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Preparation and properties of poly(urea–formaldehyde) microcapsules filled with epoxy resins

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ABSTRACT

The poly(urea–formaldehyde) (PUF) microcapsules filled with epoxy resins have potential for self-healing or toughening polymeric composites. A series of PUF microcapsules containing epoxy resins were synthesized by selecting different process parameters including surfactant type, surfactant concentration, adjusting time for pH value and heating rate. The effects of process parameters on the size and surface morphology of microcapsules were discussed. The storage stability, solvent resistance and the mechanical strength of microcapsules were investigated. The morphology of microcapsules was observed using scanning electron microscopy (SEM) and optical microscopy (OM). The results indicate that the formation of microcapsules is affected by the surfactant type. The size of microcapsules can be controlled by the surfactant concentration. The surface morphology of microcapsules can be adjusted by the surfactant concentration, the adjusting time for pH and the heating rate. The microcapsules prepared by using surfactant sodium dodecylbenzene sulfonate (SDBS) show good storage stability, excellent solvent resistance and appropriate mechanical strength.

1. Introduction

Microcapsules as means of storing and delivering healing agents to stem the spread of cracks have attracted considerable interest of researchers within aerospace and construction industries [1,2]. A microencapsulated healing agent within polymer matrix may be ruptured by the propagating crack and release the healing agent into the crack plane by capillary action. When the released healing agent comes into contact with the catalyst embedded in polymer composites beforehand, the polymerization of healing agent is initiated and bonds the crack face closed [1]. As a result, the mechanical properties of polymer composites could be maintained. Additionally, microcapsules can serve as novel tougheners for polymer matrix composites [3]. Poly(urea–formaldehyde) (PUF) microcapsules filled with dicyclopentadiene (DCPD) healing agent are the most used systems for the above-mentioned purposes. The addition of these microcapsules and Grubbs' Ru catalyst to an epoxy matrix can significantly increase the fracture toughness and improve the fatigue life through a combination of crack tip shielding mechanisms. The epoxy matrix embedded microcapsules also exhibit the ability to recover as much as 90% of its virgin fracture toughness through self-healing of fatigue damage [1,3–7]. For fiber reinforced epoxy matrix, the addition of microencapsulated healing agent and a solid chemical catalyst can yield recovery of virgin interlaminar fracture toughness [8,9]. Two PUF microcapsules systems, one containing vinyl terminated poly(dimethyl siloxane) (PDMS) resin and platinum catalyst complexes, the other containing a PDMS copolymer that crosslinks to the functional PDMS resin via the platinum catalyst, have been applied to PDMS matrix to provide an efficient autonomic healing functionality and improve the tear resistance [10]. Obviously, the polymeric composites containing microcapsules show great potential for solving some of the most limiting problems of polymeric structural materials [2].

Epoxy resins have been widely used as higher performance materials, adhesive, matrices of composites and electric encapsulating materials due to their high modulus and strength, excellent chemical resistance and so on [11–14]. They can be used as healing agents and the microencapsulated epoxy resins may be a promising candidate for self-healing or toughening polymer composites. Microencapsulated epoxy resins have been successfully synthesized [15–17]. The PUF microcapsules containing epoxy resins have been incorporated into epoxy matrix. In the case of 10 wt% microcapsules and 2 wt% $CuBr_2$(2-MeIm)$_4$ (the complex of $CuBr_2$ and 2-methylimidazole) latent hardener, the epoxy matrix exhibits a 111% recovery of its original fracture toughness. Besides, the glass fabric reinforced epoxy matrix containing microcapsules receives a healing efficiency of 68% [18].

Because the strength, diameter, the amount of liquid core and the concentration of microcapsules have significant effects on the virgin and healed fracture toughness of polymer matrix [3,19,20].

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Table 1
The composition of microcapsule prepared at different process parameters

Sample number	Surfactant	Surfactant concentration (wt%)	Heating rate (°C min^{-1})	Adjusting time for pH value (h)	Agitation rate (rpm)	Yield (%)
1-1	Unused	0.00	0.2	2–3	340	<23.0
1-2	OP-10	1.00	0.2	2–3	340	43.0
1-3	SMA	1.00	0.2	2–3	340	52.3
1-4	SDS	1.00	0.2	2–3	340	72.0
1-5[a]	SDBS	1.00	0.2	2–3	340	97.0
2-1	SDBS	0.25	0.2	2–3	340	95.6
2-2[a]	SDBS	1.00	0.2	2–3	340	97.0
2-3	SDBS	1.50	0.2	2–3	340	96.5
3-1	SDBS	1.00	0.1	2–3	380	95.0
3-2[b]	SDBS	1.00	0.2	2–3	380	97.0
3-3	SDBS	1.00	0.5	2–3	380	96.0
4-1	SDBS	1.00	0.2	5–6	380	95.5
4-2[b]	SDBS	1.00	0.2	2–3	380	97.0
4-3	SDBS	1.00	0.2	1–2	380	95.2

[a] Samples No. 1-5 and 2-2 have the same process parameters.
[b] Samples No. 3-2 and 4-2 have the same process parameters.

Selecting appropriate process parameters are important in controlling the properties of microcapsules and improving the self-healing and toughening efficiency [16,21,22].

In our previous studies [15,23,24], the effects of different prepolymers, urea–formaldehyde (U–F) weight ratio, the agitation rate and the core–shell weight ratio on the physical properties of PUF microcapsules filled with epoxy resins were investigated. The effects of diameter, surface morphology and wall thickness on the permeability and stability of microcapsules in the thermal and solvent surroundings were also discussed. In the present study, in order to perfect the preparation process of PUF microcapsules filled with epoxy resins and further investigate the properties of PUF microcapsules, the effects of some new process parameters such as surfactant concentration, heating rate and adjusting time for pH value on the properties of microcapsules were discussed. The properties of microcapsules such as the storage stability property, solvent resistance and the mechanical strength were further investigated.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A epoxy resin (DGEBPA, epoxide equivalent weight: 196 g mol^{-1}) used as core material was purchased from Wuxi Resin Plant, China. 1-Butyl glycidyl ether (BGE) as the reactive diluent of DGEBPA was bought from Shanghai Resin Plant, China. Urea and 37 wt% formaldehyde used as wall shell materials were purchased from Tianjin Chemical Plant, China. Triethanolamine for controlling the pH value of solutions was obtained from Tianjin Chemical Regents Factory, China. Surfactants such as sodium dodecylbenzene sulfonate (SDBS) (99% purity), octyl phenol ethoxylated (OP-10) and sodium dodecyl sulfate (SDS) were also supplied by Tianjin Chemical Regents Factory, China. Surfactant styrene-maleic anhydride (SMA) copolymer was kindly provided by Shanghai Jicheng Chemical Factory, China. 10 wt% sulfuric acid solutions were prepared in our laboratory to control the pH of emulsion.

2.2. Microcapsule preparation

PUF microcapsules were prepared by the following two-step process:

(1) Urea and 37 wt% formaldehyde solution were mixed in a 250-ml three-neck round-bottomed flask connected to a reflux condenser and equipped with a mechanical stirrer at room temperature. When urea was dissolved, the pH value of the resultant solution was adjusted to 8–9 by adding suitable amount of triethanolamine, then the solution was gradually heated to 60–70 °C and maintained at that temperature for 1 h to obtain the prepolymer solution of urea–formaldehyde.
(2) Under agitation, the surfactant water solution was added into the prepolymer solution of urea–formaldehyde prepared in the first step to form Solution A, then a mixture of DGEBPA and BGE (the weight ratio of BGE to DGEBPA = 0.15) was slowly added into Solution A to form an oil in water (O/W) emulsion. After stirred for 20–30 min, the pH value of the emulsion was slowly adjusted to a certain value by adding suitable amount of 10 wt% sulfuric acid solution, and the emulsion was slowly heated to the target temperature of 60–65 °C. After maintained at that temperature for 3 h, a suspension of microcapsules was obtained. Cooled down to ambient temperature, the suspension was rinsed with deionized water and acetone, subsequently, and filtered. After that the filter residue was air-dried for 24 h to obtain PUF microcapsule.

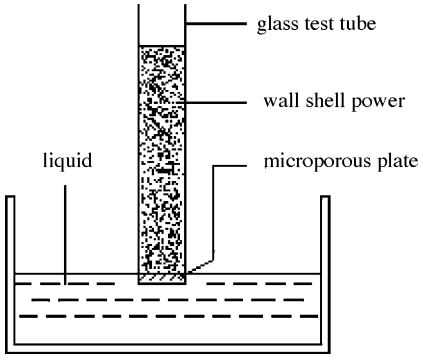


Fig. 1. Schematic of wettability of PUF powders measured by capillary rise technology.

Various PUF microcapsules prepared with different process parameters are presented in Table 1.

2.3. Characterization of microcapsules

The surface morphology of microcapsule was observed using scanning electron microscope (SEM, QUANTA200, FEI) and optical microscope (OM, XSP-XSZ, Beijing Tech Instrument Co., Ltd, China).

The microcapsule size was determined using OM equipped with image analysis software. For each type of microcapsules, its mean diameter was obtained by calculating at least 250 microcapsules.

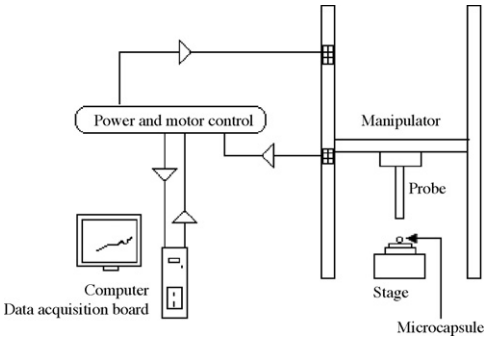


Fig. 2. Schematic of the micromanipulation rig.

2.4. Determination of core content of microcapsule

The core content of microcapsules was determined by the extracting method according to our previous study [15]. The microcapsule samples were grinded with a pestle in a mortar at room temperature, then the crushed microcapsules were collected and washed with acetone several times. After that, the microcapsules were dried at room temperature. The core content ($W_{V_{\text{core}_i}}$) of microcapsules can be calculated according to the following equations:

$$W_{V_{\text{UF}_i}} = \frac{W_{\text{UF}_i}}{W_{0_{M_i}}} \times 100\% \quad (1)$$

$$W_{V_{\text{core}_i}} = 1 - W_{V_{\text{UF}_i}} \quad (2)$$

where $W_{0_{M_i}}$ refers the initial weight of intact microcapsules, W_{UF_i} refers the weight of residual wall shell of microcapsules, and $W_{V_{\text{UF}_i}}$ is the wall shell content.

2.5. The wettability of PUF powder on core material

The wettability of PUF wall shell powders on the core mixture of DGEBPA and BGE (the weight ratio of BGE to DGEBPA = 0.15) was performed by using capillary rise technology through the Washbum's equation as shown in Eq. (3) [25,26]:

$$h^2 = \left(\frac{cr\sigma\cos\theta}{\eta}\right) t \quad (3)$$

where, c is the factor of capillary, r is the capillary radius (cm), σ is the surface tension (N m^{-1}), η is the viscosity of liquid (Pa s), θ is the contact angle of liquid on the PUF powder (°), and h is the liquid penetration distance into the capillary at different time t.

Based on the value of h along the glass column at time t, the curve of h^2 versus t according to Eq. (3) can be plotted. If the slop of the curve is coded as k, then it

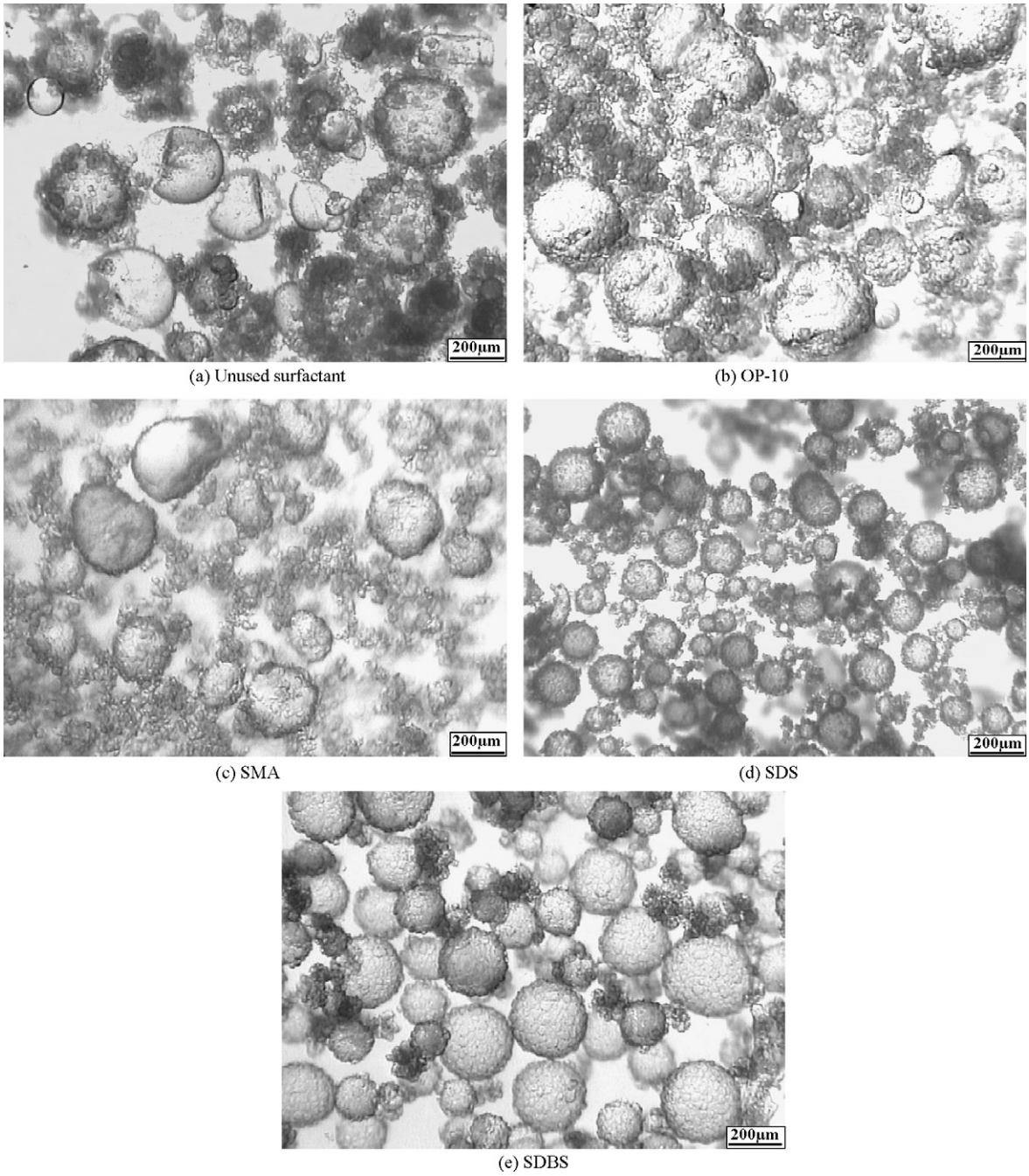


Fig. 3. OM morphologies of microcapsules prepared by selecting different surfactants (magnification: 40×).

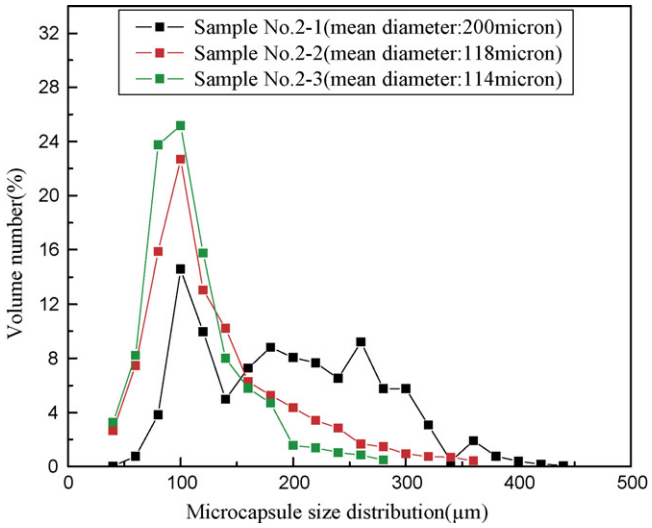


Fig. 4. Size distributions of microcapsules prepared by selecting different surfactant concentration along with the mean diameters (samples No. 2-1 to No. 2-3).

represents the penetration rate.

$$k = \frac{cr\sigma \cos\theta}{\eta} \quad (4)$$

Because the capillaries inside the column are tortuous and their radii vary within the column, so the overall penetration process is an average of the individual process, and thus k represents an average penetration rate.

Fig. 1 shows a schematic for measuring the wettability of PUF wall shell powders on the core material. The bottom end of a glass test tube (height = 20 cm, inner diameter = 6 mm) was obturated by a sintered micropore glass plate. 1.5 g PUF powders were added into the glass tube and packed manually, the measured height of packed powders was 95 mm. Here, it was assumed that the radii of pores in the packed PUF powders were the radii of the capillaries.

2.6. Mechanical property of microcapsule

In this study, the mechanical strength of microcapsule was measured by a micromanipulation technique according to Refs. [19,27]. The principle of the micromanipulation technique is compressing single microcapsule between two parallel surfaces. This technique was used to measure the bursting force and deformation of microcapsule. Microcapsule was compressed to large deformations or ruptured at a pre-set speed. Both the force imposed on microcapsule and the deformation of microcapsule were recorded simultaneously. Measurement was performed at a driving speed of 3 μm s^{-1}. In this study, we assumed that the zero of separation was at the point of the first measurable force. The relative deformation of the capsules was defined as the ratio of the deformation to the diameter of capsules. Fig. 2 shows a schematic of the micromanipulation rig.

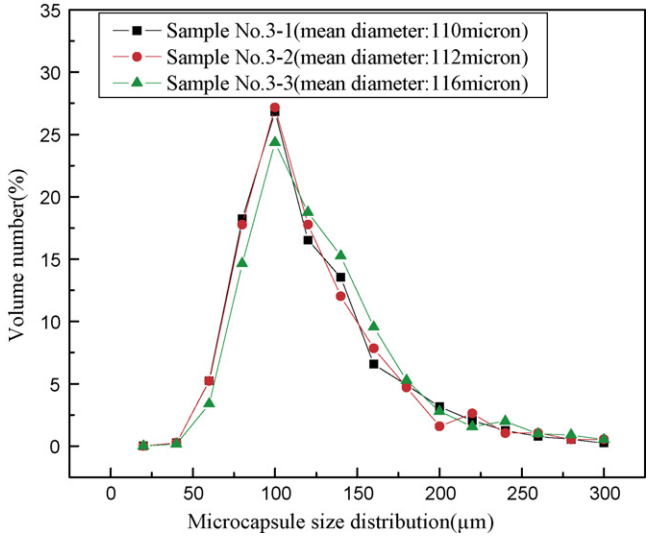
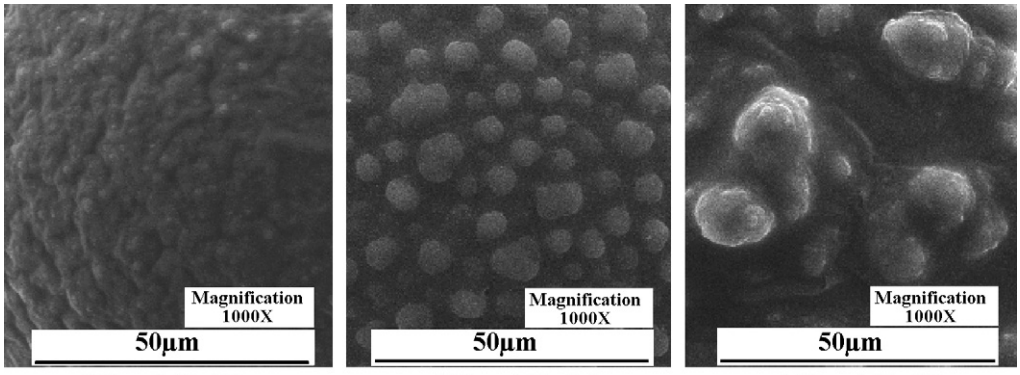


Fig. 6. Size distributions of microcapsules along with the mean diameters (samples No. 3-1 to No. 3-3).

3. Results and discussion

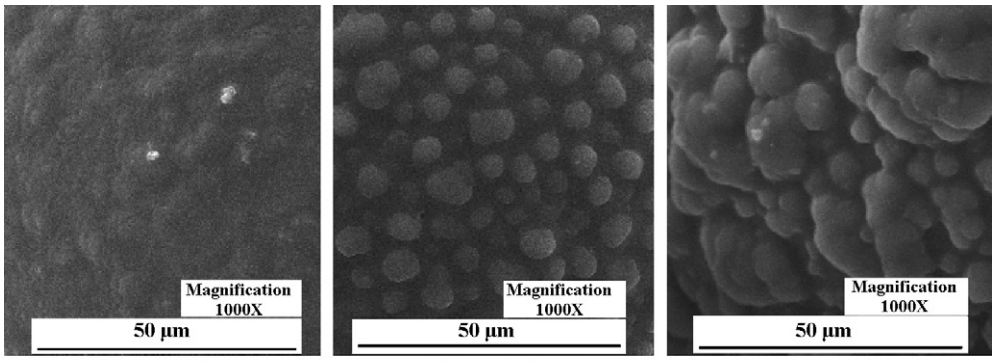
3.1. Effects of the surfactant type on the microcapsule formation

Fig. 3 shows OM micrographs of microcapsules prepared by using different surfactants such as OP-10, SMA, SDS or SDBS, respectively (samples No. 1-1 to No. 1-5). When no surfactant is used, microcapsules have irregular shapes as shown in Fig. 3(a), which indicates that the core droplets in solution are not stable even with the aid of the mechanical agitation. The larger amount of aggregated PUF nanoparticles in solution indicates that it is difficult for PUF nanoparticles to deposit on the surface of microcapsule. Obviously, the surfaces of microcapsules are not compact, so the microcapsules are easily fractured during the washing process. When OP-10 or SMA is used as the emulsifier to prepare microcapsules, the resultant microcapsules have irregular shapes, and many PUF nanoparticles aggregate in solution as shown in Fig. 3(b) and (c). Although the addition of OP-10 or SMA can decrease the surface tension and stabilize the core droplets, the solution viscosity is so high that PUF nanoparticles are prone to flocculate. In addition, both solutions of OP-10 and SMA have weak acidity (pH 6–7), which may accelerate the reaction of urea–formaldehyde resins. Due to the fast deposition of PUF nanoparticles, they cannot form a compact wall shell. When SDS is used as the emulsifier, the resultant microcapsules are spherical, but many PUF nanoparticles



(a) Sample No. 2-1 (b) Sample No. 2-2 (c) Sample No. 2-3

Fig. 5. Surface morphologies of microcapsules prepared by selecting different SDBS concentration (samples No. 2-1 to No. 2-3).



(a) Sample No. 3-1 (b) Sample No. 3-2 (c) Sample No. 3-3

Fig. 7. Surface morphologies of microcapsules (samples No. 3-1 to No. 3-3).

flocculate on the surfaces of microcapsules as shown in Fig. 3(d), which tend to release the core materials and decrease the stability of microcapsules. When SDBS is employed as the emulsifier, a great many spherical microcapsules can be observed as shown in Fig. 3(e) and the surfaces of microcapsules are relatively compact. Besides, Table 1 shows that the yield of synthesizing microcapsules by using SDBS is the largest one among those by using other materials as the emulsifier. The results can be attributed to the fact that SDBS is relatively stable no matter in alkaline solution or in neutral and weak acidic solutions, so it is beneficial to dispersing the core droplets. Based on above results, it is believed that SDBS is the optimal emulsifier in this study.

3.2. *Effects of SDBS concentration on the properties of microcapsules*

Fig. 4 shows the size distributions of microcapsules prepared by using SDBS as the emulsifier with different concentrations (0.25, 1.00 and 1.50 wt%). As SDBS surfactant concentration increases, the microcapsule size distribution becomes narrow and the mean diameter of microcapsules decreases, which are consistent with the results reported by other researches [28]. Increased surfactant concentration can form fine core droplets and reduce the collisions of smaller droplets, and accordingly, the sizes of microcapsules become smaller [29,30].

The calculated core contents of microcapsule samples No. 2-1, No. 2-2 and No. 2-3 are 75.9%, 77.0% and 76.5%, respectively. The yields of microcapsule samples No. 2-1, No. 2-2 and No. 2-3 are 95.6%, 97.0% and 96.5%, respectively. Obviously, the SDBS concentration has no significant influence on the core content and yield of microcapsules.

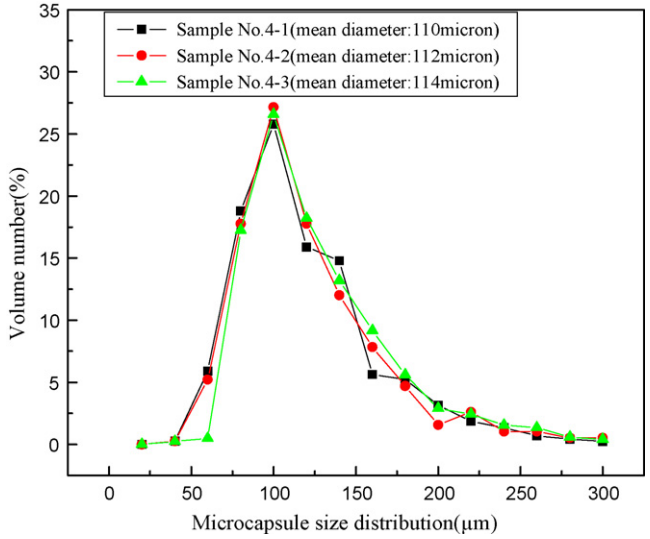
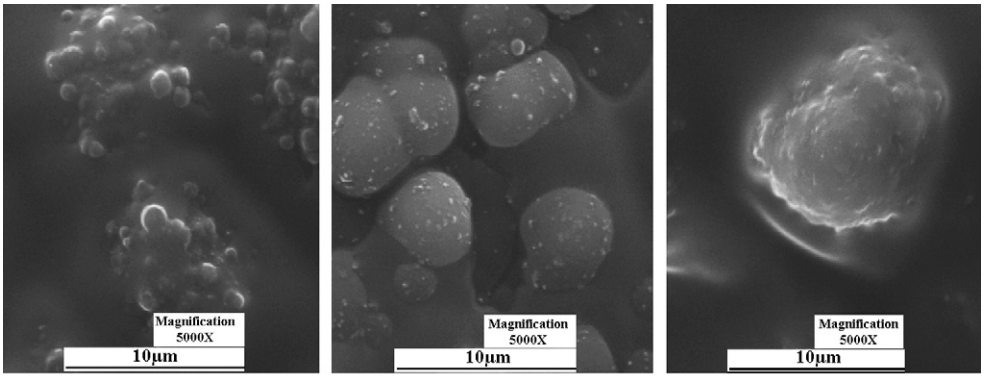


Fig. 8. Microcapsule size distributions along with mean diameters (samples No. 4-1 to No. 4-3).

Fig. 5 shows the surface morphologies of microcapsule samples No. 2-1 to No. 2-3. As the SDBS concentration increases, the surface of microcapsules becomes rough. Although the increase of SDBS concentration can improve the dispersion of core materials, the coulombic repulsion between the micelles becomes larger, leading to the formation of mixed micelles and the electroviscous property, and accordingly, the higher viscosity of the mixed system arises [31,32], resulting in the formation of rougher surface of microcapsule.



(a) Sample No. 4-1 (b) Sample No. 4-3 (c) Sample No. 4-2

Fig. 9. Surface morphologies of microcapsules (samples No. 4-1 to No. 4-3).

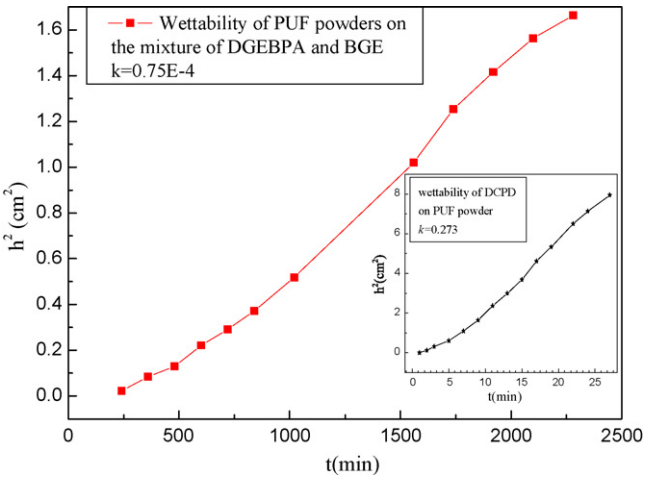


Fig. 10. The wettability of the PUF powders on the mixture of DGEBPA and BGE along with the wettability of PUF powders on DCPD.

3.3. Effects of heating rate on the properties of microcapsules

Fig. 6 shows the size distributions of microcapsules prepared with different heating rate (samples No. 3-1 to No. 3-3), and Fig. 7 gives the surface morphologies of corresponding microcapsules. The size distribution curves for all microcapsule samples are similar. As the heating rate increases, the mean diameter of microcapsules slightly increases and the surface of microcapsule becomes rougher. The reason is that with the increase of the heating rate, the condensation reaction of urea–formaldehyde resins accelerates [33], and the deposition rate of PUF nanoparticles on the microcapsule surface enhances, resulting in rougher and porous outer layer of the PUF wall shell as shown in Fig. 7(c). When keeping other parameters constant, the wall shell thickness of microcapsule with rougher and porous layer is thicker than that of microcapsule with smoother and compact surface. As a result, the size of microcapsule with rougher surface is slightly larger than that of microcapsule with smoother surface.

The calculated core contents of microcapsule samples No. 3-1, No. 3-2 and No. 3-3 are 77.4%, 77.0% and 76.8%, respectively, and the corresponding yields are 95.0%, 97.0% and 96.0%, respectively. These results suggest that the heating rate has no manifest effect on the core content and yield of microcapsules in this study.

3.4. Effects of adjusting time for pH value on the properties of microcapsules

Fig. 8 shows the size distributions of microcapsules prepared by selecting different adjusting time for pH value (samples No. 4-1 to No. 4-3). Fig. 9 shows the surface morphologies of microcapsules (samples No. 4-1 to No. 4-3). The size distributions of all microcapsule samples are similar. As the adjusting time decreases, the mean diameter of microcapsules slightly increases and the roughness of the microcapsule surface increases. The reason causing these phenomena is that the condensation rate of urea–formaldehyde resin increases with the decrease of the adjusting time for the pH value of solution [33], resulting in the deposition speed of PUF nanoparticles on microcapsule surface increases.

The calculated core contents of samples No. 4-1, No. 4-2 and No. 4-3 are 77.1%, 77.0%, and 76.6%, respectively, and the corresponding yields are 95.5%, 97.0% and 95.2%, respectively, indicating that the adjusting time for pH value has no significant effect on the core content and the yield of microcapsules.

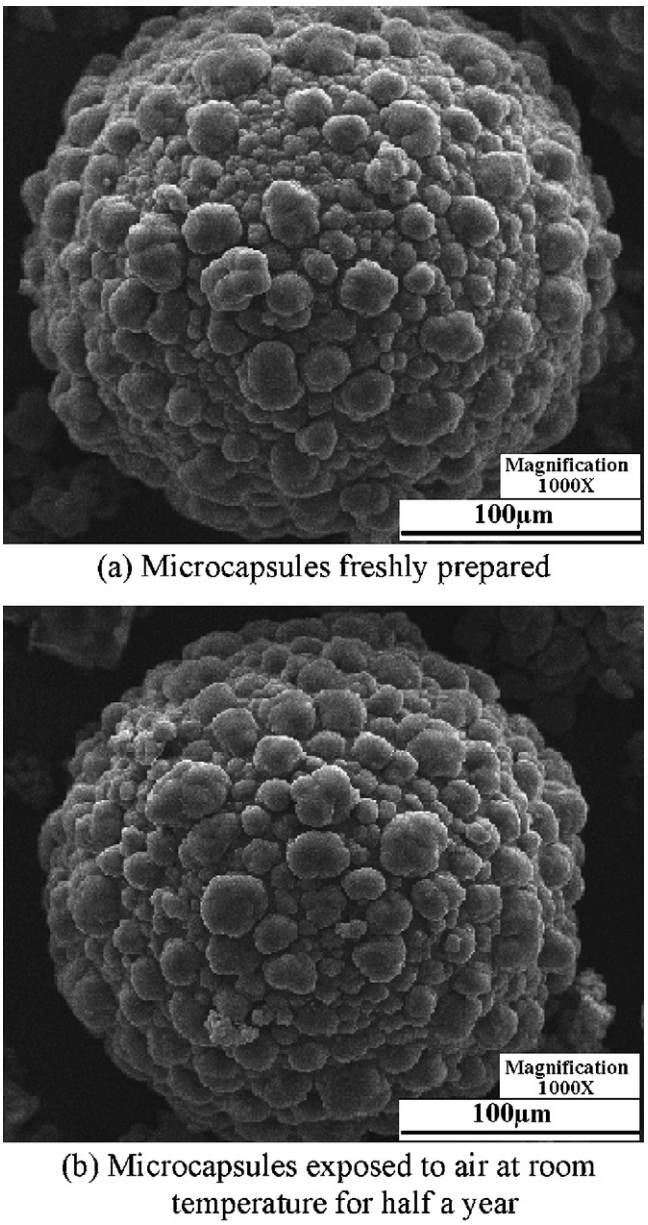


Fig. 11. SEM micrographs of microcapsules.

3.5. The wettability of core material on the PUF powders

The wettability effect of PUF powders on core material implies the storage stability of microcapsules. Fig. 10 shows the wettability of PUF powders on the mixture of DGEBPA and BGE, the wettability of PUF powders on DCPD is also given for comparison. The penetration rate (k) of PUF on the mixture of DGEBPA and BGE is 0.075×10^{-3}, which is very small when compared with that on DCPD (about 0.273), indicating that the wettability of PUF on the mixture of DGEBPA and BGE is very poor and thus microcapsules filled with epoxy resins have higher storage stability.

Fig. 11 shows the morphologies of microcapsules prepared by using surfactant SDBS after exposure to air at room temperature for half a year. Compared with that of freshly prepared microcapsules, the microcapsules exposed to air have almost the same surface morphologies, reflecting that the microcapsules can possess a long service lifetime at room temperature.

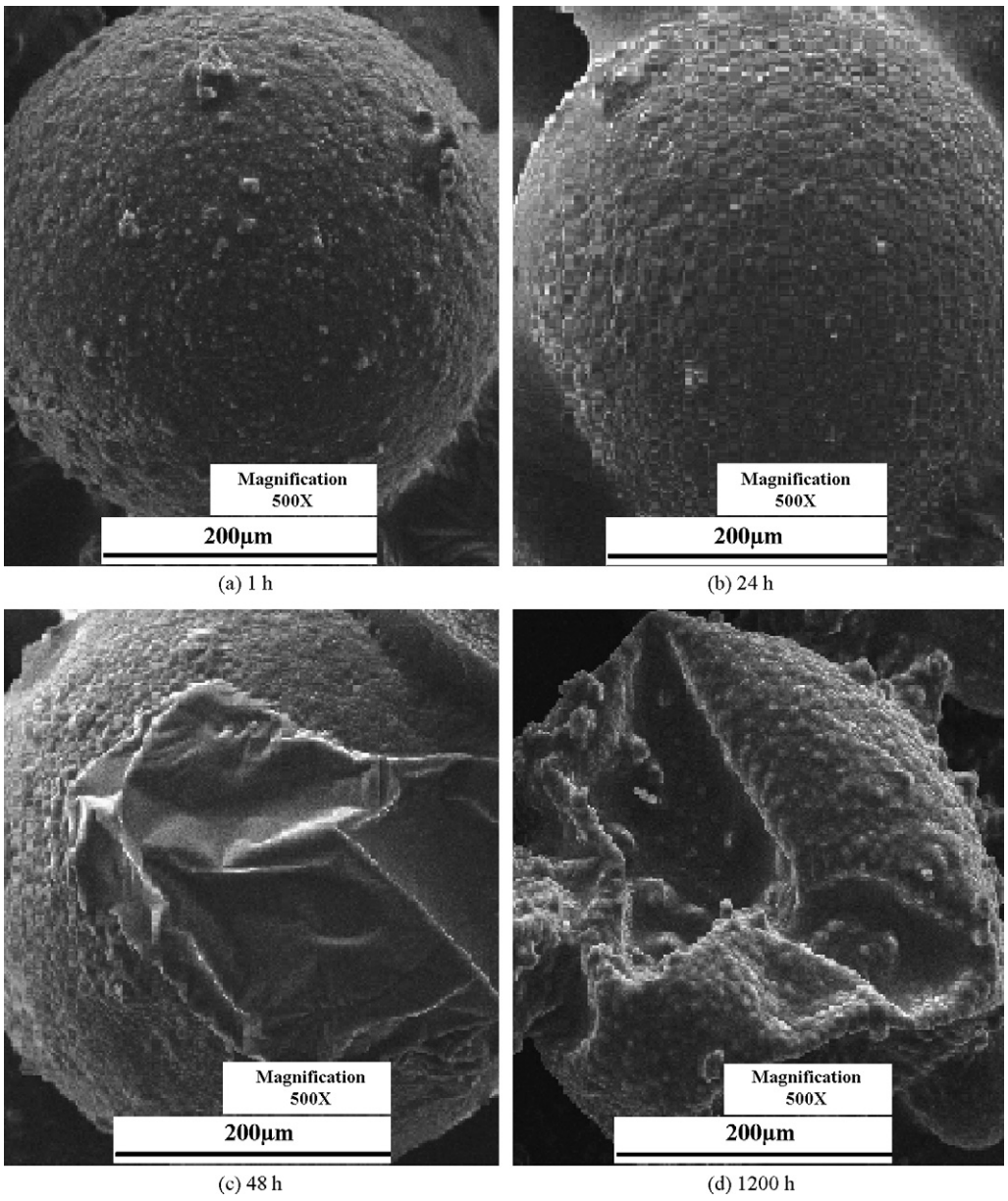


Fig. 12. SEM micrographs of microcapsules acetone-treated at different time (microcapsules with diameter of 400 ± 50 μm and wall thickness of 56 ± 5 μm).

3.6. The solvent resistance of microcapsules

When microcapsules are basic component of a polymeric composite, and the composite is fabricated by the wet method (solvent method), the solvent resistance of these microcapsules is important. Because acetone is the most often used solvent for fabricating polymeric composites by the wet method, it can be selected to evaluate the solvent resistance of microcapsules. The permeability of microcapsules in acetone has been discussed in detail in our previous article [24], but the relationship between the morphology of microcapsules and acetone-treated time has not been investigated. Fig. 12 shows SEM micrographs of microcapsules at different acetone-treated time. It can be seen that when the acetone-treated time is less than 24 h, the microcapsules remain intact as shown in Fig. 12(a) and (b), indicating that the microcapsules have very good acetone resistance, that is, there is enough time to fabricate polymeric composites containing microcapsules by the solvent method. With prolonged acetone-treated time, the dents occur on the microcapsule surfaces (Fig. 12(c)) and the amount of deformed microcapsules increases (Fig. 12(d)). The deformation of microcapsules is attributed to the diffusion of core material out of PUF wall shell and the contraction of wall shell. With careful observation, it is also found that the microcapsule with smaller diameter has less deformation than that with larger diameter, because the wall shell of the former has smaller contraction than that of the latter.

3.7. The mechanical properties of microcapsules

Microcapsules for self-healing or toughening composites should have appropriate mechanical strength, so it is necessary to investigate the mechanical properties of the microcapsules. In this study, the PUF microcapsule prepared by using surfactant SDBS was selected to study for this investigation. Fig. 13 shows the load-displacement curve when a microcapsule is compressed to

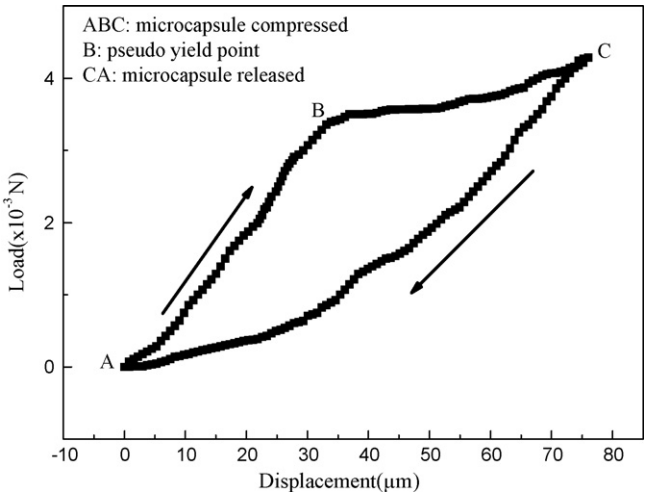


Fig. 13. Load-displacement curve (the compressed microcapsules with diameter of $400 \pm 50\,\mu m$ and wall thickness of $56 \pm 5\,\mu m$). The compression speed is $3\,\mu m\,s^{-1}$.

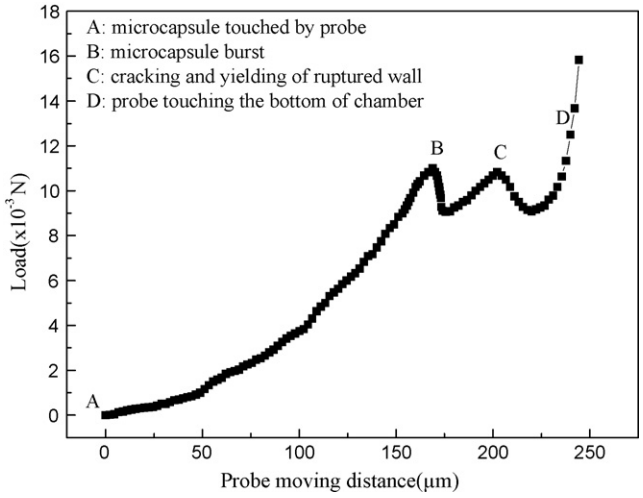


Fig. 14. Load vs. probe moving distance for compressing microcapsule to rupture (the compressed microcapsules with diameter of $400 \pm 50\,\mu m$ and wall thickness of $56 \pm 5\,\mu m$).

a relatively large deformation around 20% and then released. The load imposed on the microcapsules drops to zero when the load probe returns to its original position. A hysteresis is found in the load-displacement curve, indicating that the microcapsules have a permanent (plastic) deformation after the load put on them is completely released. A pseudo yield point (point 'B') can be observed in Fig. 13, which implies that the plastic behavior begins from the point [27], and the deformation corresponding to the yield point is about 8%.

Fig. 14 shows the plot of load versus probe moving distance for compressing microcapsule to rupture. When PUF microcapsule is compressed to a deformation around 42%, it exhibits a clear bursting represented by point 'B' in Fig. 14. Further compression shows a slight reduction in peak load reflected by point 'C', which is attributed to the localized damage such as cracking or shear yielding of the wall shell [19].

The rupture force of all studied microcapsules is $(8–11) \times 10^{-3}$ N. The deformation of microcapsule increases with the enhancement of the microcapsule diameter as shown in Fig. 15. Smaller microcapsules sustain lower load for a given displacement, the dependence of failure strength on the microcapsule diameter has good agreement with the results reported by other researchers [19]. The rougher surface of microcapsule may slightly decrease the mechanical property of microcapsule. Therefore, the mechanical strengths of PUF microcapsules can be adjusted by selecting different process parameters for synthesizing PUF microcapsules.

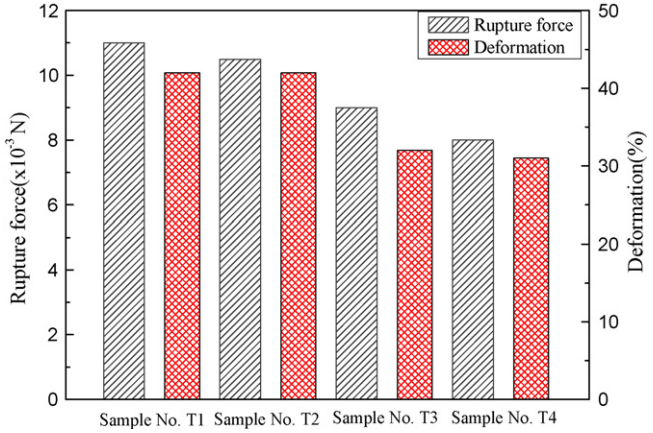


Fig. 15. The mechanical property of microcapsules with different diameter and morphology.

4. Conclusions

The synthesis and the properties of PUF microcapsules filled with epoxy resins were further investigated. Increasing the surfactant concentration can reduce the size of microcapsules and enhance the surface roughness of microcapsules. Reducing pH adjusting time and increasing the heating rate can enhance the surface roughness of microcapsules. Other process parameters such as adjusting time for pH value and the heating rate have no significant influences on the size, core content and yield of microcapsules. In the present study, SDBS is the optimum surfactant to synthesize PUF microcapsules filled with epoxy resins, the resultant PUF microcapsules can bear some load ($(8–11) \times 10^{-3}$ N) and also have good solvent resistance, and thus can be used to fabricate polymeric composites by the wet method. According to the Refs. [4,21], the PUF microcapsules with rougher surface and larger diameter are helpful to improve the self-healing efficiency of polymeric composites. So in this study, the optimal process parameters for synthesizing PUF microcapsules filled with epoxy resins are as follows: SDBS concentration: 1.0 wt%, heating rate: $0.2\,^{\circ}C\,min^{-1}$, and adjusting time for pH value: 2–3 h.

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