Optimal Preparation and Characterization of Poly(urea–formaldehyde) Microcapsules

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ABSTRACT: Microcapsules with epoxy curing agent were successfully prepared by an in-situ polymerization route with epoxy resin and poly-(urea–formaldehyde) as core and shell materials, respectively. The synthetic conditions were optimized by a comprehensive investigation on raw materials consumption, size distribution, and surface morphology. Preparation of microcapsules with high wrap ratio was also demonstrated. The as-synthesized microcapsules were studied using various characterizations techniques, including optical microscope, fourier transform infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry, and contact angle meter. Spherical microcapsules (size: $\sim$ 60 μm) with smooth surface were obtained when the stirring rate was 400 rpm and the amount of core materials is 76 wt %. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2162–2169, 2010

Key words: microcapsule; urea–formaldehyde resin; epoxy resin; contact angle

INTRODUCTIONS

Polymeric materials always inevitably have cracks and damages due to the effect of external environment during their long-term use, which leads to the degradation of mechanical properties and even loss of function. Although traditional techniques play a positive role in maintaining materials properties, it usually requires more energy and resources. To combat this challenge, self-repairing microcapsules have attracted increasing attention as they are demonstrated to more durable and reliable.[1–6] Microcapsule refers a specific type of microcontainer in which the inner and outer space is separated by shell materials. The diameter and shell thickness are usually 1–1000 μm and 0.2–10 μm,[7] respectively. One of the most important advantages of microcapsules is that the core materials can be retained inside without external influence.

Epoxy is one of the promising candidates for versatile healing because of its good adhesion to various materials; therefore, microcapsules with epoxy as shell materials become an important class of materials for self-repairing composites. To the best of the author's knowledge, current common separate method is through separation under vacuum with either a coarse-fritted filter[8] or a Buchner funnel.[9] Herein, in this article, encapsulation of epoxy resin was successfully achieved through an oil-in-water emulsion route with an improvement of polymerization.[10] Other methods were also demonstrated to obtain microcapsules with high core content. Several key experimental parameters, including core materials emulsification time, the amount of emulsifier, pH value, and solid content, were also studied in detail.[11]

EXPERIMENTAL

Raw materials and equipment

Core material: epoxy resin (E-51); wall material: urea and formaldehyde (37%); emulsifier: sodium dodecyl benzene sulfonate (SDBS) and gum Arabic; dispersion medium: deionized water; solidified agent: hydrochloric acid (HCl) and ammonium chloride (NH_4Cl); pH regulator: triethanolamine; anhydrous sodium carbonate ($NaCO_3$). All the chemicals were analytical grade and used without further purification.

Equipment: optical microscope (OM) (B $\times$51, Olympus, Japan), fourier transform infrared

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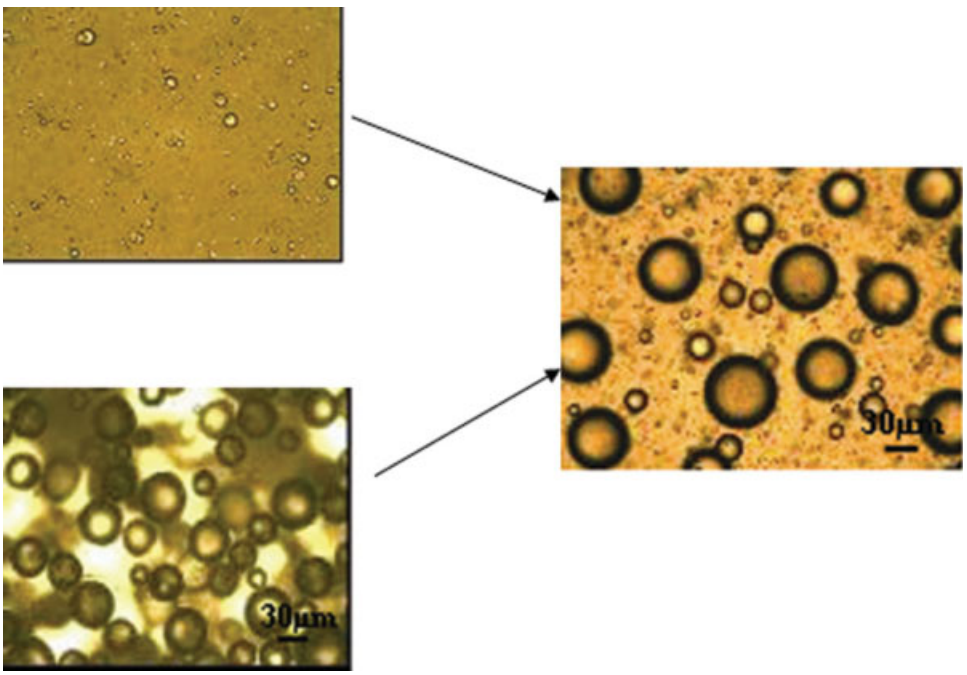

Figure 1 Optical microscope image of formation process of the microcapsules. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

spectroscopy (FTIR) (Spectrum 100, PerkinElmer, Waltham, MA), thermogravimetric analysis (TGA) (Q500, TA, New Castle, DE), and differential scanning calorimetry (DSC) (DSC-204, NETZSCH, Germany); Contact angle meter (JC2000, Shanghai zhongchen digital technic apparatus China).

Preparation of microcapsule

Prepolymer preparation

Urea (0.03 mol) and formaldehyde (0.06 mol) were added in a 100 mL three-necked flask and stirred at 80–90°C for 1 h; urea was added in batches in order to reduce the amount of free formaldehyde. The pH value of the solution was kept about 8–9 by adding triethanolamine. In order to detect the end point of reaction, a drop of the reaction solution was dropped on the slide and mixed with water at molar ratio of 1 : 2, then shaking, end the reaction as soon as the turbidity appeared.[12]

Emulsion preparation

E-51 (14.3 g), SDBS (0.73 g), gum Arabic (2.2 g), and deionized water (60 mL) were added in a 250 mL three-necked flask fitted with a stirrer, distillation

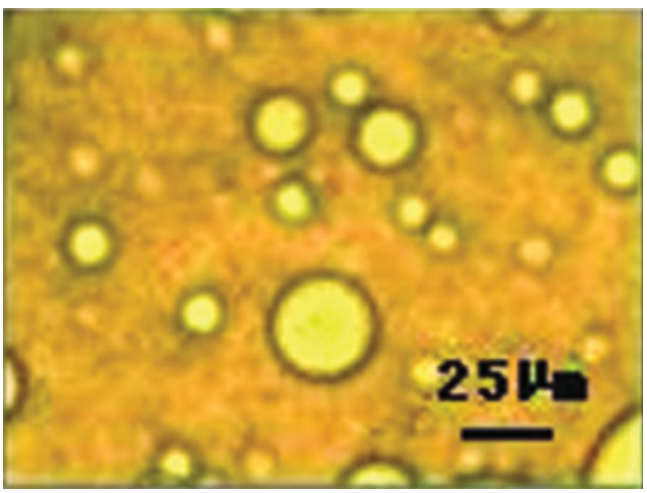

Figure 2 Optical microscope image of filtrate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

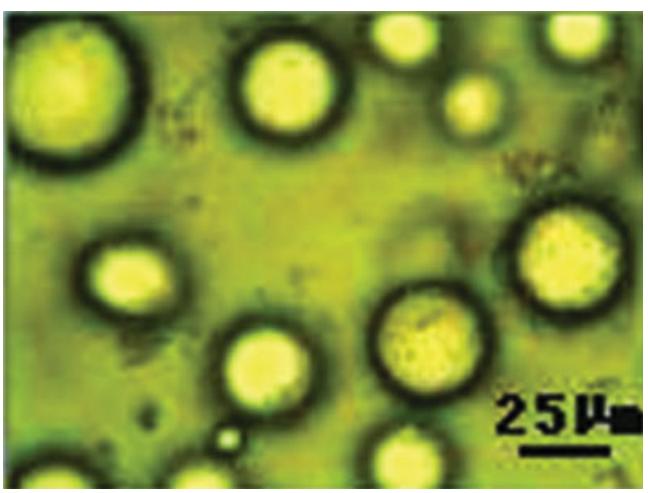

Figure 3 Optical microscope image of product on paper after filtrate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

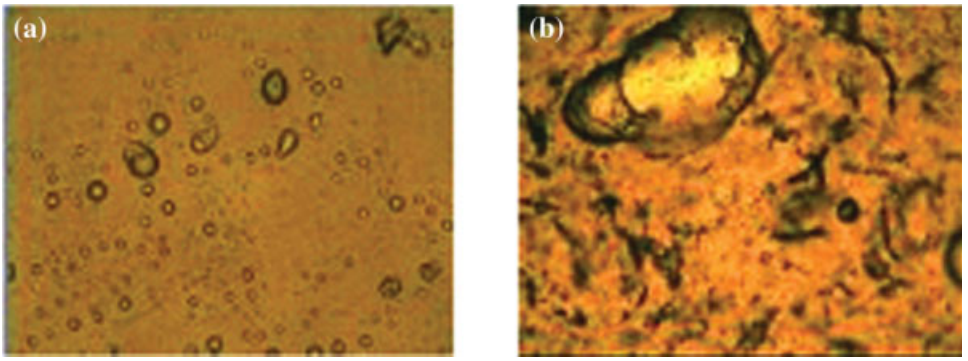

Figure 4 Optical microscope image of centrifugal separation. (a) The upper centrifugal and (b) The lower centrifugal. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

head and condenser, and stirred at room temperature for 1 h, finally the emulsion was obtained.

Synthesis of microcapsules

Prepared prepolymer was added into the above emulsion with 400 rpm continuous mechanical agitation by a three-bladed stirring paddle, reacted at 70°C for 3 h, while the pH value of solution was kept about 3 by adding batches of NH_4Cl and HCl, sampled during the course of reaction and detected microencapsulation process; eventually, the reaction mixture was cooled to room temperature, the resultant slurry was neutralized by 10% $NaCO_3$ solution, and then microcapsule powder was perceived by freeze drying method.

Extracting method of microcapsule

Different approaches were tried to separate microcapsules.

1. Acetone extraction: After cooling, the microcapsule solution was dissolved in acetone, filtered repeatedly under vacuum with Busher funnel, rinsed with deionized water, and vacuum dried for 24–48 h.
2. Centrifugal separation: Cooled microcapsule solution was dumped into a test tube with high-speed centrifuge for 30 min.
3. Spray drying: After cooling, microencapsulation solution was dried by spray dryer.
4. Freeze drying method: After cooling, add the microcapsule solution to freeze-drying machine for 24 h and then vacuum dried.

Performance test and structure characterization

Morphology and size analysis

A sufficient number of microcapsules' diameter were measured, and through statistical analysis calculated average size.[13]

$$\overline{D_n} = \sum n_i D_i \Big/ \sum n_i$$

where $\overline{D_n}$ is the average size of microcapsules, D_i is the diameter of microcapsules, and n_i is the number of microcapsules whose diameter is D_i.

Capsule core contents

Microcapsule samples were broken in a mortar at room temperature and dissolved in acetone. Then extracted by soxhlet apparatus for 72 h to remove the core material. Finally, the collected residual was wall material, vacuum dried, and weighed.

$$\text{Capsule core content} = (m_1 - m_2)/m_1 \times 100\%$$

m_1 stand for the integrity of the initial mass of microcapsules, m_2 stand for the mass of residual wall material.

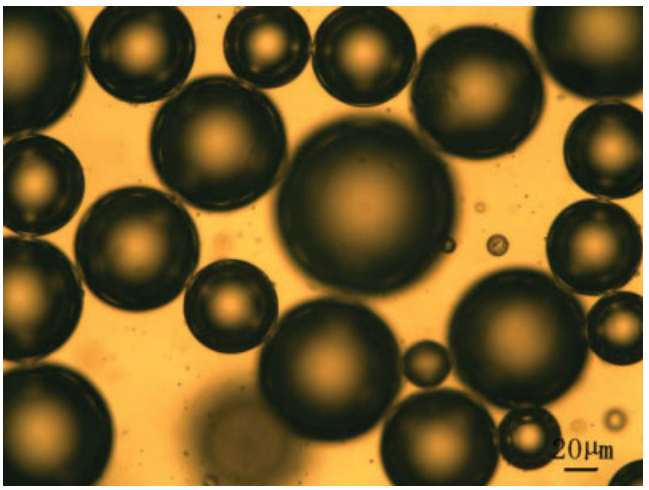

Figure 5 Optical microscope image of microcapsules. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

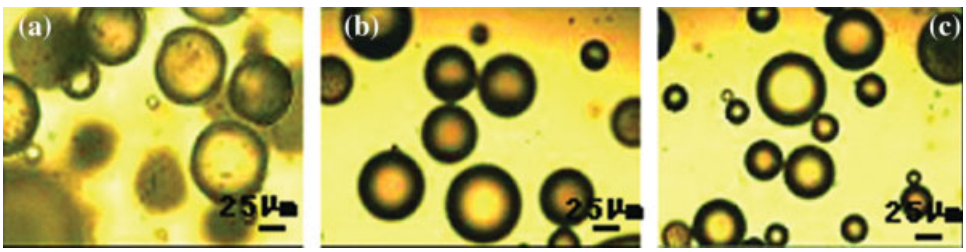

Figure 6 Optical microscope image of emulsion mixing at different time (a) 0.5 h, (b) 1 h, and (c) 1.5 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Contact angle determination

Using contact angle meter measured hydrophilic or hydrophobic property of microcapsule. First, the prepared microcapsule solvent was coated on the glass slide, and then the slide was used to measured contact angle until it was dry.

Molecular structure identification

FTIR spectrometer was used to identify the molecular structure of the microcapsule, which were prepared by grinding the samples with Potassium bromide (KBr) or by attaching the samples to a KBr disc.

Microcapsule thermal stability

TGA and DSC were used to discuss the thermal stability of microcapsule. All experiments were conducted at a heating rate of 10°C/min in a N_2 environment.

RESULTS AND DISCUSSION

Microencapsulation process and separate method

Microencapsulation process

Microcapsules are obtained through mixed prepolymers with emulsion.[14] (Fig. 1) The prepolymer has a number of small spots, and it was UF prepolymer according to judging the reaction. In the emulsion picture, the little ball is the emulsified epoxy resin microspheres, and the black region is the epoxy resin without emulsifying. Then, the prepolymer was mixed with emulsion. UF prepolymer continuously crosslinking and formed high molecular weight UF polymer and adsorbed on the surface of epoxy resin microspheres. Finally, microcapsules with smooth surface, average particle size of about 60 μm, mutual nonadhesion can be received.

Microcapsules separated

1. Acetone extraction: After Acetone extraction, white powder products were received, but the process of filtration caused more losses in filtrate, such as Figures 2 and 3.
2. Centrifugal separation: After centrifugal separation, solution was divided into two tiers from the top to the bottom, and microcapsules were broken in both layers (Fig. 4).
3. Spray drying: And get a white powder and transparent viscous liquid that is epoxy resin, which showed that microcapsules were ruptured during the drying process.
4. Freeze drying method: White powder can be got through freeze drying method.

To sum up, the general method was difficult to separate microcapsules. As the viscosity of the emulsion, the whole system should be blocked when filtrated, the liquid was hardly pumped to go. If microcapsules were filtrated repeatedly, the smaller particles went into the filtrate through the filter. some microcapsules and a large number of products adhered to the filter paper that resulted in great loss. Centrifugal separation broke the microcapsule and fails to separate microcapsule. Spray drying

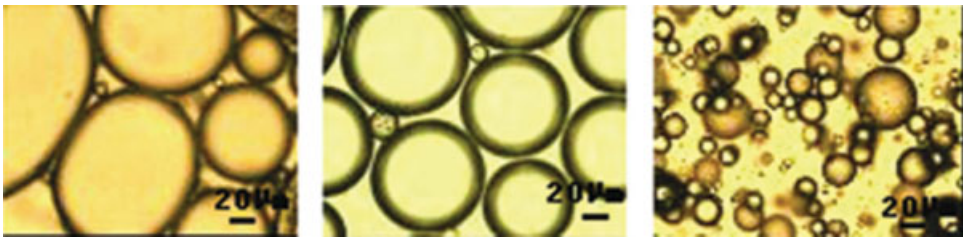

Figure 7 Optical microscope image of effect of emulsifier amount on the formation of microcapsule 0.5%, 3%, and 5%. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

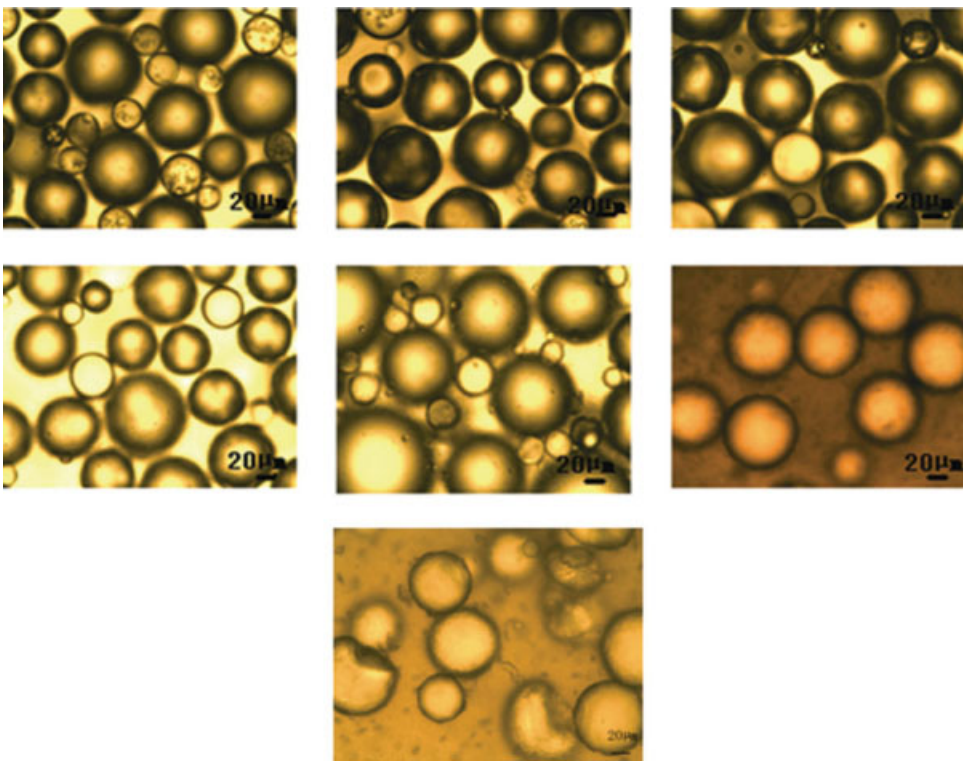

Figure 8 Optical microscope image of pH impact on microcapsules. pH = 8.0, pH = 7.0, pH = 6.0, pH = 5.0, pH = 4.0, pH = 3.0, pH < 3.0. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

rupture microcapsule during the drying process, whereas freeze drying method can get microcapsule successfully without any loss.

Size and morphology of microcapsule

The diameter of microcapsule is about 60 μm seen from OM image of microcapsule (Fig. 5).

Core contents of microcapsules

After repeated measurements, calculated average by formula above, core contents of microcapsule is about 76%.

The determination of core material emulsified time

Emulsion stirred for 0.5 h had the larger size of epoxy resin sphere, but the size distribution is not good and part of epoxy were not emulsified to sphere [Fig. 6(a)]; stirred for 1 h, epoxy resin sphere was good size distribution and had homogeneous size [Fig. 6(b)]; Stirred for 1.5 h, the size distribution was better, but particle size was uneven [Fig. 6(c)]. So, the best core material emulsified time is 1 h.

The effect of emulsifier amount on the formation of microcapsules

Gum Arabic and SDBS were used as emulsifier. The amount of emulsifier that had effect on the formation of microcapsules was studied in detail.

Emulsifier could decrease the interface tension between water and oil phase and formed stable oil-in-water emulsion,[15] which facilitated the interface reaction. If the amount of emulsifier is too small, it was difficult to emulsify the dispersed phase into a stable tiny droplets that lead to failure of microcapsule forming; with excessive amount of emulsifier,

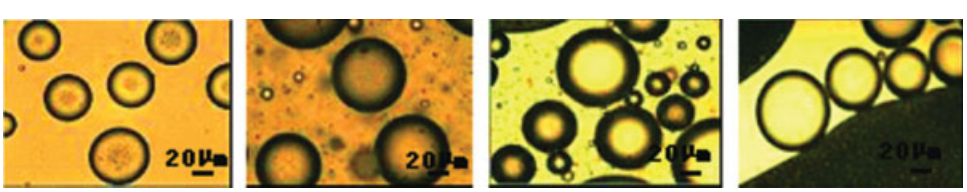

Figure 9 Optical microscope image of impact of solid content on microcapsules 27.7%, 35.7%, 45.9%, 53.1%. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

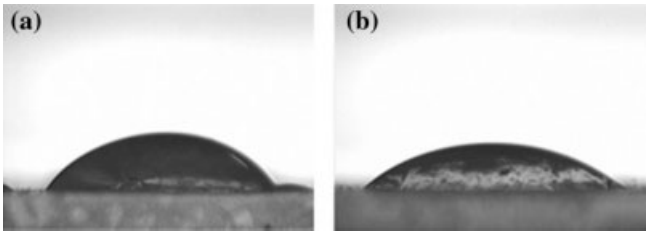

Figure 10 Pictures of contact angle. (a) Contact angle of E-51 emulsion and (b) Contact angle of microcapsule.

the system has high viscosity, and microcapsules cannot be formed either.

When emulsifier was 0.5 wt % (0.48 g), the shape of microcapsules was irregular, connected closely and distributed unevenly; when emulsifier was 3 wt % (2.93 g), the microcapsules had even size; when the emulsifier was 5 wt % (4.8 g), the microcapsules size was too small and distributed unevenly (Fig. 7), so 3 wt % emulsifier was the best amount.

The effect of pH value on microcapsules

In the early stages, the microcapsule system is alkaline, at this time for the deposition of UF, and the microcapsules wall is relatively thick, which is because untight deposition of UF resin. With the lower pH system, microcapsules wall is obviously thin that showed that UF resin have been deposited compactly on epoxy resin. When the pH value is 3, microcapsules with smooth wall are formed. We conclude that the lower the pH value the more the regular shape and morphology of microcapsules, but to some extent, if pH is below 3.0, it will undermine the microcapsules (Fig. 8).

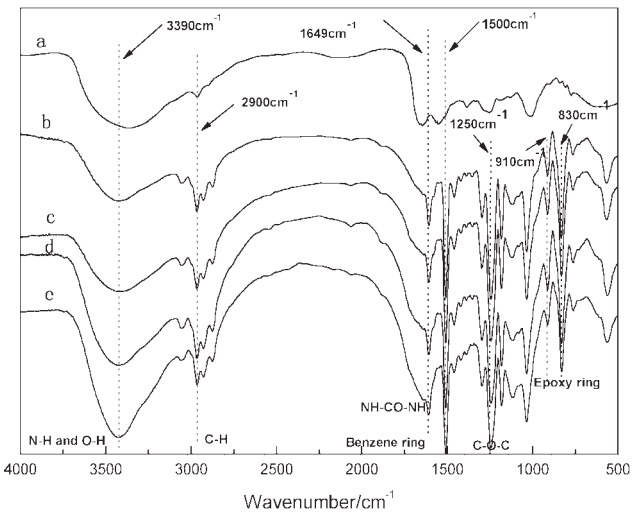

Figure 11 FT-IR spectra of (a) UF, (b) microcapsule without heat treatment, (c) microcapsule with heat treatment at 100°C, (d) microcapsule with heat treatment at 140°C, and (e) microcapsule with heat treatment at 180°C.

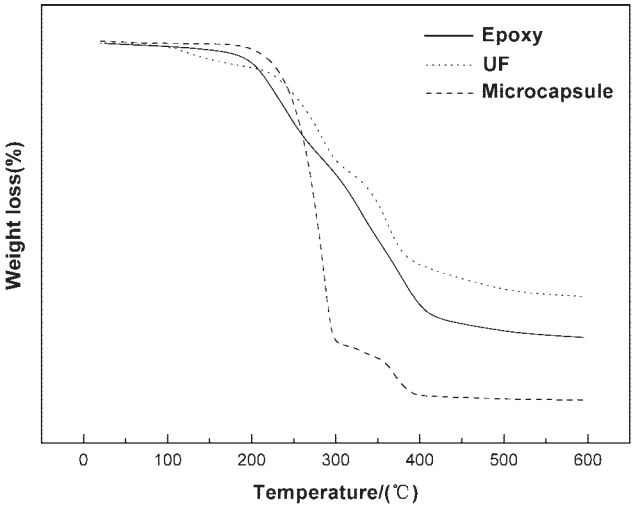

Figure 12 TGA curve of microcapsule compared with the shell wall and core material.

The effect of solid content on the formation of microcapsules

It can be seen in Figure 9 when solid content is too low, it generates a small number of microcapsules with unevenly size distribution and the thinner outer wall. whereas, when the solid content is too high most were not coated with epoxy resin during the process of microcapsules formation. When the solid content is between 35.7 and 45.9%, the microcapsules distributed evenly, microcapsules extraction was also easily, and the amount of solid products also increased. so, solid content from 35.7 to 45.9% was suitable.

Determination of contact angle

Figure 10 showed that the contact angle of E-51 emulsion is bigger than microcapsule, because epoxy resin is lipophilic whereas urea–formaldehyde resin is hydrophilic, which can confirm the microcapsule have been prepared successfully.

Structure identification of microcapsule

Infrared spectrum of microcapsule

FTIR (Fig. 11) analysis showed that the products contained —OH and —NH group (3390 cm^{-1}), –CH group (2900 cm^{-1}). 1649 cm^{-1} and 1500 cm^{-1} was the characteristic absorption of PUF and benzene ring, respectively. Absorption peak at 1250 cm^{-1} was ν_{C-O-C}, and the two peaks at $\nu = 910$ cm^{-1} and 830 cm^{-1} are ascribed to epoxy ring. From the spectrum can be analyzed that microcapsule shell material and microcapsule had been synthesized. The FTIR spectra of microcapsule with heat treatment was almost similar to the untreated one. The

TABLE I
Temperature Corresponding to Weight Loss in TGA

Items	Material					
	Epoxy		UF		Microcapsule	
Weight loss (%)	95	50	95	50	95	50
Temperature (°C)	220	278	165	366	199	345

characteristics of epoxy peak (910 cm^{-1} and 830 cm^{-1}) still existed after heat treatment; it mean that microcapsules had good chemical stability between 100–180°C. As E-51 had high thermal stability (>200°C), chemical structure of microcapsule was relatively stable even heated at 200°C.

Thermal analysis

Thermal analysis can help to understand both phase transition temperature and thermal decomposition temperature of microcapsule, so the right temperature application range would be chosen.

TGA curves of shell material (PUF) and core material (E-51) were compared (Fig. 12). Thermal stability of microcapsule was lower than pure PUF and higher than pure E-51, which was due to microcapsule was mixture of PUF and E-51, and its thermal stability will between the PUF and E-51. There are three main microcapsule weight lost stages: 70–200°C, microcapsule products have a very small amount of residual water, 5% weight loss was found at 199°C; 200–400°C, 50% weight loss was found at 345°C (Table I), as a result of thermal decomposition of wall material, as well as the crosslinked polymer generated by core material polymerization. A total of 5% of the mass loss was found at 199°C that indicated that the microcapsule had good heat tolerance. The DSC curve (Fig. 13) showed two distinct exothermic peaks and an endothermic peak, the little peak at low temperature may be due to the existence of a small amount of water. At 228.1°C, the exothermic peak caused by the rapid polymerization of core material, 264.6°C endothermic peaks may due to the wall material decomposition. 303°C exothermic peak caused by production produced by thermal decomposition of wall material had self-etherification reaction at a high temperature, such as ammonia, a methyl amine, and dimethyl amine as well as the capsule core.[16]

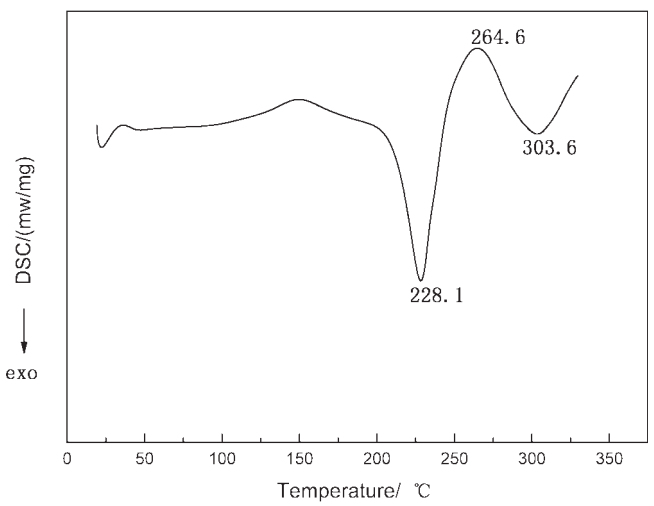

Figure 13 DSC curve of microcapsule.

Combination of TG and DSC analysis, PUF microcapsules neither decomposed nor had other reaction until heated at high temperature, so microcapsule had better thermal stability.

CONCLUSIONS

1. Urea and formaldehyde are easy to get and costs less are used as raw materials of microcapsule synthesis,
2. Urea is added at three times for formaldehyde completely transformed, so that free formaldehyde content of UF wall material can be reduced.
3. To sum up, in the process of using in-situ polymerization to prepare microcapsule, core material emulsified time, emulsifier amount, pH value, and solid content have a significant impact on the microencapsulation process and the final product morphology. UF [n (urea) : n (formaldehyde) = 1 : 2] is used as the wall material, epoxy resin is as the core material [m (wall material): m (core material) = 3 : 10], DBS and gum Arabic is as the emulsifier, gum Arabic (2 wt %), DBS (1 wt %), microcapsules with size and core content are about 60 μm and 76%, respectively, can be synthesized successfully.

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