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Effects of Processing Conditions on the Properties of Epoxy Resin Microcapsule

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Abstract: In order to improve the healing performance and increase the service life of the polymer matrix composites, microcapsules were prepared by interfacial polymerization process with urea formaldehyde resin and epoxy resin E-51 as the wall material and core material separately. The effects of core/shell mass ratio and emulsifier on the distribution, topography and encapsulation rate of microcapsules were investigated. By optimizing the conditions, microcapsules with little particle size, well dispersion and compact surface were prepared. The distribution, topography, stability and compositions of the microcapsules were characterized using Nano-2s, optical microscope, scanning electron microscopy, thermal analysis and Fourier transform infrared spectroscopy. The osmosis performance of the microcapsules was evaluated. The experimental results showed that the ratio of core/shell materials (1:1) and 1% DBS as emulsifier were optimum preparation conditions and the encapsulation rate was 62.5%. The microcapsules can be synthesized successfully with mean diameter 548.6 nm and exhibit a good chemical stability below 225 ℃. The FTIR result indicated that urea-formaldehyde resin was formed and the core materials were successfully encapsulated in urea-formaldehyde shell. Osmosis performance evaluation showed that the microcapsules were well coated and slowly osmosed.

Key words: epoxy resin; microcapsule; interfacial polymerization process

1 Introduction

The concept of composite materials with self-healing capabilities was proposed first by US military in the mid-1980s and the development of self-healing materials is an area of great interest because of their self-healing capabilities in the case of a damage event[1-8]. The healing agent is embedded into self-healing materials and when the conditions of environment change, the repair agent will be released to respond to the stimulation and achieve the purpose of repair. The present research work is mainly focused on the study of the self-healing system and the preparation method of microcapsule.

Yuan YC[9] studied the self-healing system prepared by in-situ emulsion polymerization with melamine-formaldehyde and epoxy resin and thio-alcohol as the wall material and curing agent separately. The mean particle size of the microcapsule was about 93 μm and the repair strength was high. Li H[10] studied the self-healing system prepared by in-situ emulsion polymerization with polyurea formaldehyde as the wall material and cyclopentadiene as core material and the surface of microcapsule was modified with organosiloxane KH-550. The results showed the amino groups on the microcapsule surface could increase the binding force between the microcapsules and epoxy resin substrate.

However, there are common problems in self-healing systems[11]. Firstly, the particle size of microcapsule is relatively large (50-400 μm), which can only be applied in thick coating, and the microcapsule will collapse after releasing the healing agent and catalyst, which will cause new problems. Secondly, the cracks usually occur on the surface of the coating and the amount of larger particles of microcapsules are restricted in their coating because

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the distribution of larger particle size microcapsule in the coating can hardly form a continuous arrangement, so the microcapsule can not burst in rift and is unable to provide healing agent.

Recently, sonication technique was used to produce the fine particle size microcapsules. The sonication technique can transfer the ultrasonic energy from the probe to the solution medium with a specified time and energy. After this modification, microcapsules as fine as 600 nm were produced[12]. The study showed that the smaller the particle size of microcapsules, the better the compatibility with coating matrix.

Compared with sonication technique, interfacial polymerization technique is the easiest and best process of encapsulation. In this paper, microcapsules were prepared by interfacial polymerization with urea formaldehyde resin and epoxy resin E-51 as the wall material and core material separately. The effects of the core/shell mass ratio and emulsifier on the particle size, distribution, morphology and structure of epoxy resin microcapsules were studied. Microcapsules with fine particle size, good dispersion and compactness surface were prepared by optimizing the preparation conditions. The distribution, topography, stability and compositions of the microcapsules were characterized using Nano-2s, optical microscopy, scanning electron microscopy, thermal analysis and Fourier transform infrared spectroscopy. The osmosis performance of microcapsule was evaluated.

2 Experimental

2.1 Raw materials

Epoxy resin (E-51) was supplied by SanMu Group Corporation of Jiangsu, China. Sodium dodecyl sulfate, sodium dodecylbenzenesulfonate, Tween-80 and Arabic gum used as emulsifier were supplied by Guangzhou Chemical Reagent, China. Triethanolamine, sodium chloride, hydrochloric acid, acetone, resorcinol and n-octanol were supplied by Damao Chemical Reagent of Tianjin, China. Urea and 37% formaldehyde used for the preparation of urea-formaldehyde prepolymer were supplied by Guangzhou Chemical Reagent, China. All commercial chemicals were used without further purification.

2.2 Preparation of epoxy resin microcapsule by interfacial polymerization process

At room temperature, urea (U) and 37wt% formaldehyde (F) were mixed in a 250 mL three-necked round-bottomed flask with mechanical stirring equipment. The weight ratio between urea and formaldehyde was 1:2. After the urea dissolved, the pH of the mixed solution was adjusted to 8-9 by drop-wise addition of triethanolamine. The temperature of the system was raised to 70 ℃ and kept for 90 minutes, and a milky viscous prepolymer solution was obtained.

E-51 was dissolved into the solution of thinner and emulsifier and dispersed by the ultrasonic equipment for 20 minutes, and then stirred by the mechanical stirring equipment for 20 minutes; the oil-in-water emulsion (O/W emulsion) was obtained. U-F pre-polymer was added into the above O/W emulsion with 500 r/min continuous mechanical agitation at 50 ℃. Resorcinol (0.5 g) and NaCl solution (4wt%) were added into the solution. After the solution was stirred for 20 min at the agitation ratio of 500 raps, the pH of solution was adjusted slowly to 3.0 by 10wt% hydrochloric acid solution, and then the solution was heated to 60 ℃ and kept at this temperature for 3 h. The microcapsules were rinsed with deionized water and acetone, filtered and air-dried for 24 h.

2.3 Method for encapsulation rate of microcapsules

Encapsulation rate determination of microcapsule was established by the method of extraction and acetone was used as an extraction solvent. The samples were crushed and washed with acetone several times, and then dried at room temperature for 24 h.

$$\text{Encapsulation rate} = (m_1 - m_2) / m_1 \times 100\%$$

where, m_1 is the initial mass of the complete microcapsules; m_2 is the quality of the wall material remained.

2.4 Performance test and structure characterization

2.4.1 Molecular structure identification

FTIR (FT-IR, N4icolet Avatar 360) spectrometer was used to identify the molecular structure of microcapsule. The samples were ground and dispersed in KBr, followed by compression to consolidate the formation of the pellet. FTIR spectra were obtained in the wave number range from 400 cm^{-1} to 4 000 cm^{-1}.

2.4.2 Analysis of microcapsule size and shell morphology

Microcapsule size analysis was carried out with a particle size analyzer (Nano-2s). The surface morphology, shell thickness and the size of microcapsules were determined by optical microscopy (OM) and scanning electron microscopy (SEM).

2.4.3 Thermal analysis of microcapsule

Microcapsules were analyzed using thermal analysis (DTA-TG, ZRY-2P) in nitrogen environment with a sample weight of about 8.0-10.0 mg. Heating rate was maintained at 10 ℃/min in the temperature range of 25-600 ℃. The flux of nitrogen of the method was 60 mL/min.

2.4.4 Osmosis performance evaluation of microcapsule

A certain amount of microcapsules were dispersed in anhydrous alcohol at room temperature for a certain time, then the microcapsules were filtered, dried and weighed and then the operation was repeated. According to the experiment data, the curve of microcapsule quality changing with time was made.

3 Results and discussion

The effects of different processing parameters (core/shell mass ratio and emulsifier) on the distribution, topography and encapsulation rate of microcapsules were investigated.

3.1 Effects of core/shell mass ratio on the formation of microcapsules

In the synthesis process, the core/shell mass ratio directly influences the encapsulation rate, particle size, distribution and morphology of the microcapsule. Table 1 and Fig.1 show the effects of different core/shell mass ratio (varied from 0.5:1 to 1.2:1) on the encapsulation rate and morphology of microcapsules. In this case, the emulsifier is DBS and the concentration of DBS is 1%.

Table 1 Effects of core/shell mass ratio on the encapsulation rate

Core/shell mass ratio	0.5∶1	0.7∶1	1∶1	1.2∶1
Encapsulation rate	46.09%	50.78%	62.50%	42.97%

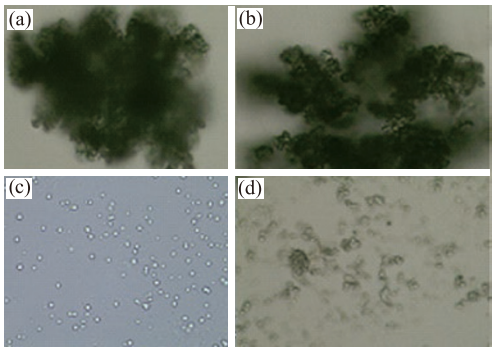

Fig.1 OM of microcapsule with different core/shell mass ratios: (a) 0.5:1; (b) 0.7:1; (c) 1:1; (d) 1.2:1

According to the results of Table 1 and Fig.1, the encapsulation rate, particle size, distribution and morphology of the microcapsule are different at different core/shell mass ratios. The encapsulation rate of microcapsules is 62.50% and the particles are relatively fine and highly dispersed with the core/shell mass ratio of 1. When the core/shell mass ratios reduce to 0.5 and 0.7, the shell material is relatively excessive and the encapsulation rate of microcapsules reduce to 46.09% and 50.78%, separately. In this case, agglomeration occurs and it is difficult to see the particles dispersed individually. These are attributed to that too little core material is used for microencapsulation and a large amount of urea-formaldehyde resin will agglomerate by itself in water with decreasing core/shell mass ratio. When the core/shell mass ratio increases to 1.2, the encapsulation rate of microcapsules reduces to 42.97%. In this case, the agglomeration of microcapsule is slightly better compared to that at the ratios of 0.5 and 0.7. The particles of microcapsules are unevenly dispersed because of the excessive amount of the core material. With increasing core/shell mass ratio (1:1), the amount of core material increase in solution and core material could contact with urea formaldehyde easier which is very beneficial for the formation of microcapsule. When the core/shell mass ratio continues to increase (1.2:1), it is easier to form larger microcapsules or the shell of the microcapsule is relatively thin or incompletely coated, due to the reduction of the shell material. The microcapsules prepared under this condition are easily cracked under shear stress, resulting in the core material of the microcapsule agglomerated. Therefore, the appropriate core/shell mass ratio has important influence on the formation of microcapsule. According to the results of Table 1 and Fig.1, the optimal of core/shell mass ratio is 1:1.

3.2 Effects of emulsifier on the formation of microcapsules

Emulsifier plays a very important role in microcapsule synthesis with interfacial polymerization method. At first, the core material is dispersed into small droplets and exists stably as disperse phase. The formation of droplets is set by not only external agitation but also the emulsification of emulsifier. The core material is liquid material and its surface tension has a constant value. When the discrepancy of the surface tension between the core material and shell material is larger, the formation of microcapsules is easier. The suitable emulsifier can increase the surface tension of core material, which can affect the particle size, distribution, shape, and morphology of microcapsules directly.

In this paper, non-ionic surface active agents (gum

Arabic, Tween-80) and an anionic surfactant (SDBS, DBS) as emulsifiers were used and the effects of different emulsifiers on the formation of an epoxy resin microcapsules were investigated. The results of the encapsulation rate, particle size and distribution with different emulsifiers are shown in Table 2 and Fig.2.

Table 2 Effects of emulsifier on the encapsulation rate

Emulsifier	Gum Arabic	Tween-80	SDBS	DBS
Encapsulation rate	28.12%	31.25%	21.87%	62.50%

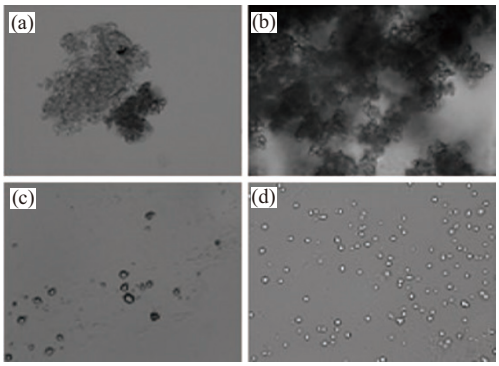

Fig.2 OM of microcapsule with different emulsifiers: (a) Gum Arabic; (b) Tween-80; (c) SDBS; (d) DBS

It can be seen that the microcapsules prepared with different emulsifiers have different encapsulation rates. The lowest encapsulation rate of the microcapsules is only 21.87% prepared with SDBS as the emulsifier. The encapsulation rate of the microcapsules prepared with gum Arabic and Tween-80 as the emulsifiers increases slightly reaching 28.12% and 31.25%, respectively. The highest encapsulation rate of the microcapsule is up to 62.50% prepared with DBS as emulsifier. Fig.2 shows that the agglomeration phenomenon of the microcapsules prepared with non-ionic surfactant Tween-80 and Arabic gum as emulsifiers is very serious, which is very unfavorable for the self-healing of applications. Anionic surfactants (SDBS or DBS) as emulsifiers are very favorable for the formation of the microcapsules. It could be observed that the microcapsules prepared with SDBS or DBS as emulsifier show better dispersion (Figs.2(c)-2(d)). The particle size of the microcapsule prepared with DBS as emulsifier is smaller and more evenly distributed compared to that with SDBS as emulsifier

Studies[13] have shown that ionization reactions will not occur between non-ionic surfactants and water. The shell material is difficult to cover the core material when the shell material deposites on the surface of the core material droplets because of the steric hindrance. Negative charge could form on the surface of core material droplet because of the addition of anionic surfactant, which is not only favorable for the positive charge of the shell material conducive to negative electric field of the core droplets, but also helpful for the stability of the core material droplets. In addition, the reduction of the surface tension of surfactants can reduce the oil-water interfacial tension, which is favorable for the dispersion of the core material in the aqueous phase. This may be the reason that the microcapsules had fine particle and dispersed better using anionic surfactant DBS as the emulsifier. Therefore, DBS is used as the optimal emulsifier in this paper.

3.3 Effects of emulsifier concentration on the formation of microcapsules

According to the results of 3.2, DBS was used as the emulsifier for the preparation of microcapsules. The effects of emulsifier concentration (1%, 1.5%, and 2%) on the encapsulation rate, particle size and distribution were investigated. The results of Table 3 show that with increasing DBS concentration, the encapsulation rate of the microcapsules decreases. Fig.3 shows that when the concentration of DBS is 1%, the epoxy resin microcapsule has fine particle size and distributed uniformly. When the concentration of DBS increases to 1.5%, the microcapsule size increases and the size is not uniform. When the concentration of DBS increases to 2%, the formation of microcapsules decreases significantly. Therefore, the optimal amount of DBS is 1% in this paper.

Table 3 Effects of DBS concentration on the encapsulation rate

Emulsifier concentration	1%DBS	1.5%DBS	2%DBS
Encapsulation rate	62.5%	50.78%	39.06%

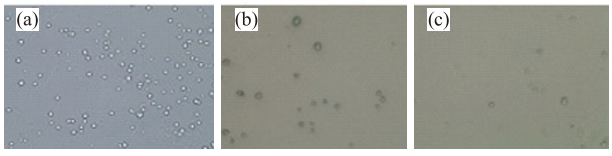

Fig.3 OM of microcapsule with different DBS concentrations: (a) 1.0%; (b) 1.5%DBS; (c) 2.0%DBS

3.4 Performance test and structure characterization of epoxy resin microcapsule

Based on the experimental results of 3.1-3.3, the performance test and structure characterization of epoxy resin microcapsule were conducted under the conditions with the core and shell mass ratio of 1:1, and DBS as the emusifier with the concentration of 1%.

3.4.1 Analysis of microcapsule size

The particle size of the microcapsules was

characterized by a Malvern particle size analyzer (Nano-2s) and the results are shown in Fig.4. Fig.4 shows that the average size of the epoxy resin microcapsule particle is 548.6 nm, the highest proportion is 422.8 nm and the particle size of the microcapsules shows a normal distribution.

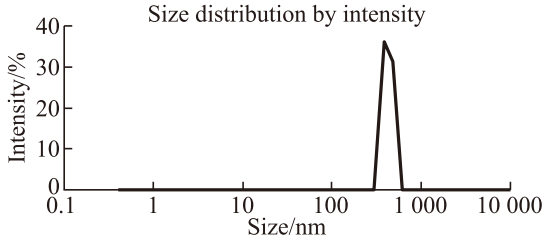

Fig.4 Particle size distribution of epoxy resin microcapsule

3.4.2 SEM analysis

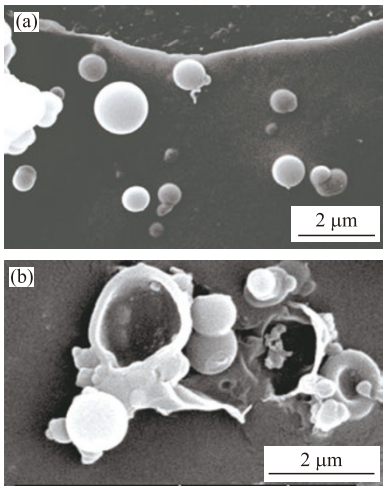

Fig.5 SEM images of epoxy resin microcapsule (a) and crushed (b)

The morphology of the microcapsules was characterized by SEM and the results are shown in Fig.5. Fig.5 (a) shows that microcapsule shows uniform round, narrow particle size distribution and smooth surface, which will guarantee that the microcapsules can be uniformly dispersed in the matrix in a certain extent. Fig.5(b) shows that the shell of the microcapsule is thin and such microcapsules could coat more epoxy resin.

3.4.3 DTA and TG of epoxy resin microcapsules (DTA-TG)

The thermal stability of microcapsules plays an important role in their applications in self-healing composites materials. Fig.6 shows the curves of TG and DTA. The TG curves of the microcapsules shows that the microcapsules have a quick decomposition process between 225-375 ℃, which is due to the shell material being cracked or destructed, resulting in the rapid release of the core material. The decomposition temperature of the microcapsules exceeds the decomposition temperature of the core material 170 ℃, which indicates that the core material is coated on the shell material and the decomposition temperature of the microcapsules improves because of the protection of the shell material. Then there is a further weight loss between 375-600 ℃ because of the decomposition of shell material. In view of the above results, it was established that the core materials are successfully encapsulated in urea-formaldehyde. The decomposition temperature of microcapsules is about 225 ℃ and the microcapsules can be safely stored and used below this temperature. In the DTA curve of microcapsules, there are two endothermic peaks appeared. For the two endothermic peaks, the first endothermic one is due to the rapid release of the core material, when the shell is cracked or damaged. The second one is due to the decomposition of shell materials. By comparing the two curves, the microcapsules are chemically stable below 225 ℃, indicating that the microcapsules have a good thermal stability.

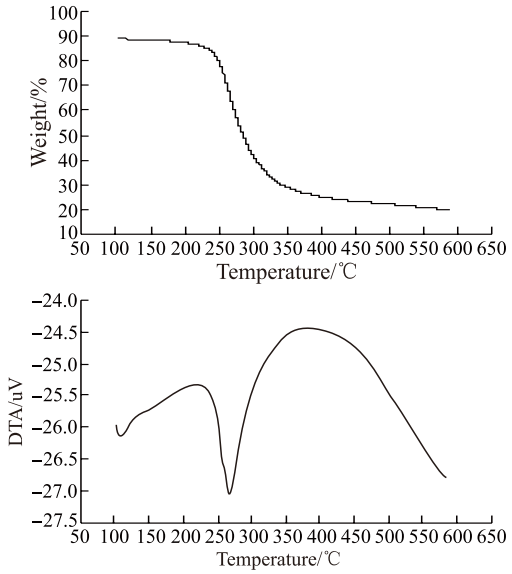

Fig.6 DTA and TG curves of epoxy resin microcapsules

3.4.4 IR spectra of epoxy resin microcapsules (FTIR)

Fig.7 shows the FTIR spectrum of epoxy resin microcapsules. The peaks at 3 357 cm^{-1}, 2 960 cm^{-1}, 1 643 cm^{-1}, and 1 284 cm^{-1} are the characteristic absorption peaks of -OH, -CH, -C=O, and -C-N, respectively. The four primary peaks indicate the formation of urea-formaldehyde polymer. In addition the peaks at 915 cm^{-1} and 835 cm^{-1} are the absorption peak of epoxy ring, which shows that the core materials are successfully encapsulated in urea-formaldehyde shell.

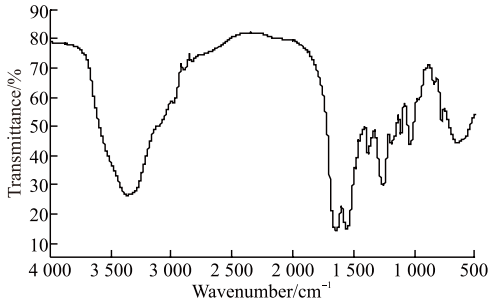

Fig.7 FTIR spectrum of epoxy resin microcapsules

3.4.5 Osmosis performance evaluation of microcapsule

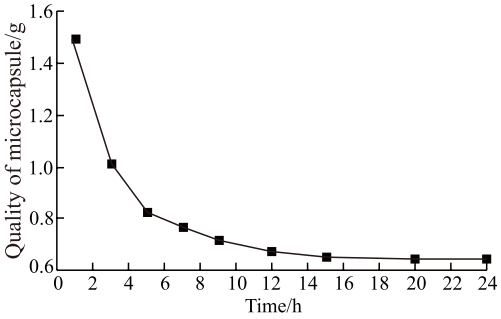

Fig.8 Osmosis performance evaluation of microcapsule

Fig.8 shows the osmosis performance evaluation of microcapsule. According to the results of Fig.8, there is comparatively large quality change in the first two hours. This is largely because part of the core material was not well covered and directly dissolved in ethanol. In the next twenty-two hours, the quality of microcapsules is largely unchanged. So it is certainly that the microcapsules are well coated and slowly osmosed, which is helpful for storage and using.

4 Conclusions

a) The ratio of core/shell materials (1:1) and 1% DBS as emulsifier were the optimum conditions. The microcapsules prepared under those conditions showed little particle size, well dispersed and compact surface and the encapsulation rate of microcapsules was 62.5%.

b) The microcapsules can be synthesized successfully with mean diameter 548.6 nm and exhibit a good chemical stability below 225 ℃. The result of FTIR indicated that urea-formaldehyde resin was formed and the core materials had been successfully encapsulated in urea-formaldehyde shell. Osmosis performance evaluation showed that the microcapsules were well coated and slowly osmosed.

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