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ORIGINAL CONTRIBUTION

Synthesis and characterization of microencapsulated dicyclopentadiene with melamine–formaldehyde resins

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Abstract Microcapsules containing healing agents have been used to develop the self-healing polymeric composites. These microcapsules must possess special properties such as appropriate strength and stability in surrounding medium. A new series of microcapsules containing dicyclopentadiene (DCPD) with melamine–formaldehyde (MF) resin as shell material were synthesized by in situ polymerization technology. These microcapsules may satisfy the requirements for self-healing polymeric composites. The chemical structure of microcapsule was identified by using Fourier transform infrared (FTIR) spectrometer. The morphology of microcapsule was observed by using optical microscope (OM) and scanning electron microscope. Size distribution and mean diameter of microcapsules were determined with OM. The thermal properties of microcapsules were investigated by using thermogravimetric analysis and differential scanning calorimetry. Additionally, the self-healing efficiency was evaluated. The results indicate that the poly(melamine–formaldehyde) (PMF) microcapsules containing DCPD have been synthesized successfully, and their mean diameters fall in the range of 65.2~202.0 μm when the adjusting agitation rate varies from 150 to 500 rpm. Increasing the surfactant concentration can decrease the diameters of microcapsules. The prepared microcapsules are thermally stable up to 69 °C. The PMF microcapsules containing DCPD can be applied to polymeric composites to fabricate the self-healing composites.

Keywords Microcapsule · Melamine–formaldehyde resins · Dicyclopentadiene · Characterization

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Introduction

Microcapsules are tiny particles that contain core materials encapsulated by coatings or shells. The core materials of microcapsules can be drugs, fragrant oils, salts, enzymes, or dyes, etc. Because the core materials can be protected by the coatings or shells from the damages of environment or can be released under a controlled condition, microcapsules have been applied to various areas, such as the pharmaceutical and biomedical industries [1, 2], food additives [3], catalysts [4], dyes [5, 6], and so on. Recently, new applications of microcapsules have been developed. Poly (melamine–formaldehyde) (PMF) microcapsules containing polyaniline particles [7, 8] and poly(methyl methacrylate) microcapsules containing polyaniline [9] have been used for electrorheological materials. Microcapsules containing oil or titanium dioxide (TiO_2) using melamine and formaldehyde, or urea, melamine, and formaldehyde (UM/F) as wall shell materials [10, 11] have been used for electronic ink display technique. Especially, poly(urea–formaldehyde) (PUF) microcapsules containing self-healing agent dicyclopentadiene (DCPD) have been used to fabricate the self-healing epoxy composites, and PUF microcapsules containing styrene have been used to heal the microcrack planes in polyester matrix [12–16]. The application of microcapsules containing self-healing agents to polymeric composites is very interesting. The self-healing is accom-

plished by incorporating a microencapsulated healing agent and a catalytic chemical trigger within polymeric composites. Owing to the promising technical applications of microcapsules containing self-healing agents to polymeric composites, the syntheses of microcapsules containing self-healing agents have attracted more and more attentions from researchers.

Polymeric composites can be fabricated at different temperatures and pressures. The requirements for microcapsules containing healing agents are various according to the processing procedure of polymeric composites. The mechanical and thermal properties must be adequate to retain the intactness of microcapsules during the manufacturing of composites, and the microcapsules must rupture when the damages occur. For polymeric composites processed at higher temperature and pressure, the used microcapsules must possess higher mechanical and thermal properties to resist higher temperature and pressure. The shell materials play an important role in obtaining high physical property of microcapsules. Among the various shell materials for microcapsule preparation, urea–formaldehyde (UF) resins and MF resins are widely used owing to their perfect techniques. Because PMF are superior to PUF in hardness and heat resistance [17, 18], the mechanical properties and stability of PMF microcapsules may be higher than that of PUF microcapsules when they contain the same core materials.

In this study, to synthesize microcapsules with high physical property, which can endure the processing conditions of polymeric composites, MF resins are adopted as shell materials to encapsulate DCPD healing agent. The chemical structure, morphology, and thermal stability of synthesized microcapsules were investigated by using Fourier transform infrared (FTIR), scanning electron microscope (SEM), and thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively. We hope that the PMF microcapsules containing DCPD can be used in polymeric composites fabricated at room and middle temperature or high pressure.

Experimental

Materials

Melamine and 37.0 wt% formaldehyde aqueous solution, used as shell-forming monomers, were purchased from Tianjin Resin Factory and Tianjin Chemical Reagent Factory, China, respectively. Sodium dodecyl benzene sulfonate (SDBS) used as an emulsifier and poly(vinyl alcohol) (PVA, Mw.1500) used as a protective colloid were obtained from Tianjin Chemical Reagent Factory, China. Some 10.0 wt% $NaCO_3$ aqueous solution and 10.0 wt% HCl aqueous solution as pH controllers were prepared in our laboratory. DCPD used as core material was obtained from Shanghai Resin Factory, China, and used without any further purification. Resorcinols used as inhibitor and 1-octanol used to eliminate surface bubbles were purchased from Tianjin Chemical Reagent Factory, China. Epoxy resins [diglycidyl ether of bisphenol A: DGEBPA (E-51, epoxide equivalent weight: 196 g/mol)] were purchased from Wuxi Resin Plant, China. 2-Ethyl-4-methylimidazole (2E4MZ) used as curing agent of epoxy resins was obtained by Tianjin Chemical Reagent Factory, China. The catalyst system $WCl_6/WOCl_4$-$AlEt_3$ was provided by Shanghai New Tianhe Resin, China.

Preparation of microcapsules

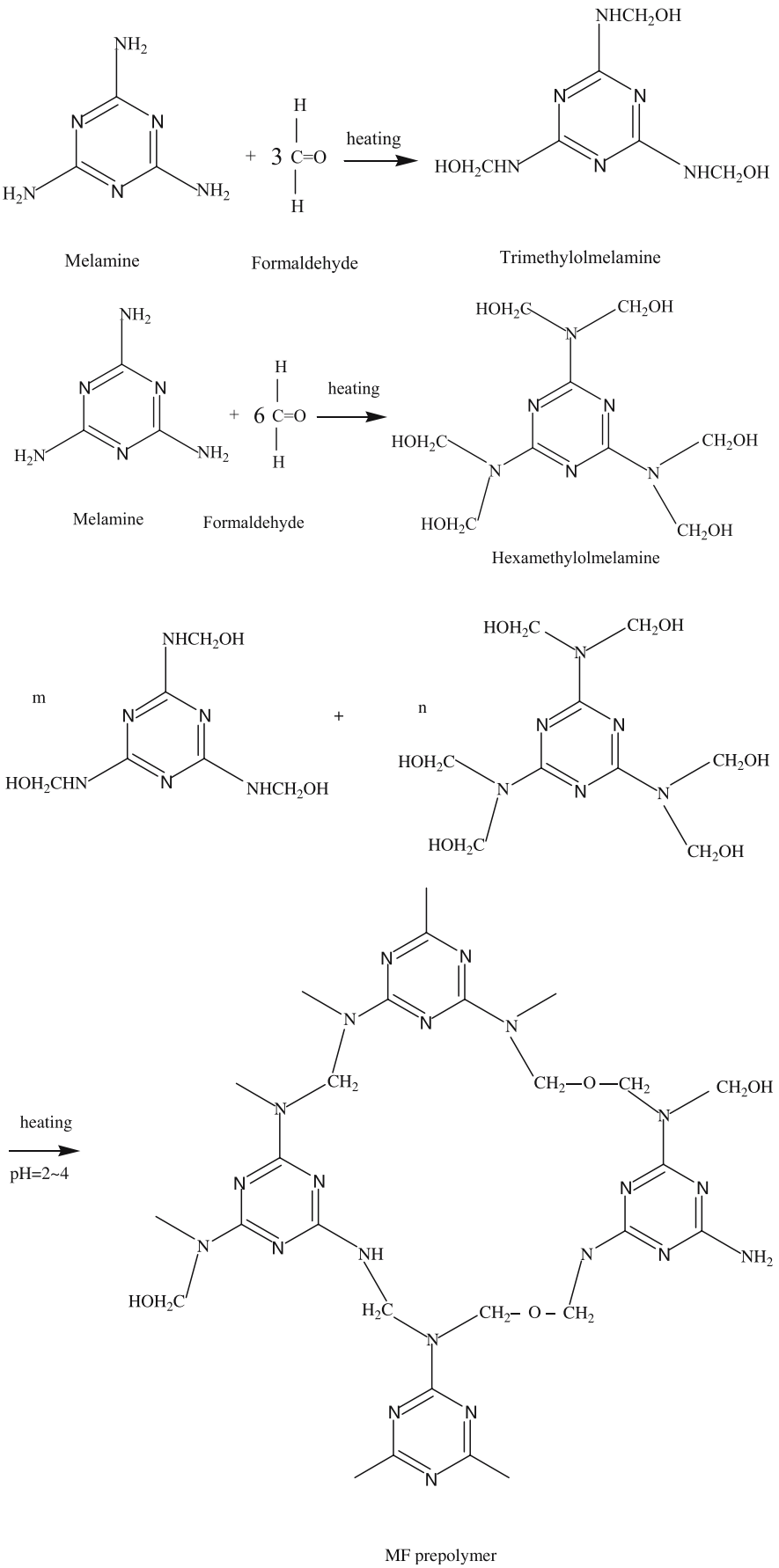
Measurements of 0.06 mol melamine, 0.2 mol formaldehyde, and 20 ml distilled water were added to the three-neck round-bottomed flask equipped with a mechanical stirrer. When melamine was dissolved, the pH value of the solution was adjusted to 8.5~9.0 with 10.0 wt% $NaCO_3$ aqueous solution, while the solution was slowly heated to the target temperature of 65 °C. After 20~30 min, the prepolymer solution of MF was obtained. Figure 1 shows the mechanism of polymerization of MF resins.

Under agitation, 100 ml of aqueous solution of SDBS was added to the prepolymer solution. Some 20 ml DCPD and 0.002 mol resorcinol were added to form an emulsion and allowed to stabilize for 20~25 min. During the emulsification of DCPD, one drop of 1-octanol was added to eliminate surface bubbles, and 10 ml PVA aqueous solution was added to protect the colloids. The pH of the resultant emulsion was slowly adjusted to approximately 4.0 by 10.0 wt% HCl aqueous solution; meanwhile, the resultant emulsion was heated to the target temperature of 65~68 °C. After 3 h of continuous agitation, the reaction was ended. The microcapsule slurry was decanted, washed with water to remove DCPD on the surface of microcapsule, and air-dried at room temperature for 24 h.

Characterization

FTIR spectrometer (WQF-310) was used to identify the chemical structure of the microcapsule specimens. The FTIR spectra of microcapsule samples were compared with the spectra of DCPD and PMF wall shell material. The structural characteristic of PMF was also characterized by proton magnetic resonance spectrometry (^{1}H-NMR VARIAN INOVA-400) by using $CDCl_3$ as solvent and tetramethylsilane as an internal standard. The thermal properties of microcapsules were investigated by using TGA (Q50, TA) at a heating rate of 10 °C/min and DSC (NETZSCH 200 PC) at a heating rate of 10 °C/min in a

Fig. 1 Mechanism of polymerization of MF resins



nitrogen atmosphere. The microcapsule morphology and wall thickness were observed by using an SEM (QUANTA 200, FEI) and an optical microscope (OM, XSP-XSZ, Beijing Tech Instrument, China). Particle size distribution and mean diameter of the microcapsules were determined by using an OM equipped with an image analyzer.

Determination of core content and wall thickness of microcapsules

The theoretical core material content ($W_{I_{DCPD}}$) of microcapsule was measured via TGA at 400 °C according to Cho et al. [19, 20]; DCPD can been decomposed entirely at this temperature. The prepared microcapsule core content ($W_{V_{DCPD}}$) was also determined by extracting method and using acetone as extracting solvent. Microcapsule samples were ground with a pestle in a mortar at room temperature. The crushed microcapsules were collected and washed with acetone several times, then dried at room temperature and obtained the residual wall shell material. Knowing the initial weight of intact microcapsules ($W_{0_{Microcapsule}}$) and the weight of residual wall shell (W_{MF}) of microcapsules, the wall shell content ($W_{V_{MF}}$) and $W_{V_{DCPD}}$ of microcapsule could be calculated as:

$$W_{V_{MF}} = \frac{W_{MF}}{W_{0_{Microcapsule}}} \cdot 100\% \tag{1}$$

$$W_{V_{DCPD}} = 100 - W_{V_{MF}} \tag{2}$$

The theoretical wall shell thickness can be calculated according to Eq. 3 [21],

$$h = \frac{W_{I_w}}{W_{0_{Microcapsule}} - W_{I_w}} \cdot \frac{\rho}{\rho_w} \cdot \frac{d}{6} \tag{3}$$

where h is the theoretical wall shell thickness, W_{I_w} is the weight of wall shell material, ρ_{w} is the density of the wall

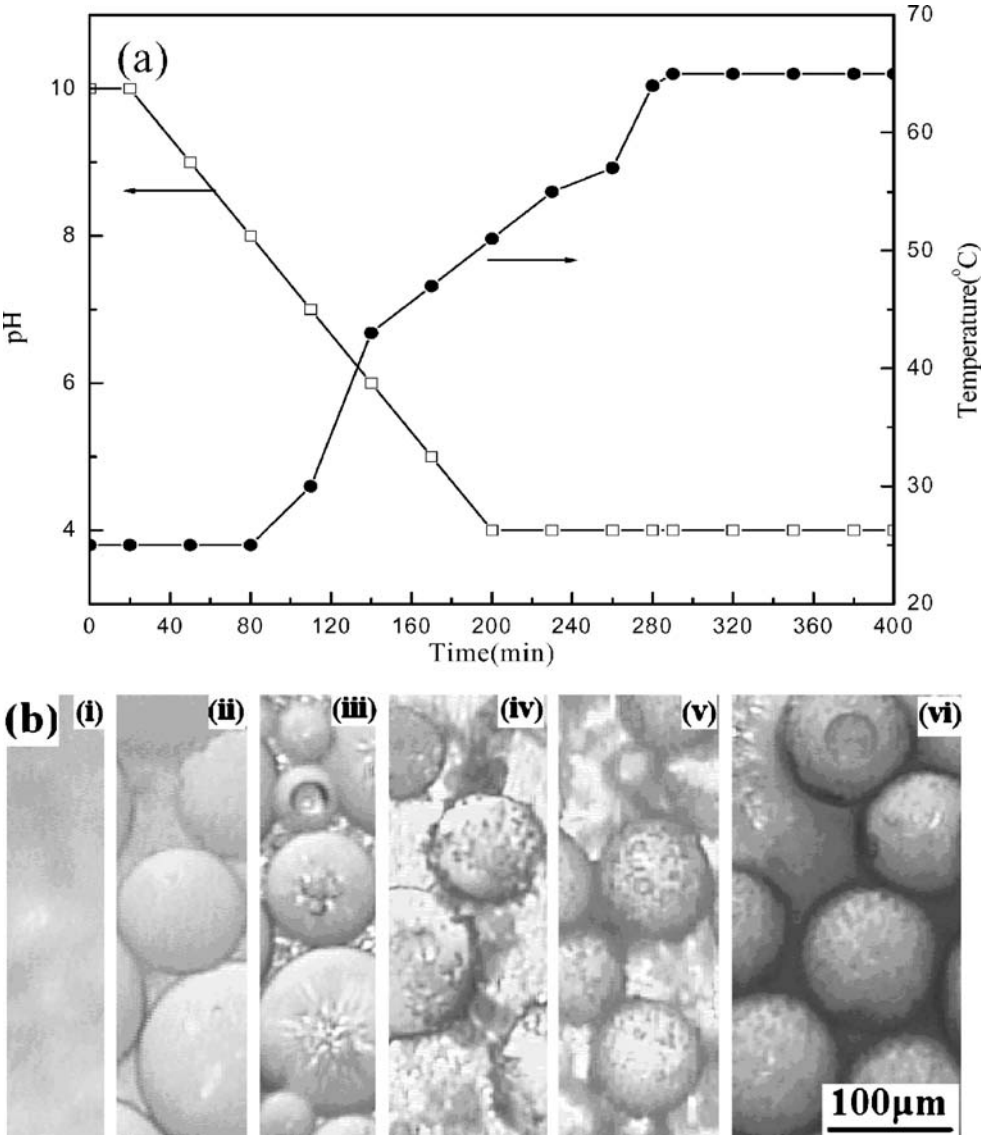


Fig. 2 Aliquot OM images during microencapsulation process along with pH and temperature. **a** Temperature and pH value during microencapsulation process. **b** Aliquot OM images during microencapsulation process (magnification:×40). *(i)* Solution of prepolymer; *(ii)* DCPD droplets in prepolymer solution and no shell formation (0~60 min); *(iii)* PMF nanoparticles begin to precipitate out solution and the solution becomes an emulsion (60~120 min); *(iv)* Microcapsules begin to form (120~200 min); *(v)* Microcapsule shell increases (200~280 min); *(vi)* PMF nanoparticles attach further to the wall shell and the solution turns clear (280~400 min)

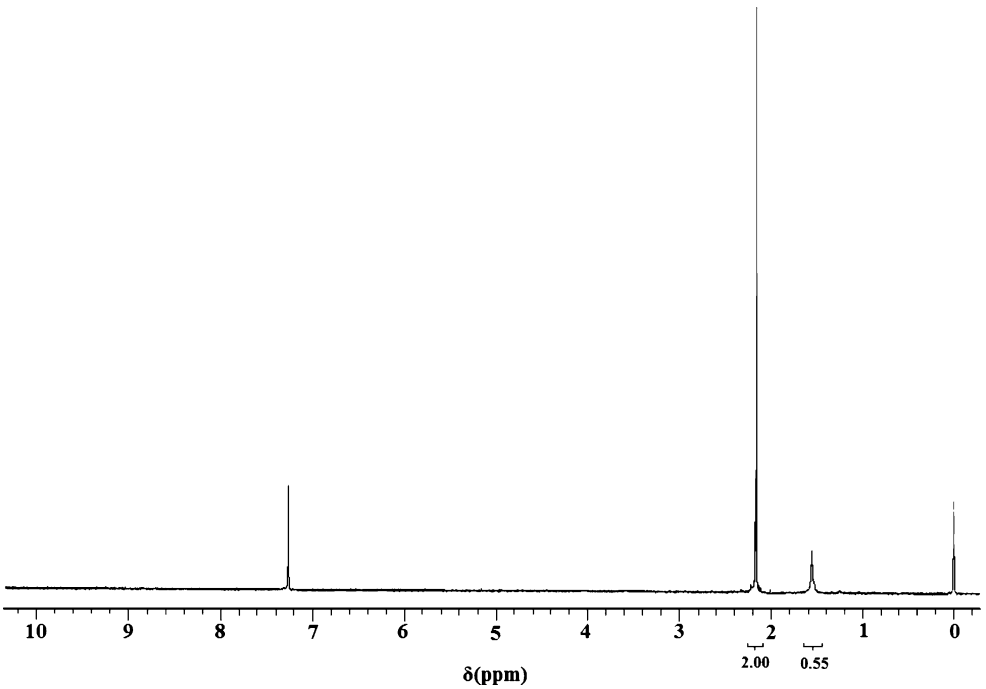


Fig. 3 ^{1}H-NMR spectra of PMF

shell materials, which can be determined by densimeter, ρ is the density of core material, and d is the mean diameter of microcapsules. It is assumed that the weight of melamine is M_{M}, and the mole ratio of formaldehyde to melamine is n, and then W_{I_w} can be calculated as:

$$W_{I_w} = M_M + \frac{M_M}{m_1} \cdot n \cdot m_2 - \frac{M_M}{m_1} \cdot \frac{n}{2} \cdot m_3 \tag{4}$$

where m_1, m_2, and m_3 are the molecular weights of melamine, formaldehyde, and water, respectively.

It is assumed that the initial weight of core materials is R. Transforming Eq. 3 using Eq. 4 and R, and then Eq. 5 can be obtained.

$$h = \frac{dM_M}{6R} \cdot \frac{\rho}{\rho_w} \cdot \left[1 + \frac{(2m_2 - m_3)}{2m_1} \times n\right] \tag{5}$$

The value of h can be calculated according to Eq. 5.

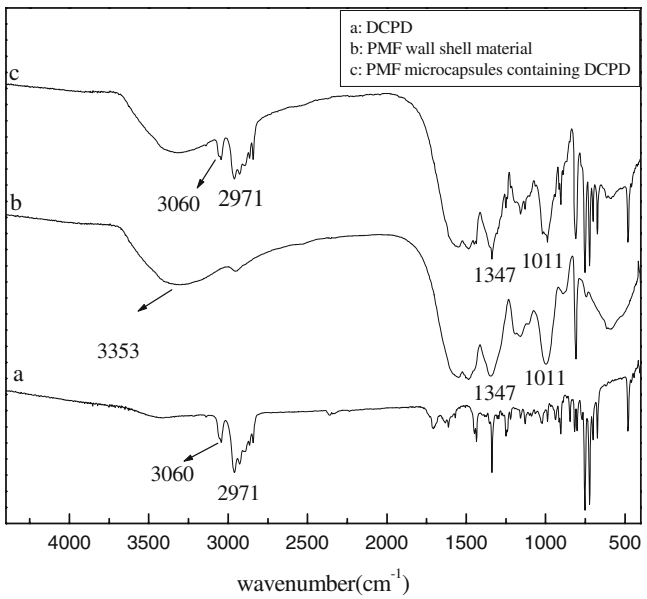


Fig. 4 FTIR spectra of DCPD, PMF wall shell material, and PMF microcapsules

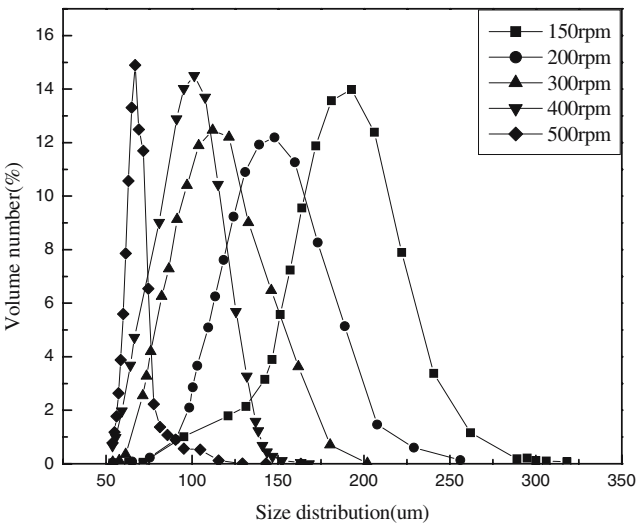


Fig. 5 Size distributions of microcapsules prepared by selecting different agitation rates

Determination of self-healing efficiency

The self-healing composite systems were prepared by mixing DGEBPA with PMF microcapsules containing DCPD, 8.0 wt% of 2E4MZ, and 3.0 wt% of WCl_6/$WOCl_4$-$AlEt_3$. The mixture was degassed, poured into a closed glass mold, and cured for 2 h at 100 °C followed by 4 h at 150 °C. After curing, the self-healing systems were removed from the mold. Tapered double cantilever beam (TDCB) specimens were made for self-healing experiments. The mean thickness of specimens was about 4 mm. Healed fracture tests were performed after 2 weeks of the fracture event. The crack healing efficiency (η) can be evaluated by adopting a measurement of the ability to recover fracture [22]. For the TDCB specimens with the same geometry, η can be calculated as [23]:

$$\eta = \frac{P_C^{Healed}}{P_C^{Virgin}} \tag{6}$$

where P_C^{Virgin} is the critical fracture load of the virgin specimen, and P_C^{Healed} is the critical fracture load of healed specimen. The fracture toughness test was performed using an Instron Model 8502 tensile test machine in displacement control at a rate of 2 mm/min.

Results and discussion

The microencapsulation process of DCPD was monitored by using OM. Figure 2 shows a sequence of aliquot images along with temperature and pH profile. When DCPD is added to the solution at room temperature, microeddies with a range of length scales are present in the flow. DCPD droplets can be observed in the time range of 0~60 min. During this time period, the pH reduces from 10.0 to 8.5; no wall shell forms. As the solution temperature increases slowly from 25 to 35 °C and the pH decreases from about 8.5 to 6.5 in the time range of 60~120 min, the solution becomes an emulsion owing to the formation of PMF nanoparticles in suspension, indicating that PMF prepolymer begins to precipitate out solution. When the pH reduces from 6.5 to 4.0 and the temperature continuously increases from 35 to 51 °C, the microcapsules begin to form owing to the increase of the molecular weight of prepolymer. The microcapsules can be obviously observed during 200~280 min when the temperature increases from 51 to 65 °C and when the pH is kept at 4. The reason is the deposition of most of PMF nanoparticles on the surfaces of microcapsules. However, the microcapsules are easily fractured or deformed due to the thinner shell if the deposition of PMF nanoparticles is stopped. Stabilizing the temperature (about 65 °C) and pH value (about 4) in the time range of 280~400 min, the wall shell of microcapsule becomes thicker and reaches its maximum owing to the further reaction of prepolymer and the deposition of PMF nanoparticles on the surface of the microcapsule. Moreover, the suspension gradually becomes clear, and the microcapsules are easily separated.

Figure 3 shows the ^{1}H-NMR spectra of PMF wall shell material. The peak at about 2.17 ppm represents the protons

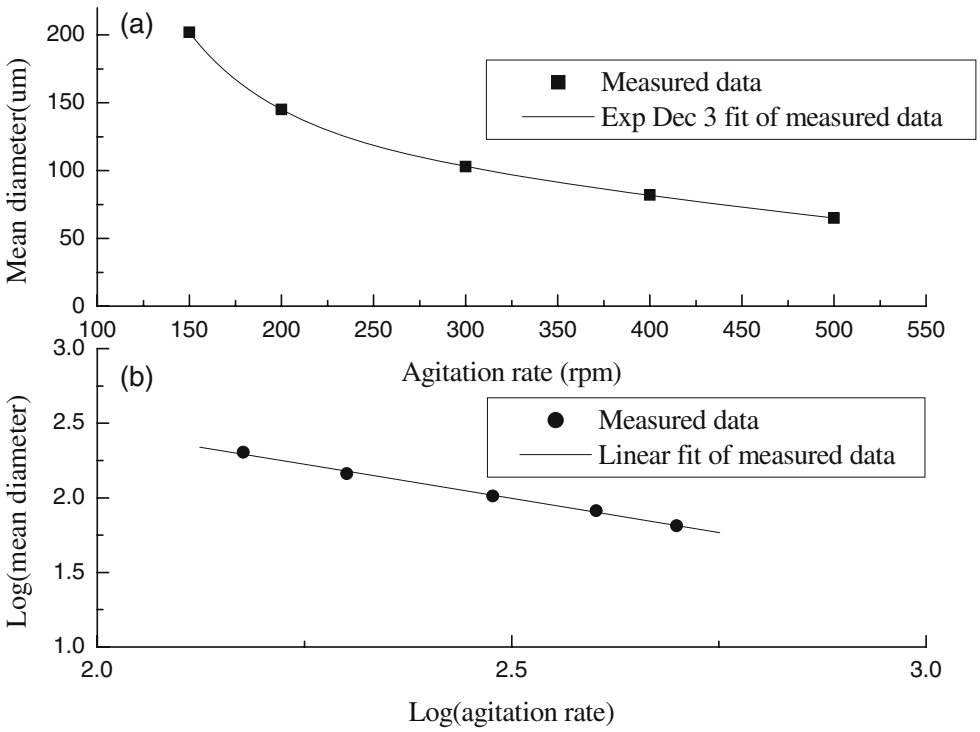


Fig. 6 The relationship of mean diameter and agitation rate

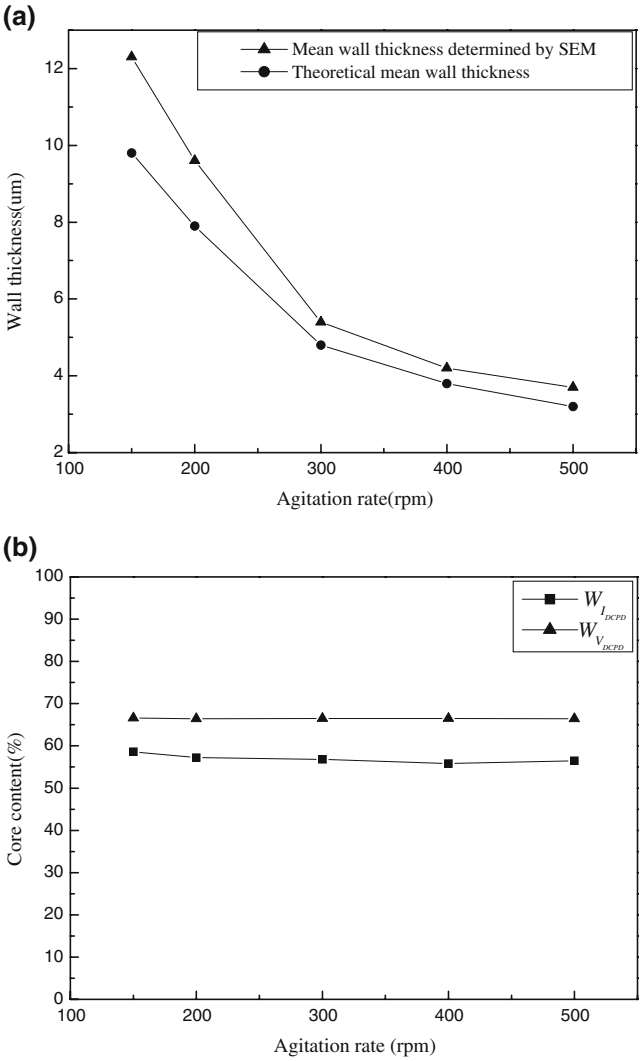


Fig. 7 Mean wall thicknesses and core contents of microcapsules prepared by selecting different agitation rates. **a** Mean wall thicknesses of microcapsules determined by SEM and Eq. 5. **b** Core contents of microcapsules evaluated by TGA and Eq. 2

for methylene ether bridges, which indicates the polymerization of melamine and formaldehyde. Figure 4 shows the spectra of DCPD, PMF wall shell material, and PMF microcapsules containing DCPD. The spectrum of DCPD (curve a) reveals C=C stretching vibration peak at about 3,060 cm^{-1}, C–H stretching vibration peak at 2,971 cm^{-1}, and =C–H bending vibration peak at about 1,340 cm^{-1}. The spectrum of PMF wall shell material (curve b) indicates the board stretching vibration peaks of N–H and –OH at about 3,353 cm^{-1}, the stretching vibration peak of C–N and the bending vibration peak of N–H at about 1,347~1,592 cm^{-1}, and the vibration peak of –C–O–C– at about 1,011 cm^{-1}. Knowing that the characteristic peaks of DCPD and PMF wall shell material, it can be found that the spectrum of microcapsules (curve c) not only well defines the characteristic peaks of PMF but also shows the characteristic peaks of DCPD, which indicates that DCPD is microencapsulated with PMF.

Figure 5 shows the size distributions of microcapsules prepared by adjusting agitation rates between 150 and 400 rpm. The size distribution of each microcapsule sample is in a wide size range. Because the fluid flow around the propeller is turbulent, in the region of flow away from the propeller, many larger microeddies exist, and in the vicinity of the propeller blades, many smaller microeddies exist; as a result, the size of microcapsules are in a wider length scale [24, 25]. The microcapsule size can be controlled by adjusting agitation rate during microencapsulation [26, 27]. The mechanical agitation can provide energy for emulsion and bring two immiscible phases into contact, resulting in the formation of oil drops. The size of oil drops depends on many variables including the agitation speed. An increase in the agitation speed promotes breakup of oil droplets and favors the formation of finer emulsion [28–32]. As a result, the amount of microcapsules with smaller particle size increases, the particle size distribution shifts toward smaller sizes, and the size distribution becomes narrower, which are in accordance with the results reported by Kawashima et al. [33]. In this study, microcapsule diameters are in the range of 54.3~318.2 μm, and the mean diameters of microcapsules are in the range of 65.2~202.0 μm by selecting a different agitation rates between 150 and 500 rpm.

Figure 6 shows the relationship between the mean diameter and the agitation rate. As the agitation rate increases, a finer emulsion is obtained, and the mean diameter of microcapsules decreases with the increase of the agitation rate. The relationship between mean diameter and agitation rate is third-order exponent decay as shown in Fig. 6a and linear in log–log scale as shown in Fig. 6b, which are in accordance with the results reported by Brown et al. [12]. Figure 7a shows the mean wall shell thicknesses

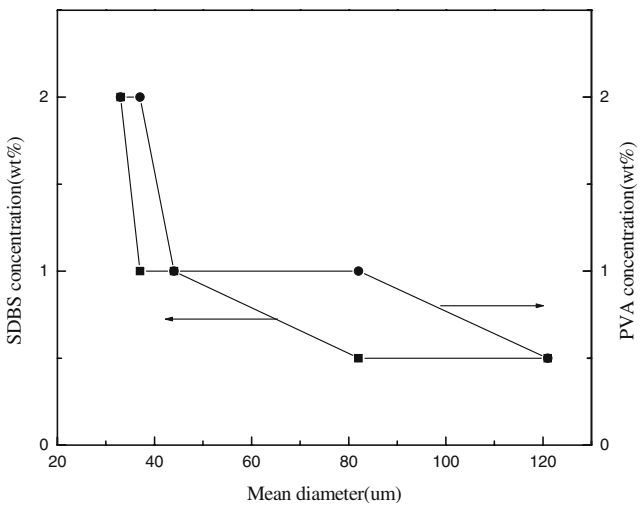


Fig. 8 Mean diameters of microcapsules prepared at different surfactant concentrations

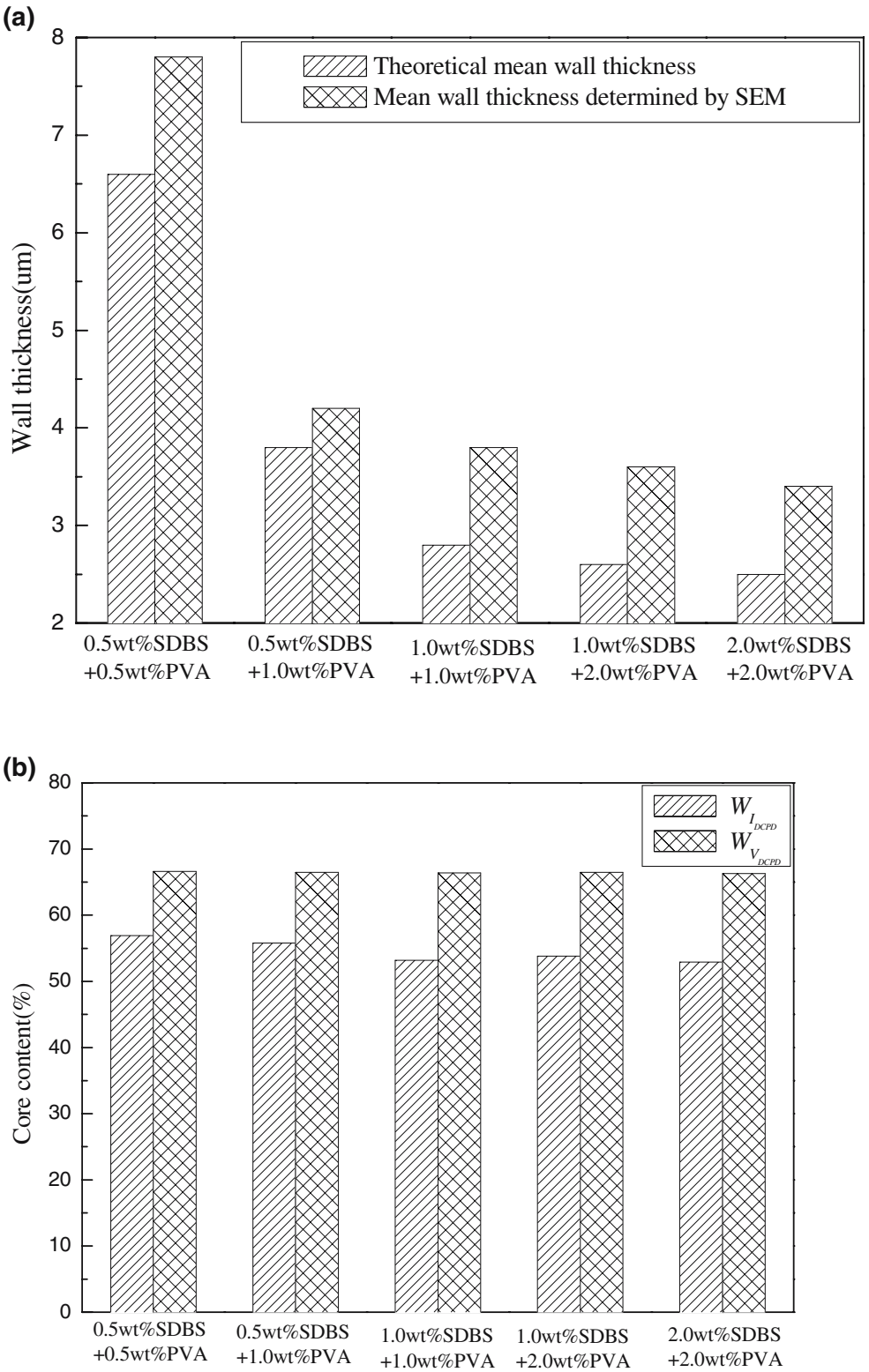


Fig. 9 The mean wall thickness and core contents of microcapsules prepared by selecting different surfactant concentrations. **a** Mean wall thicknesses of microcapsules determined by SEM and Eq. 5. **b** Core contents of microcapsules evaluated by TGA and Eq. 2

determined by SEM and the theoretical mean wall thicknesses of the corresponding microcapsules prepared by selecting different agitation rates. The mean wall thickness decreases as the agitation rate increases. The main reason probably is the fact that the total surface area of oil drops increases due to the formation of more smaller oil. Figure 7b shows the core contents of microcapsules prepared by selecting different agitation rates. They are evaluated by TGA and Eq. 2, respectively. The agitation rate has no significant influence on the core contents of

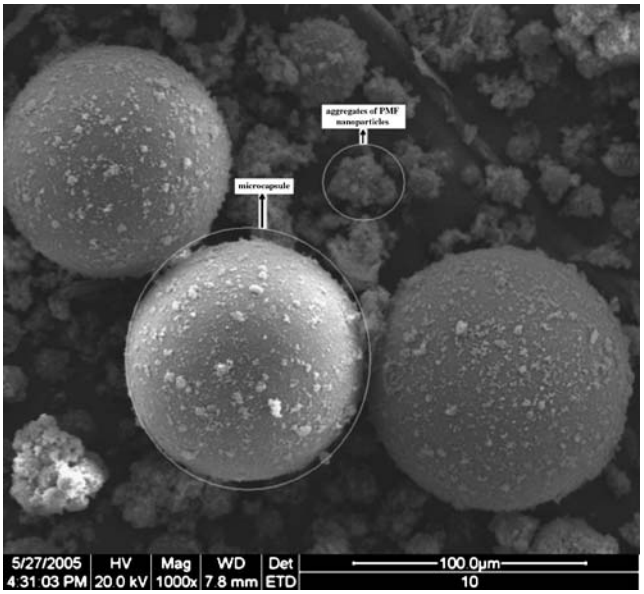


Fig. 10 SEM micrograph of microcapsules

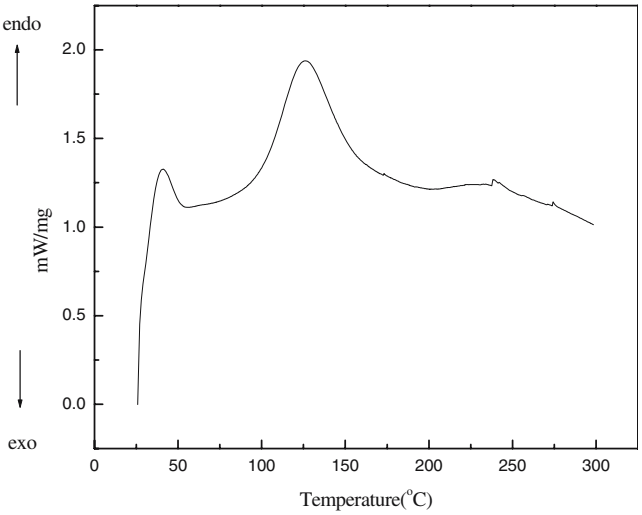


Fig. 12 DSC diagram of PMF microcapsules containing DCPD

microcapsules. The reason probably is the fact that the density of wall shell materials is smaller, compared with the core materials, and little change in the amount of wall shell materials has a slight effect on the core content.

Figure 8 shows the mean diameters of microcapsules prepared at different surfactant concentrations (0.5, 1.0, and 2.0 wt%). As the surfactant concentrations of SDBS and PVA increase from 0.5 to 2.0 wt%, the microcapsule size distribution becomes narrow and the mean diameter of microcapsules decreases. The reason is the fact that increasing the surfactant concentration can improve the core material dispersion in water and reduce the flocculation of core material, which can help to form the smaller microcapsules. In general, the larger the surfactant concentrations, the smaller are the core droplet and the microcapsule size [34]. The mean diameter of microcapsules changes slightly when the SDBS and PVA concentration values are above 1.0 and 2.0 wt%, respectively. It can be explained by the fact that the surfactant concentrations satisfy the maximum dispersion of core droplets; the increase of surfactant concentration cannot play a significant role in dispersion of core droplets. Figure 9a shows the mean wall shell thicknesses determined by SEM and the theoretical mean wall thicknesses of the corresponding microcapsules prepared by selecting different surfactant concentrations. In general, the mean wall thickness of microcapsules decreases as the surfactant concentrations increase. The

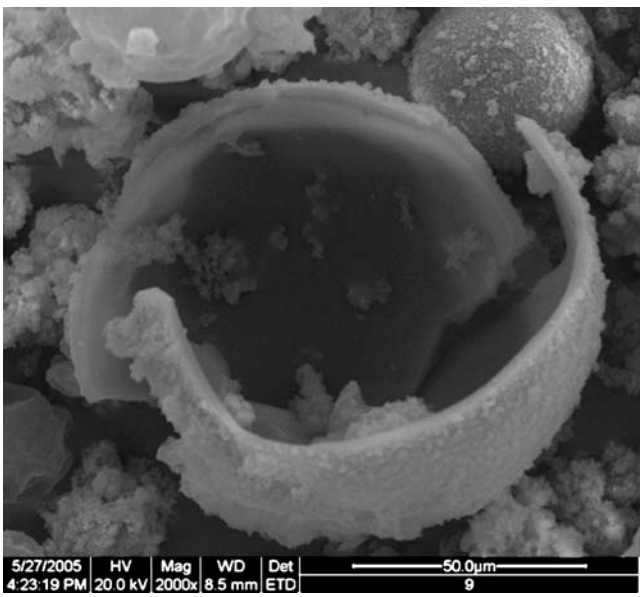


Fig. 11 SEM micrograph of the wall shell of microcapsule

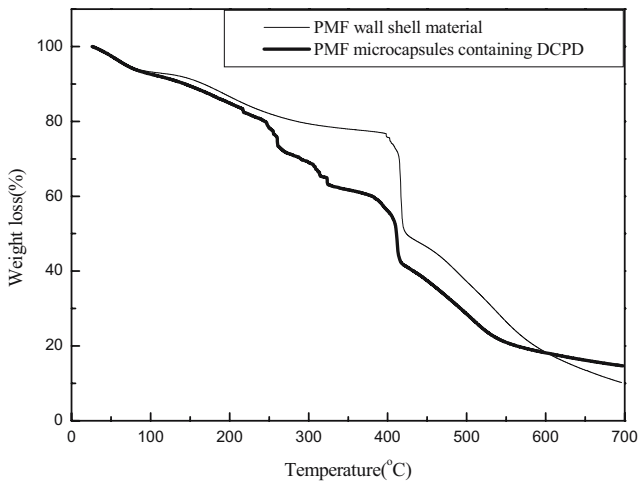


Fig. 13 TGA diagrams of PMF wall shell material and PMF microcapsules containing DCPD

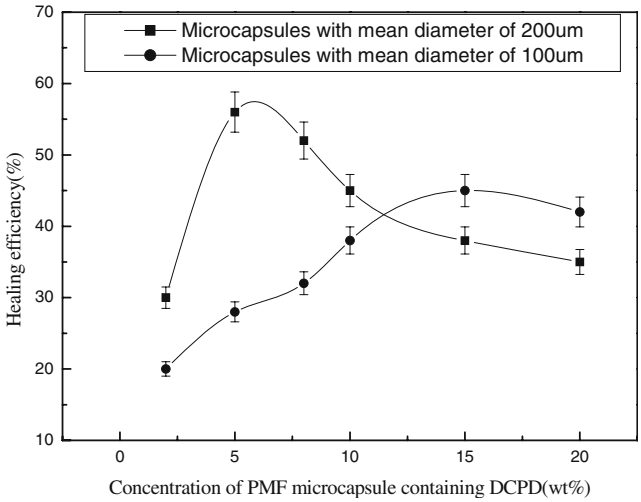


Fig. 14 The self-healing efficiency of the self-healing epoxy system

main reason probably is the fact that the total surface area increases owing to the formation of the more smaller oil drops when the surfactant concentration is higher. Figure 9b shows the core contents of microcapsules prepared by selecting different surfactant concentrations, which are evaluated by TGA and Eq. 2, respectively. The surfactant concentrations have slight influences on the core contents of microcapsules. The reason probably is the fact that little change in amount of the wall shell material with smaller density has a slight effect on the core content.

Additionally, Figures 7a and 9a show that the mean wall shell thickness determined by SEM is larger than the theoretical mean wall thicknesses without reference to the agitation rate and surfactant concentration. The reason is that during the practical microencapsulation, PMF nanoparticles deposited on the surface of microcapsule form a rough and porous outer layer of PMF shell, not an ideal compact wall shell, which results in the increase of the wall shell thickness. Figures 7b and 9b show that the theoretical mean core contents are slightly smaller than the measured mean core contents of microcapsules without reference to the agitation rate and surfactant concentration. The reason is that the weight of the elimination of adsorbed water and formaldehyde existing in microcapsules is included in the calculated core material content [35–37]. During the experiment, it was found that PMF microcapsules containing DCPD exposed to ambient laboratory conditions for 1 month lost 1.0~2.0 wt% core weight, which is lower than the weight loss of PUF microcapsules containing DCPD (about 2.3 wt%), indicating that the ambient stability of PMF microcapsules containing DCPD is higher than that of PUF microcapsules containing DCPD [12].

Figure 10 shows the SEM micrographs of microcapsules. The shapes of microcapsules are spherical, and their surfaces are smooth. Figure 11 shows the SEM micrograph of fractured wall shell; the wall thickness is about 5.4 μm. The inner surface of microcapsule is smooth though some debris on the inner surface can be found due to the faulty preparation of microcapsule sample. The wall thicknesses of microcapsules prepared by selecting different agitation rates between 150 and 500 rpm are in the range of 2.8~30.0 μm.

Figure 12 shows the DSC diagram of microcapsules. The DSC curve indicates two manifest endothermic peaks in the range of 25~300 °C. The first one of the two manifest endothermic peaks at about 41 °C is the melt point of DCPD, and the second one at about 125 °C is mainly due to the evaporation of DCPD. A weak peak at about 240 °C occurs on DSC curve probably due to the decomposition of a part of DCPD. Owing to the high thermal decomposition temperature of PMF wall shell material (>300 °C), the endothermic peaks of PMF decomposition do not occur obviously below 300 °C.

Figure 13 shows the TGA diagrams of PMF wall shell material and microcapsules. The weight loss below 100 °C for PMF is mainly attributed to the evaporation of adsorbed water. The weight loss in the range of 100~320 °C is mainly due to the free formaldehyde. The weight loss in the range of 320~430 °C is attributed to the decomposition of a part of melamine. The weight loss in the temperature range of 430~660 °C is attributed to thermal degradation of PMF, and PMF progressively deaminates forming cyameluric structure. Above 660 °C, PMF undergoes extensive degradation [36, 37]. As for the microcapsules, the weight loss below 100 °C is mainly attributed to the evaporation of adsorbed water, the weight loss in the range of 100~240 °C is mainly caused by the evaporation or decomposition of a part of DCPD, and the weight loss in the temperature range of 240~300 °C is due to the further decomposition of DCPD.

The 5 wt% weight loss temperature (T_d) of PMF microcapsules is at about 69 °C. Compared with the PUF microcapsules containing DCPD, the T_d of PMF microcapsules is higher than that of PUF microcapsules (59 °C, which have been investigated in our laboratory). The reason is probably the higher cross-linking density and compactness of PMF, which can reduce the diffusion of DCPD.

To evaluate the self-healing efficiency of PMF microcapsules containing DCPD applied to polymeric composites, the microcapsules with different mean diameters were embedded in epoxy matrix to fabricate the self-healing composites. Figure 14 shows the self-healing efficiency of cured epoxy resins mixed with different mean diameter microcapsules. The microcapsule diameter has a significant influence on the self-healing efficiency. The higher self-healing efficiency can be obtained by adding a lower content of microcapsules with larger diameter or by adding a higher content of microcapsules with smaller diameter, and increasing microcapsule diameter can improve the

maximum self-healing efficiency. These phenomena are in accordance with the results reported by Brown et al. [23]. In this study, the self-healing efficiency is in the range of 20~56%.

Conclusions

PMF microcapsules containing DCPD were prepared successfully by in situ polymerization technology in an oil-in-water droplet interface. Microcapsules with mean diameter in the range of 65.2~202.0 μm and shell thickness of about 2.8~30.0 μm can be obtained by adjusting agitation rates between 150 and 500 rpm. Increasing the surfactant concentration can decrease the diameters of microcapsules. Due to the high thermal stability of cross-linked PMF and the formation of smooth surface, PMF microencapsulated DCPD has better thermal stability, and its T_d is enhanced by 10 °C in comparison with PUF microcapsules containing DCPD. PMF microcapsules containing DCPD could be applied to polymeric composites fabricated at room temperature and middle temperature (50~100 °C). In general, the research provides novel microcapsules for the self-healing composites, and the effects of the microcapsules on the polymeric composites will be further examined in our future study.

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References

1. Biju SS, Saisivam S, Maria NS, Rajan G, Mishra PR (2004) Eur J Pharm Biopharm 58:61
2. Yutaka U, Kenichi H, Kageyosi S, Kazunori A, Yoshikazu T, Mutsuo S (2001) Surgery 130:13
3. Yúfera M, Fernández-Díaz C, Pascual E (2005) Aquaculture 248:253
4. Ji HB, Kuang JG, Qian Y (2005) Catal Today 105:605
5. Sawada K, Urakawa H (2005) Dyes Pigm 65:45
6. Yamamoto T, Dobashi T, Kimura M, Chang CP (2002) Colloids Surf B 25:305
7. Choi HJ, Lee YH, Kim CA, Jhon MS (2000) J Mater Sci Lett 19:533
8. Lee YH, Kim CA, Jang WH, Choi HJ, Jhon MS (2001) Polymer 42:8277
9. Park SY, Cho MS, Kim CA, Choi HJ, Jhon MS (2003) Colloid Polym Sci 282:198
10. Jang IB, Sung JH, Chio HJ (2005) J Mater Sci 40:1031
11. Kim KS, Lee JY, Park BJ, Sung JH, Chin I, Choi HJ, Lee JH (2006) Colloid Polym Sci 284:813
12. Brown EN, Kessler MR, Sottos NR, White SR (2003) J Microencapsul 20:719
13. White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, Brown EN, Viswanathan S (2001) Nature 409:794
14. Kessler MR, Sottos NR, White SR (2003) Composites Part A 34:743
15. Brown EN, White SR, Sottos NR (2005) Compos Sci Technol 65:2474
16. Jung D, Hegeman A, Sottos NR, Geubelle PH, Whites SR (1997) Compos Funct Grad Mater 80:265
17. Pizzi A (1994) Advanced wood adhesives technology. Marcel Dekker, New York, pp 2–3
18. Dunky M (1998) Int J Adhes Adhes 18:95
19. Cho MS, Cho YH, Choi HJ, Jhon MS (2003) Langmuir 19:5875
20. Cho YH, Cho MS, Choi HJ, Jhon MS (2002) Colloid Polym Sci 280:1062
21. Madan PL, Luzzi LA, Price JC (1974) J Pharm Sci 63:280
22. Wool RP, O'Conner KM (1982) J Appl Phys 52:5953
23. Brown EN, Sotts NR, White SR (2002) Exp Mech 42:372
24. Taylor GI (1932) Proc R Soc Lond Ser A 138:41
25. Dobetti L, Pantaleo V (2002) J Microencapsul 19:139
26. Dietrich K, Herma H, Nastke R, Bonatz E, Teige W (1989) Acta Polym 40:243
27. Dietrich K, Bonatz E, Geistlinger H, Herma H, Nastke R, Purz HJ, Schlawne M, Teige W (1989) Acta Polym 40:325
28. Johnson GR (1980) J Vinyl Addit Technol 2:138
29. Chatzi EG, Kiparissides C (1994) Chem Eng Sci, Part 2, 49:5039
30. Wieringa JA,Van Dieren F, Janssen JJM, Agterof WGM (1996) Chem Eng Res Des, Part A, 74:554
31. Zhou GW, Kresta SM (1998) Chem Eng Sci 53:2063
32. Yang B, Takahashi K, Takeishi M (2001) J Appl Polym Sci 82:1873
33. Kawashima Y, Niwa T, Handa T, Takeuchi H, Iwamoto T, Itoh K (1989) J Pharm Sci 78:68
34. Holtzscherer CH, Candau FJ (1988) J Colloid Interface Sci 125:97
35. Zhang XX, Tao XM, Yick KL, Wang XC (2002) Colloid Polym Sci 282:330
36. Devallencourt C, Saiter JM, Fafet A, Ubrich E (1995) Thermochim Acta 259:143
37. Costa L, Gamino G (1998) J Therm Anal 34:423