healing agent from the microcapsules [1]. This microcapsule-based approach could be easily integrated in many polymer systems, although the healing agent is locally depleted after a single damage event [2]. The attractive features of such technology include prolonging the service life-span of the materials and reducing the cost of repair or replacement of failed component.

Designing a microcapsule-based self-healing material requires a number of considerations. The first is to design the microcapsules, followed by incorporating them into the polymer matrices. Next, the viable mechanical characterization of the polymer during the occurrence of cracks should be studied. Finally, the extent of self-healing reactions must be determined and verified. Thus, the suitable encapsulation method for a particular healing agent must first be identified. One must consider the operation parameters such as solubility, reactivity, viscosity, and volatility of the healing agent. In the next step, the microcapsules should be integrated into the matrix host without being broken during mixing and must be well distributed. Microcapsules produced by encapsulating the healing agent in urea-formaldehyde (UF), melamine-formaldehyde/melamine-urea-formaldehyde (MF/MUF), and

poly(urethane) (PU) microcapsules have been shown as being capable of withstanding processing conditions in thermoset resins as well as in composite materials. The mechanical properties, triggering mechanism, and self-healing performance of the material should be characterized to ensure the usefulness of the innovation. The overall properties of the healed materials, such as fracture toughness, tensile strength, and hardness could be affected by the microcapsules [2].

1.1 Types of microcapsules for self-healing

Different types of microcapsule systems have been applied in self-healing materials; these include the microcapsule-catalyst system, dual/multi-capsule system, and microcapsules with latent hardener. Grubb's catalyst was first reported in a self-healing material containing micro-encapsulated dicyclopentadiene (DCPD) (White et al., [3]). Later, a self-healing epoxy adhesive was designed by incorporating 15 wt. % micro-encapsulated DCPD and 2.5 wt. % Grubbs' catalyst. A significant increase in the initial fracture toughness after 24 h of healing at ambient temperature was observed [4]. Healing process at elevated temperature of 110°C was applied in a rubber-toughened epoxy adhesive. To withstand specific epoxy hash curing conditions, the DCPD was encapsulated in a double-walled polyurethane (PU)/UF shell. Recovery of 20–58% of virgin fracture toughness was obtained after assessment with width-tapered double cantilever beam (WTDCB) test [5].

The microcapsules and catalyst self-healing system was found to have certain shortcomings. For instance, poor dispersion of the catalyst and the hardener (diethylenetriamine, DETA) could lead to a drop in healing efficiency. Thus, an alternative method of encapsulating the catalyst was introduced [6], by addition of wax microspheres into the epoxy matrix. The wax-catalyst microspheres were found to improve the dispersion, which resulted in efficient healing (up to a maximum of 93%) with significantly lower amount of embedded catalyst than the non-wax-encapsulated catalyst. Although the Grubbs' catalyst has excellent selectivity, it is costly and toxic. Therefore, these drawbacks have limited its use in high-volume commercial composite and polymeric parts.

Tungsten (VI) chloride was used as an alternative catalyst for DCPD; it is more cost-effective, widely available, and more tolerant to moderate temperature changes. It was used for catalyzing the ring-opening metathesis polymerization of *exo*-DCPD and achieved an *in situ* healing efficiency of approximately 20% with 15 wt. % microcapsules [7].

A different type of chemistry was involved when metal triflates were used as Lewis acid catalyst, to initiate the curing of diglycidyl ether of bisphenol A (DGEBA) and epoxy resins. It was easily available and thus chosen due to its high catalytic activity, and of relatively low cost, low toxicity, and high stability [8]. The DGEBA, ethyl phenyl acetate microcapsules, and scandium(III) triflate catalyst particles were embedded into epoxy matrix. The achieved healing performances were comparable to the more expensive and less robust (air and moisture-sensitive) Grubbs' catalyst/DCPD-capsule system [9].

Multi-capsule self-healing systems have also been reported. For example, a two-part resin system containing microcapsules of an epoxy resin and its hardener with poly(melamine-formaldehyde) (PMF) shell was employed. The PMF shell was inert toward the two types of cores. It was reported that at 20°C for 24 h of reaction time, 43.5% healing efficiency was achieved at 1 wt. % capsule content, and 100% healing efficiency at 5 wt. % capsule content [10]. Pang and Bong have used a similar approach earlier but with the healing agent loaded inside hollow fibers instead of microcapsules [11].

In another example of two-component microcapsule system, epoxy and boron trifluoride diethyl etherate ($(C_2H_5)_2O{\cdot}BF_3$) as hardener were used in self-healing

epoxy composites. Boron trifluoride diethyl etherate has been commercially available as a cationic catalyst for low-temperature chain polymerization of epoxy resins. A remarkable recovery of 80% of impact strength was achieved within 30 min at 20°C at only 5 wt. % epoxy and 1 wt. % ($(C_2H_5)_2O{\cdot}BF_3$)-loaded microcapsules. The only shortcoming of this system was that the high reactivity of the healing agents resulted in limited shelf life [12].

Another approach is to encapsulate the epoxy resin and amine hardener separately without the need of another catalyst. The epoxy microcapsules were prepared by the classic *in situ* polymerization method, while the hardener-microcapsules were prepared by vacuum-infiltrating the amine into hollow PUF microcapsules. High healing efficiency with 91% recovery of mode-I fracture toughness was achieved with 7 and 10.5 wt. % amine and epoxy microcapsules, respectively. The microcapsules have shown 6-month storage stability at ambient conditions [13].

Recently, to overcome the challenges in encapsulating the hardener for epoxy resins, poly(methyl methacrylate) (PMMA) was used instead of the amino resins. The PMMA microcapsules can withstand 6–12 months of storage at room temperature [14]. They have obtained 43.5 and 84.5% fracture toughness recovery with 5 and 15 wt. % microcapsules, respectively, at room temperature for 24 h of curing [15].

The third type of self-healing system is the microcapsule-latent functionality where the healing agent is encapsulated or dispersed as particles, and the polymerizer is residual reactive functional groups in the matrix. This approach was introduced by Yin and colleagues. Encapsulated epoxy resin was used as curing agent and a well-dispersed latent hardener, which is also epoxy-based, was distributed in the matrix. Repair of the cracked sites was achieved through the cross-linking reactions of the released epoxy resin from the fractured microcapsules [16]. Another example of this system utilizes solvents together with the healing agent. Here, residual amine functionality in an epoxy matrix is used to initiate polymerization with healing agent [17]. Other works have incorporated meltable, thermally polymerizable epoxy microspheres into epoxy composite materials to induce self-healing [18] and also water-soluble, self-curing epoxy-amine adduct particles in a protective coating on a steel substrate [19].

The fourth type of self-healing system comprises a simplified processing method of capsule-catalysts. Here, the catalyst and the healing agent were dispersed throughout the matrix. Although encapsulated-catalyst healing system was used, the siloxane-based healing agents, that is, hydroxyl end-functionalized polydimethylsiloxane (HOPDMS) and polydiethoxysiloxane (PDES) mixture were not encapsulated. Due to their low solubility, the siloxane-based polymers and the encapsulated butyltin dilaurate catalyst mixture were directly blended with the vinyl ester prepolymer, forming a distribution of stable phase-separated droplets and protected catalyst (**Figure 1**). No reactions took place between the HOPDMS and PDES prior to exposure to the catalyst. A stable healing chemistry in humid or wet environments and a stable system for elevated temperature (important for higher temperature thermoset-curing system) was reported. The siloxane-based polymers are also widely available and comparatively low in cost [20].

1.2 Self-healing epoxy coating

Self-healing epoxy coating is another attractive application of the self-healing property. This system was first introduced when microvascular networks were included into epoxy coating. These networks then released the healing agent when cracks occurred, flowed to fill the gaps, and cross-linked to mend the damages [21]. Another work reported the healing of cracks in paint film by linseed oil released from microcapsules that ruptured under simulated mechanical action.

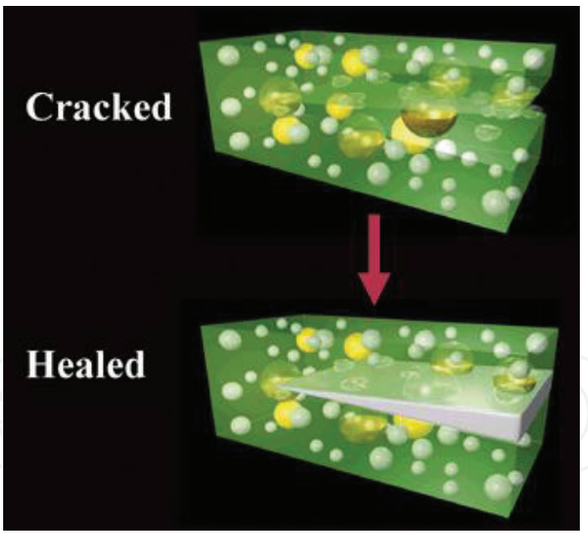

Figure 1.
Polydimethylsiloxane (PDMS)-based self-healing is achieved through the tin-catalyzed polycondensation of phase-separated droplets. Reproduced from Cho et al. ©2006 Wiley-VCH.

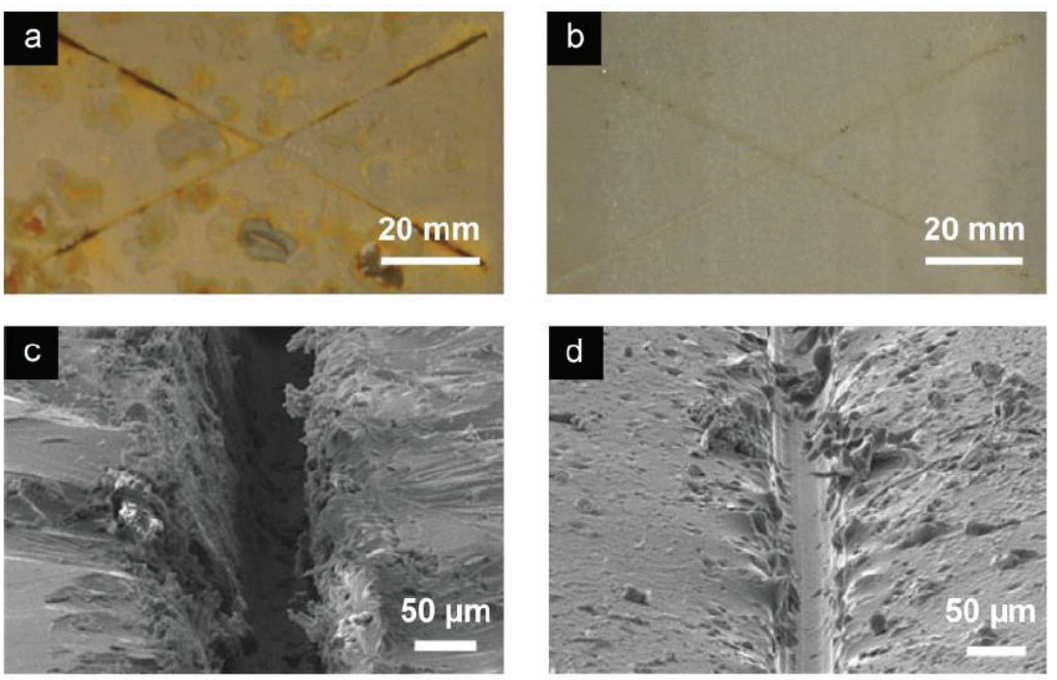

Figure 2.
Optical images after 120 h of immersion in salt water of (a) control sample (b) self-healing coating; SEM images of the scratched region of (c) the control coating (d) the self-healing coating after healing. Reproduced from Cho et al. © 2009 Wiley-VCH.

The healed area was able to protect the substrate from corrosion [22]. In another investigation, the encapsulated linseed oil along with solvents and dispersing agent were added to the epoxy coating. This was compared to another epoxy coating filled with talc at similar level. Results showed that the coating containing encapsulated linseed oil formed fewer and smaller cracks. The enhanced impact resistance of the microcapsule-filled coating might be due to higher elasticity of microcapsule containing linseed oil compared to the harder inorganic filler particles. Based on preliminary salt spray exposure of coatings, the addition of microcapsules to the epoxy binder matrix has not compromised the coating performance [23].

The possibilities of sonication to produce nanocapsules containing linseed oil as healing agent in epoxy coating was examined by Boura et al. [24] Capsules of smaller sizes provide easier dispersion for better healing performance for the coating matrix and had better wet adhesion and corrosion resistivity than those of larger sizes [24]. Tung oil was also encapsulated to impart self-healing ability in epoxy paint films. Scratches were healed efficiently with satisfactory anti-corrosive properties [25].

Encapsulated Grubbs' catalyst and DCPD in silica-coated micron- and sub-micron-size capsules had been demonstrated by Jackson and co-researchers [26]. Silica served as a protective and functional layer to the capsules and catalyst, and significantly improved dispersion in the epoxy matrix. The particles were successfully incorporated into the epoxy matrix without significant loss of healing agent. It also enabled the capsules and particles to be dispersed at higher concentrations with little loss of reactivity.

The concept of phase-separated self-healing was extended to an anti-corrosion epoxy coating. A dramatic reduction in corrosion of metal protected by the coating is shown by the optical images in **Figure 2** [27].

2. Microencapsulation of healing agent

Microencapsulation is the process of coating small solid particles, liquid droplets, or gas bubbles with a thin film of shell materials. The term microcapsule is used to describe particles with diameters between 1 and 1000 μm [28]. It consists of a core-shell structure where the active reagent is surrounded by a membrane (reservoir system) [29]. The shell of the microcapsules and the process of encapsulation are selected according to the physical properties of the core and the intended application.

Microcapsules containing self-healing agent are embedded into polymeric materials. When crack occurs in the polymer matrix due to an external force such as sudden physical impact or stretch, some of these microcapsules along the crack line are ruptured and the liquid curing agent flows into cracks and reacts with the catalyst or the matrix itself to form solid that fills the gaps. The healing agents could be monomers, dyes, catalysts, or hardeners, and they are encapsulated to suit the chemistry of the intended matrix and applications. These healing agents behave like adhesives that glue the polymeric matrix from inside the system. Ionomers, concrete, ceramics, metals, and polymers are among known materials that have been developed to have self-healing ability.

There are many methods to prepare the microcapsules such as interfacial polymerization, coacervation, *in situ* polymerization, extrusion, and sol-gel methods. Among these methods, the *in situ* polymerization was the most frequently used technique, because it is the easiest process, and does not require sophisticated equipment [30].

The shells of microcapsules were synthesized via *in situ* polymerization. The core material in the form of water-immiscible liquid (or solid) was dispersed in an aqueous phase that contains urea, melamine, water-soluble urea-formaldehyde condensate, or water-soluble urea-melamine condensate. At the same time, a suitable additive that could enhance shell formation is added to the aqueous phase if necessary. Shell formation begins to occur when formaldehyde is added and the pH adjusted to between 2 and 5 with a dilute mineral acid. The system is maintained at 40–60°C for several hours. Condensation reaction occurs in the aqueous phase to produce oligomers that deposit on the surface of the dispersed core particles and continue to polymerize to form a water-insoluble, cross-linked hard polymeric shell. The process has been used commercially to manufacture a wide range of microcapsules [28].

2.1 Resins for encapsulation

Amino resins are most widely used in making microcapsules for self-healing materials [30]. They are also known hardeners for epoxy resins. Their reactions occur first through the etherification process with loss of water or alcohol and second through the addition reaction of *N*-methylol groups to the epoxide group [31]. These resins are produced by the reactions of amino groups, thus they are compounds with -NH functionality such as urea, melamine, thiourea, aniline, and guanamines, which can react with formaldehyde. Urea-formaldehyde (UF) and melamine-formaldehyde (MF) are the two most popular amino resins, and their structures are shown in **Figure 3**.

Both UF and MF resins are light in color and exhibit enhanced water and heat resistance. They are widely used in industries as adhesives, impregnating resins, molding materials, strengtheners for building materials, flame-retardant coatings, foamed resins for many purposes, grinding wheels, ion-exchange resins, sewage flocculants, and microcapsule production [32, 33]. UF resin was also used in specialized application such as in the fabrication of natural fiber-reinforced plywood and chip-boards [34].

In preparing the microcapsules, UF can be cross-linked to form hard shells that protect the healing agent in the cores. Some UF nanoparticles would deposit on the shell to form a rough surface that facilitates the adhesion of microcapsules to the polymer matrix [35, 36]. During the preparation process, a low-molecular weight oligomer is first formed from the condensation of urea and formaldehyde. Subsequently, the oligomer becomes attached onto the surface of the dispersed core material and gradually polymerizes to form the shell [37].

A number of modifications of poly(urea formaldehyde) (PUF) resin for encapsulation has been reported, for example, by mixing urea with melamine-formaldehyde prepolymer forming poly(melamine-urea-formaldehyde) (PMUF). 5-ethylidene-2-norbornene (ENB) and its cross-linking agent were encapsulated for self-healing purpose [38]. PMUF shells are more robust, stronger, and easier to handle than PUF shells. Up to 12 wt. % urea was replaced with melamine in the formulation, to encapsulate an epoxy resin. The resultant PMUF microcapsules exhibited better resistance against solvent, acid, and alkali [39]. Other researchers had replaced 1–5% urea with a commercially available melamine resin, Cymel 303®, in producing shell materials for microcapsules containing DCPD. The microcapsules were strong enough to withstand the mechanical mixing with a viscous restorative dental resin [40]. Both PUF and PMUF resins have been used to prepare microcapsules of epoxy resins, DCPD, linseed oil, and alkylglycidyl ether. Here, it is

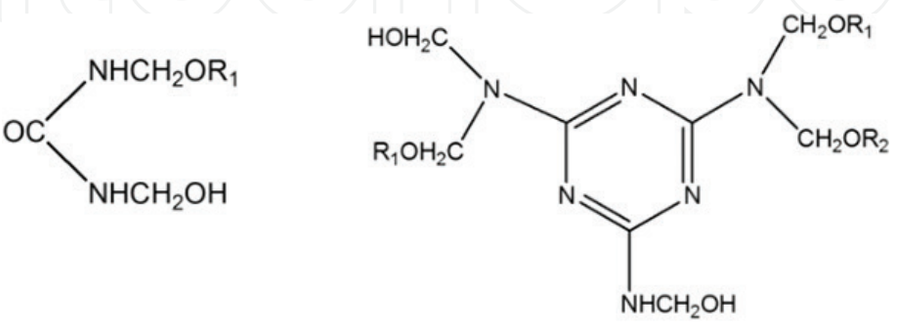

Figure 3.
Chemical structures of UF and MF resins.

also reported that PMUF shells were more stable than PUF shells and resulted in the production of higher yield of microcapsules [36].

2.2 Parameters affecting microencapsulation

There are several processing parameters that could affect the formation and the size of the microcapsules. These factors are discussed briefly as follows. The core/shell weight ratio was calculated based on the weight of core over the weight of the total raw materials forming the shell. Brown and his colleague have used a 6.2/1 ratio in the UF *in situ* polymerization [37]. This ratio has been adopted by a number of other researchers [39, 41, 42]. The tendency to form thicker and porous layers that cause agglomeration was noted by some researchers. A higher ratio of 6.45/1 was reported to produce more spherical and well-formed microcapsules [43].

The size of microcapsules was found to change with the weight ratio of core-shell material. The higher amount of core material results in larger size of microcapsules. Fixing the other processing parameters, an increase in the core/shell weight ratio increases the size of core droplet in emulsion. Consequently, the core material and the size of microcapsules increase. However, excess core materials may cause poorer dispersion, and there is relatively less oligomer to coat and fully polymerize to hard shell, resulting in more aggregation of core droplets, leading to lower yield of good microcapsules. The final microcapsules would have thinner shell wall and become fragile [44].

The concentration of emulsifiers has played a crucial role during *in situ* polymerization; if it is too low, the droplets will tend to agglomerate into bigger sizes, thus an increase in concentration may be required to maintain the sizes of the droplets within a certain range [45, 46]. Sodium dodecyl benzene sulfonate (SDBS) is one of the surfactants used in the production of microcapsules by *in situ* polymerization [44], while sodium dodecyl sulfate (SDS), gum Arabic, and gelatin are normally used in coacervation method [45, 47]. Poly(vinyl alcohol) (PVA), that serves to adjust the viscosity of the medium, is also used in PUF encapsulation [16, 22]. However, polyelectrolyte species are the most commonly used emulsifiers in the production of PUF microcapsules, such as ethylene maleic anhydride (EMA) copolymer, methylvinyl ether maleic anhydride copolymer, and styrene maleic anhydride copolymer [48].

The use of surfactants lowers the interfacial tension between the two phases (oil and water phases) and serves to prevent the regrouping of the particles formed. The adsorption at the interface between water and air reduces the surface tension [48]. When the concentration of stabilizer is increased, finer emulsion could be formed. Consequently, the size of microcapsules will be reduced and their size distribution will be narrower [44, 49]. However, an increase in nanoparticle formation will also occur, which will cause problem during separation by filtration [23]. Another study has reported the observed pH variation when concentration of EMA was increased [50].

The effect of emulsifier concentrations has been investigated. At low emulsifier concentration (<2 wt. %), agglomeration of particles tends to occur and the microcapsules were reported to have irregular shapes and sizes. Increasing the concentration to 3 wt. % has improved the size distribution. However, at much higher emulsifier levels, the microcapsules might become very small and with uneven size distribution [51]. Overall, it is necessary to optimize the concentration of emulsifier to obtain the desired size, shape, and a good yield.

The successful production of desired microcapsules is affected by the method of production. It is difficult to generalize on the relative importance of the different aspects of the procedure. The relative viscosities of the organic (alkyd/ oils/ others) and the aqueous phases have been reported to be significant parameters [28, 52]. Only the viscosity of the aqueous phase can be more easily controlled or adjusted by the use of emulsifier or viscosity adjuster.

On the other hand, the viscosity of the organic phase is determined by the type of core content used. Commonly encapsulated materials such as inks, fragrances, and pesticides are liquids with low viscosity. According to Ghosh (2009), monomers as self-healing reagents should have low viscosity in order to have the ability to flow into the microcracks, once the microcapsules are ruptured [53]. For this purpose, encapsulated healing agents are mostly liquids, which have low viscosity, such as DCPD, linseed oil, and amine. Although some of the commonly available healing agents could be resins of high molecular weights with medium to high viscosity, they need to be diluted with either reactive or non-reactive diluents, prior to encapsulation. For example, DGEBA resin was diluted with 1-butyl glycidyl ether (BGE) as a reactive diluent with 0.2/1 wt. ratio of BGE/DGEBA [44]. In another example, 40 g of E-51 (bisphenol-A epoxy resin) was diluted with 800 mL of sodium polyacrylate prior to encapsulation to produce self-healing epoxy composites [16].

An undiluted epoxy resin, diglycidyl tetrahydro-o-phthalate (DTHP), with 0.36 Pa·s viscosity, was encapsulated for self-healing epoxy composites [10]. In a subsequent work, the effect of using epoxy resins with different viscosities (but with similar epoxide value) on the healing efficiency was studied. EPON 828, Epoxy 731, and Epoxy 711 resins with viscosity values of 12.5 , 0.85 and 0.53 Pa·s, respectively, were used without any dilution. The lowest viscosity epoxy resin (Epoxy 711) achieved the highest mixing efficiency (83.4%), as compared with Epoxy 731 (79.3%) and EPON 828 (63.7%). The healing efficiency would be favored when the encapsulated epoxy prepolymer has lower viscosity, as the healing agent would be able to flow more easily to fill the gaps in the cracks [54].

A work investigated a number of solvents as diluents for epoxy resins (EPON 828 and EPON 862) and concluded that solvents should ideally have dielectric constant (ε) between 5 and 38. The selection is based on three parameters: dielectric constant (ε), boiling point, and flash point. The solvents chosen for their study included chlorobenzene, phenylacetate (PA), and ethyl phenylacetate (EPA). The combination of 60 mL of epoxy resin-15 pph EPA was concluded as the best combination for solvent-promoted self-healing epoxy material [43].

Using PDMS resin, which has high molecular weight and high viscosity, as healing agent, it was diluted with 30 and 53 wt. % xylenes, respectively, prior to encapsulation. The addition of solvent would lower the relative quantity of healing agent delivered. These microcapsules with solvents were compared with microcapsules containing only PDMS resin as control. The control showed best microcapsule production with good shape, free flowing property, and little debris. On the other hand, microcapsules containing solvent were less uniform in shape, with more debris, and had a tendency to cluster. Solvent also lowered the thermal stability of the microcapsules. However, PDMS with 30% xylene showed the highest healing efficiency at certain loading limit and the efficiency decreased when the content loading exceeded 0.3 mg/cm^3. This observation was explained as follows. The strength of PDMS resin increases with molecular weight during polymerization but the viscosity of the core would also increase, thus solvent would be required to improve the flow. The use of solvents generally degrades capsule quality and thermal stability [55].

In a separate study, Nesterova et al. encapsulated different healing agents for epoxy coating, which include linseed oil, 5-ethylidene-2-norbornene (ENB), DGEBA diluted with BGE, and DCPD. They concluded that the stability of microcapsule is very dependent on the core material. Higher stability was observed in microcapsules formed with more viscous cores. This was possibly due to the higher elasticity of more viscous compounds, which can absorb more stress on the shell material during handling of the capsules [36].

The encapsulation process is uniquely dependent on the core used and the process needs to be optimized. A low-viscosity core is preferred for efficient

self-healing application and the core viscosity can be adjusted with suitable diluents. However, the inclusion of diluents may or may not have an impact on the production of microcapsules as well as the healing efficiency.

Finally, the agitation rate also has a great influence on the formation of microcapsules. As the stirring rate is reduced, the core/water interfacial surface is lowered. Thus, the reaction between urea and formaldehyde will occur mostly in the aqueous phase instead of on the interfacial surface. This will result in lots of aggregates, which consequently will reduce the amount of well-formed microcapsules [56]. A high agitation rate can produce smaller core droplets and subsequently smaller microcapsules. However, very high agitation rates would lead to more frequent collisions that cause the deposition of PUF and core content on the stirrer and reactor's wall, leading to lower yield of microcapsules [37]. The increase in collisions of the droplets may also lead to more agglomeration of the microcapsules, which also will reduce the yield [57]. Brown et al., in their study, have established a correlation between average diameter and agitation rate, which is linear in log-log scale [37].

3. Conclusion

The development of self-healing smart polymeric materials has attracted much attention during the last decade. The attractive features of such technologies include prolonging the service life-span of the materials and reducing the cost of repair or replacement of failed component. Currently, the most widely employed technique is by embedding microcapsules that contain a healing agent into the bulk polymer matrix. When cracks develop in the polymer matrix, the curing agent is released from the microcapsules to fill the gaps and subsequently cross-link through suitable reactions to repair the cracks. This microcapsule-based approach can be easily integrated in many polymer systems, such as the epoxy composites and coating, and has a vast potential to be explored and applied commercially. Microencapsulation is a robust technique that can be achieved by optimizing the encapsulation method by *in situ* polymerizing the potential shell material with the healing agent in the core. The two most popular amino resins for encapsulation of the core healing agent are urea-formaldehyde (UF) and melamine-formaldehyde (MF).

The microcapsules were synthesized via *in situ* polymerization to form the shell. The water-immiscible core material was dispersed in an aqueous phase that contains urea or melamine or a combination of both, before the calculated amount of formaldehyde is added. The system is heated for several hours at 40–60°C, preliminary reactions occur in the aqueous phase, producing condensation oligomers that deposit on the surface of the dispersed core particles and continue to polymerize gradually to produce a water-insoluble, cross-linked hard polymer shell. The microcapsules could then be separated by sieving and dosed into the epoxy formulations for composite or coating application.

There are several processing parameters that could affect the yield and the size of the microcapsules. These include core/shell weight ratio, the emulsifier type and concentration, pH, and the stirring speed during microencapsulation.

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Conflict of interest

The authors declare no conflict of interest.

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