The Effect of Synthesis Condition on Physical Properties of Epoxy-Containing Microcapsules

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ABSTRACT: The physical properties of microcapsules are largely influenced by the synthesis conditions such as weight ratio of core/shell material, agitation rate, reaction time, and different emulsifier. Different synthesis condition would lead to different property. It is an important issue for application in composites that require self-healing microcapsules possessing rough surface morphology, less adhesion, less core material permeability, appropriate diameter and core content, and adequate shell thickness. The properties of microcapsules influenced by the synthesis conditions were investigated systematically in this article. According to orthographic factorial design, the most influencing factor on microcapsule's yield, core material, average shell thickness and average diameter, are concluded, respectively. The synthesis parameters when the epoxy-containing microcapsules exhibit the optimum properties are concluded: 1.4 : 1 for the weight ratio of core/shell material, 250 rpm for the agitation rate, 3 h for the reaction time and 1.5% content for the emulsifier DBS. The chemical structure of resultant microcapsules is confirmed by FT-IR, and core material of microcapsule exhibits reactivity through DSC measurement. Subsequently, the microcapsules are characterized by SEM, OM, and contact angle experiment so as to provide parameters of microcapsule's physical properties for making binary self-healing materials. As a result, the resultant microcapsules are suitable for fabricating self-healing materials. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1866–1879, 2012

Key words: microencapsulation; emulsion polymerization; synthesis; physical properties; self-healing

INTRODUCTION

In recent years, active polymeric materials incorporating self-healing functionality have attracted more and more attention because they represent a new paradigm for structural materials that require long-term durability and reliability.[1–4] For the key element of self-repairing, the healing agent should be kept active at the healing temperature and be protected from external environment. It is a general approach to be encapsulated by the polymeric wall shell material via chemical synthesis.[5–8] While the composite with the embedded self-healing microcapsules and catalyst is fabricated, microcracks propagate throughout the microcapsules and healing agent releases into microcracks so as to bond microcracks as a result of catalytic action.

A series of approach of encapsulation of healing agent have been reported in the literature. Microcapsules are typically synthesized by *in situ* condensation polymerization of urea or melamine and formaldehyde in an oil-in-water emulsion,[9] interfacial polymerization of diisocyanate and amine,[10] etc. Microencapsulation of epoxy resin and epoxy resins with a solvent is a fundamental step toward self-healing in thermoset epoxies. New synthesis method such as encapsulating epoxy is also carried out by interfacial polymerization via UV resins.[11]

Much of the work in self-healing materials has focused on binary systems such as endo-dicyclopentadiene and its catalysts,[12–17] epoxy and its curing agents.[18–21] In each of these systems, the microencapsulation of epoxy resin has increasingly attracted because epoxy resins are reactive monomers and can be reacted with wide variety of curing agents or hardeners such as amines of differential functionalities and anhydrides at different temperatures. Epoxy-containing microcapsules are successfully prepared first by Yuan via *in-situ* polymerization.[22] Subsequently, new method of encapsulating epoxy resins is reported by Xiao et al.[11] For the encapsulating curing agents, several strategies have been reported in the literature such as microencapsulation of a reactive liquid-phase amine,[10] polythiol,[23] and active $(C_2H_5)_2O$ BF_3.[24] Xiao et al. report a smart approach to envelop an extremely active catalyst $(C_2H_5)_2O$ BF_3 through catalyst-loaded vegetable fibers coating by polystyrene.[25]

The physical properties of microcapsules are largely influenced by the synthesis conditions such as weight ratio of core/shell material, agitation rate,

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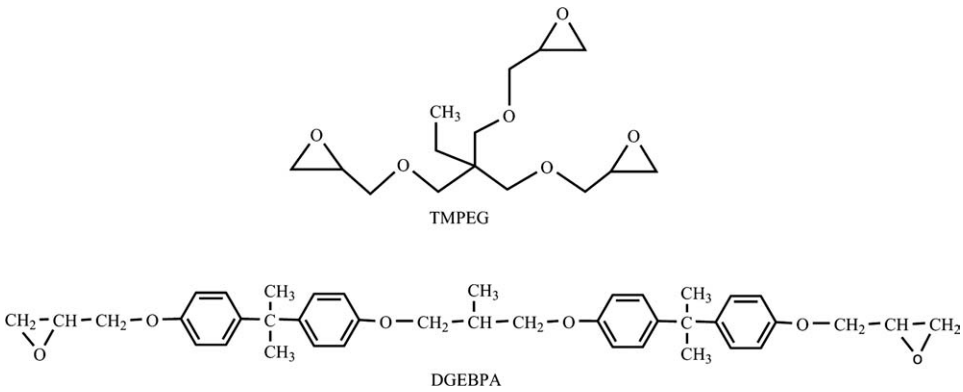

Figure 1 Chemical structure of DGEBPA and TMPEG.

reaction time, and different emulsifier. Different synthesis condition would lead to different property. It is an important issue for application in composites that require self-healing microcapsules possessing rough surface morphology, less adhesion, less core material permeability, appropriate diameter and core content, and adequate shell thickness.[22,26,27] Therefore, to prepare accordant microcapsule by controlling the synthesis conditions is vital importance for the application in composite. To the authors' knowledge, however, the influencing factors of synthesis conditions on epoxy-containing microcapsule's physical properties by the method of *in-situ* polymerization of urea and formaldehyde have not been systematically investigated yet. In our work, the microcapsule's physical properties (surface morphology, adhesion, core material permeability, size distribution, average diameter, core content, and average shell thickness) influenced by synthesis condition were investigated in detail. Through the method of orthographic factorial design, we conclude the most influencing factor on microcapsule's yield, core content, average shell thickness and average diameter, respectively. Then the effect of the most influencing factors on microcapsule's physical properties was investigated. Finally, the most optimum synthesis conditions of epoxy-containing microcapsule are concluded.

In this article, the epoxy-containing microcapsules were prepared by *in situ*-polymerization of urea and formaldehyde in an oil-in-water emulsion. The influence of synthesis conditions on microcapsule's physical properties was systematically investigated. The chemical structure and core material reactivity of microcapsules were investigated by FT-IR and DSC, respectively. The physical properties of the resultant microcapsules synthesized under the optimum condition were examined by SEM, OM, and contact angle experiment so as to provide parameters of microcapsule's physical properties for making binary self-healing composites in the subsequent works.

MATERIALS AND METHODS

Materials

Epoxy resin (diglycidyl ether of bisphenol A: DGEBPA, E-51) used as core material was purchased from Wuxi Resin Plant, China. Trimethylolpropane triglycidyl ether (TMPEG) used as reactive diluent of DGEBPA, was purchased from Anhui Xinyuan Chemical Plant, China. Urea (U) and 37 wt % formaldehyde (F) used as shell material were obtained from Tianjin Chemical Plant, China. Triethanotamine (TEA) (Tianjin Nankai Chemical Plant, China) was used to control the pH of solution. Sodium dodecyl sulfate (SDS) is purchased from Tianjin Kemeng Chemical. Sodium dodecyl benzene sulfonate (SDBS) is purchased from Tianjin Kemiou Chemical. Nearly 10 wt % hydrochloric acid solutions were prepared to control the pH value of emulsion. Triethylenetetramine (TETA) was purchased from Tianjin Yixin Tenglong Chemical Plant, China. All the materials are commercial products and used without further purification. Figure 1 shows the chemical structures of DGEBPA and TMPEG.

Preparation of epoxy-containing microcapsules

U and 37 wt % F were mixed in a 250-mL three-neck round-bottomed flask with mechanical stirring at room temperature. The weight ratio between U and F was 1 : 2. The pH of mixed solution was adjusted to 8–9 with TEA. The temperature of system was raised to 70°C and kept for 1 h, and then the UF prepolymer solution was obtained.

A prepared mixture of DGEBPA and TMPEG (weight ratio of TMPEG to DGEBPA : 0.2) was added to a prepared mixture of deionized water (40 g) and 1.5% emulsifier under the agitation ratio of 250–350 rpm for 15–30 min. A prepared prepolymer solution was added into the solution, and then 0.5 g resorcinol as solidify promoter was added. The pH of the solution was adjusted slowly to 3.0–4.0 $\times$ 10 wt % hydrochloric acid solution, and then the

TABLE I
Creation of an Orthographic Factorial Design of Four Factors and Three Levels for Microcapsules Preparation

	Factor			
	Weight ratio of core/shell material	Agitation rate (rpm)	Reaction time (h)	Emulsifier
Level	A	B	C	D
1	1.2 : 1	250	3	SDBS
2	1.4 : 1	300	2	SDS
3	1.6 : 1	350	1	None

solution was heated to 60°C. The microcapsules were rinsed with deionized water for several times, filtered and air-dried for 24 h.

To optimize and evaluate the effect of the preparing conditions on the yield, core content, average shell thickness, and average diameter of microcapsules, an orthographic factorial design of four factors (i.e., weight ratio of core/shell material, agitation rate, reaction time, and emulsifier) and three level was used (Table I). The microcapsules' yield was calculated by eq. (1):

$$Y_{\text{microcapsule}} = W_m/W_0 \times 100\% \quad (1)$$

where W_0 represents the theoretical weight of the resultant microcapsules, i.e., the input weight of core material and shell-formers, W_m represents the weight of the obtained microcapsules after removing the unreacted shell-formers, residual shell material, and unencapsulated DGEBPA and TMPEG.

Characterization

FTIR spectrometer (AVATAR 370 THERMO NICOLET) was used to identify the chemical structure of microcapsule which was prepared by grinding the sample with a potassium bromide (KBr). Surface morphology, shell thickness of microcapsules, and fractured surface of self-healing epoxy were observed by SEM (QUANTA 200 ESEM, FEI). Samples were prepared on an aluminum slice, dried in a vacuum oven, and sputtered a coat with gold-palladium. The structure of microcapsules was observed using OM (BX51, OLYMPUS). Size distribution of microcapsules was investigated with laser particle size analyzer (Mastersizer2000), and refractive index of microcapsules is 1.52. The content of core material was characterized by weighting the microcapsules and the shell materials after extraction. The core material permeability was characterized by measuring the weight of microcapsules which were soaked into the solvent ethanol for different times. The contact angle between core material and shell material was measured by Contact Angle Measuring Instrument (DCAT 21, DATAPHYSICS). The shell material was obtained by grinding microcapsules, subsequently rinsed by acetone. The resultant shell material was compacted to a flake by pressing machine. The reaction activity of core material was investigated by differential scanning calorimetry (DSC) (DSC141, Setaram). Samples were combusted in N_2 at a heating rate of 10°C min^{-1} from 25 to 200°C.

RESULTS AND DISCUSSION

Influencing factors of preparation of microcapsules on the yield

The poly (urea-formaldehyde) (PUF) microcapsules were synthesized by *in-situ* polymerization of UF prepolymer at the oil-water interface. Detailed descriptions of the mechanism and the fabrication conditions for UF prepolymer had been reported in the literature.[9] The weight ratio of core/shell material, agitation rate, reaction time, and emulsifier would influence on the yield of microcapsules. Therefore, the influencing factors of preparation of epoxy-containing microcapsules were investigated in this section. For this purpose, orthographic factorial design was applied and the microcapsule yield was set as the response of the designed experiments.

Table II shows the results and analysis of the effects of the four factors at three levels on microcapsule's yield (refer to Table I). According to the theory, the bigger N_i is, the more important factor is. Therefore, the importance of factor from high to low in turn is emulsifier, reaction time, weight ratio of core/shell material, and agitation rate. Figure 2 shows the influence of different levels of the four factors (see Table I) on the averaged microcapsule yield (that was taken from the values of R_{ij} listed in Table II). It is found that emulsifier has a very evident influence on the yield of microcapsules. The emulsifier could decrease the Gibbs free energy at the interface of oil-in-water emulsion and keep stabilization of the emulsion. Comparing with no emulsifier, the stabler the emulsion is, the larger the microcapsules' yield is. Similarly, lower yields are attained by changing emulsifier as a result of increasing the Gibbs free energy at the interface of oil-in-water. In general, the differences in the yield at different levels are moderate except for the emulsifier.

As a consequence from the experiment based on the microcapsule's yield, the optimum conditions for preparing epoxy-containing microcapsules can be easily given from Figure 2: 1.2 : 1 for the weight ratio of DCPD/UF prepolymer, 250 rpm for the agitation rate, 3 h for the reaction time, and emulsifier DBS. However, it does not mean that the optimum conditions can thus be concluded because of the

TABLE II
The Result of the Orthographic Factorial of Microcapsules

	Factor				Results			
No.	A	B	C	D	Core content (%)	Average diameter (μm)	Average shell thickness (μm)	Yield %
1	1	1	1	1	74.4	203	7.3(±1)	88.4
2	1	2	2	2	61.1	182	6.2(±1)	68.2
3	1	3	3	3	<9.4	–	4.9(±2)	<17.8
4	2	1	2	3	<11.0	–	6.8(±2)	<22.2
5	2	2	3	1	75.4	215	5.9(±1)	63.5
6	2	3	1	2	64.3	174	4.5(±1)	67.8
7	3	1	3	2	62.8	245	6.2(±1)	56.4
8	3	2	1	3	<15.4	–	5.0(±2)	<28.7
9	3	3	2	1	76.2	170	3.7(±1)	79.1
Result analysis of microcapsule yield								
K_{i1}	174.4	167.0	184.9	231.0	–	–	–	–
K_{i2}	153.5	160.4	169.5	192.4	–	–	–	–
K_{i3}	164.2	164.7	137.7	68.7	–	–	–	–
R_1	58.1	55.7	61.6	77.0	–	–	–	–
R_2	51.2	53.5	56.5	64.1	–	–	–	–
R_3	54.7	54.9	45.9	22.9	–	–	–	–
N_i	6.9	2.2	15.7	54.1	–	–	–	–

K_{ij} denotes the sum of microcapsule yield with factor i and level j.
R_{ij} denotes the average of K_{ij}. $R_{ij} = K_{ij}/n_i$, n_i is the number of level j with the same factor i.
$N_i = \mathrm{Max}(R_{ij}) - \mathrm{Min}(R_{ij})$, ($i$ = A, B, C, D; j = 1, 2, 3).

complicated situation in practice. For example, the weight ratio of core/shell material is an important factor for the capsule yield and the lower weight ratio of core/shell material results in higher yield, but the resultant microcapsule is easier to be adhered together as a result of the residual UF prepolymer keeping on the polymerization on the surface of microcapsules. Similarly, higher weight ratio of core/shell material results in lower yield because shell material is not adequate for encapsulating core material. Therefore, the effects of synthesis condition on microcapsule's properties are discussed as follows to find out the most optimum synthesis condition.

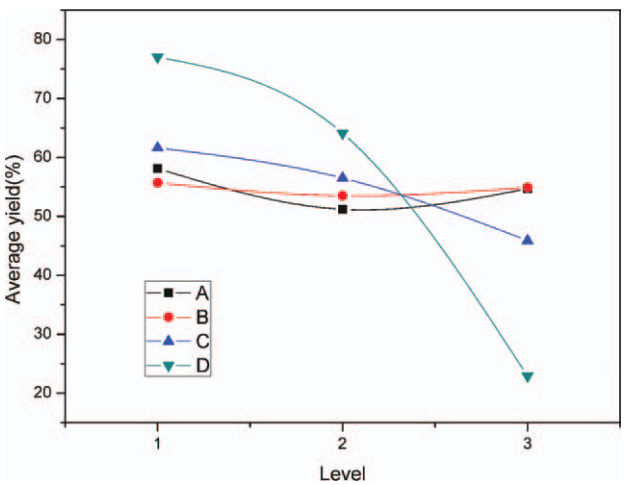

Figure 2 Influence of different levels of the four factors (see Table I) on the averaged capsule yield (that was taken from the values of R_{ij} listed in Table II). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To estimate the most influencing factor of core content of microcapsule, the result analysis of orthographic experiment of core content is carried out (Table III). The importance of factor from high to low in turn is weight ratio of core/shell material, reaction time, and agitation rate. Similarly, from the Table IV, the importance of influencing factor on average diameter from high to low in turn is agitation rate, reaction time, weight ratio of core/shell material. Because emulsifier greatly influence microcapsule's yield, the effect of varying emulsifier on core content and average diameter are not considered in this section.

The shell thickness of microcapsules plays an important role in the self-healing process, which must be made sure that the microcapsule can keep structural integrality during the fabricating composite. The diameter of microcapsule which is selected to measure the average shell thickness is as close as possible to the average diameter of microcapsule sample. Subsequently, we used graph digitizer software to gain the two-point coordinate of wall shell from the SEM photographs. Then the shell thickness of microcapsules was calculated by the distance formula of two points, i.e., $d = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2}$.

TABLE III
The Result Analysis of Orthographic Experiment of Core Content of Microcapsule (%)

	Factor			
No.	A	B	C	D
K_{i1}	144.9	148.2	154.1	226.0
K_{i2}	150.7	151.9	148.3	188.2
K_{i3}	154.4	149.9	147.6	35.8
R_1	48.3	49.4	51.4	75.3
R_2	50.2	50.6	49.4	62.7
R_3	51.5	50.0	49.2	11.9
N_i	3.2	1.2	2.2	–

K_{ij} denotes the sum of core content of microcapsule with factor i and level j.
R_{ij} denotes the average of K_{ij}. $R_{ij} = K_{ij}/n_i$, n_i is the number of level j with the same factor i.
$N_i = \text{Max}(R_{ij}) - \text{Min}(R_{ij})$, ($i$ = A, B, C, D; j = 1, 2, 3).

TABLE V
The Result Analysis of Orthographic Experiment of Average Shell Thickness of Microcapsule (μm)

	Factor			
No.	A	B	C	D
K_{i1}	18.40	20.30	16.80	16.90
K_{i2}	17.20	17.10	16.70	16.90
K_{i3}	14.90	13.10	17.00	16.70
R_1	6.13	6.77	5.60	5.63
R_2	5.73	5.70	5.57	5.63
R_3	4.97	4.37	5.67	5.57
N_i	1.16	2.40	0.10	0.06

K_{ij} denotes the sum of average shell thickness of microcapsule with factor i and level j.
R_{ij} denotes the average of K_{ij}. $R_{ij} = K_{ij}/n_i$, n_i is the number of level j with the same factor i.
$N_i = \text{Max}(R_{ij}) - \text{Min}(R_{ij})$, ($i$ = A, B, C, D; j = 1, 2, 3).

Finally, the average shell thickness of microcapsules was obtained by calculating the mean value of maximum and minimum of shell thickness. Table V shows the result analysis of orthographic experiment of average shell thickness. The importance of factor from high to low in turn is agitation rate, weight ratio of core/shell material, reaction time, and emulsifier. It is found that the influence of reaction time and emulsifier on microcapsule's shell thickness is tiny (from N_i value listed in Table V). Therefore, the influences of agitation rate and weight ratio of core/shell material on microcapsule's average shell thickness were only discussed.

The effect of weight ratio of core/shell material on microcapsules' properties

As discussed above, the weight ratio of core/shell material is the most influencing factor on core content of microcapsules. In this section, the microcapsule's properties including the core content, adhesion, size distribution, average diameter, and average shell thickness of microcapsules influenced by weight ratio of core/shell material were investigated.

To estimate the effect of varying weight ratio of core/shell material on the size distribution and average diameter of resultant microcapsules, size distribution of microcapsules at varying weight ratio of core/shell material was shown in Figure 3. Raising the core/shell ratio would increase the average diameter of microcapsules and broaden their size distribution. The main reason is that the size of core droplet in emulsion is larger when the weight ratio of core/shell material is higher and the other

TABLE IV
The Result Analysis of Orthographic Experiment of Average Diameter of Microcapsule (μm)

	Factor			
No.	A	B	C	D
K_{i1}	385	448	377	588
K_{i2}	389	397	352	601
K_{i3}	415	344	460	–
R_1	193	224	189	196
R_2	195	199	176	200
R_3	208	172	230	–
N_i	15	52	41	4

K_{ij} denotes the sum of average diameter of microcapsule with factor i and level j.
R_{ij} denotes the average of K_{ij}. $R_{ij} = K_{ij}/n_i$, n_i is the number of level j with the same factor i.
$N_i = \text{Max}(R_{ij}) - \text{Min}(R_{ij})$, ($i$ = A, B, C, D; j = 1, 2, 3).

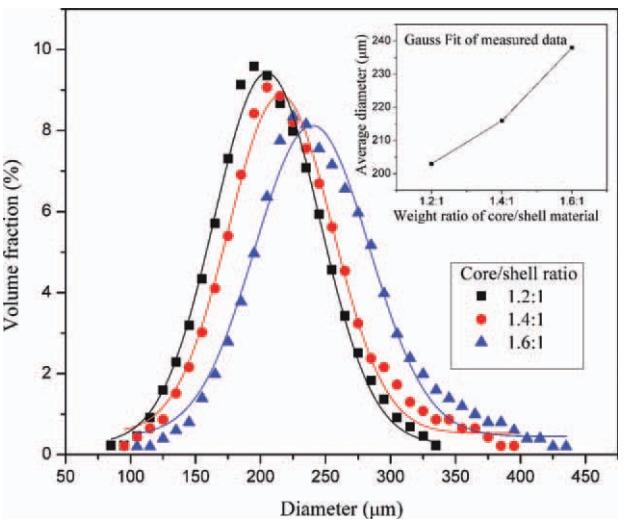

Figure 3 Size distribution of epoxy-containing microcapsules at varying weight ratio of core/shell material. Synthesis condition: 250 rpm for the agitation rate, 3 h for the reaction time, and emulsifier SDBS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

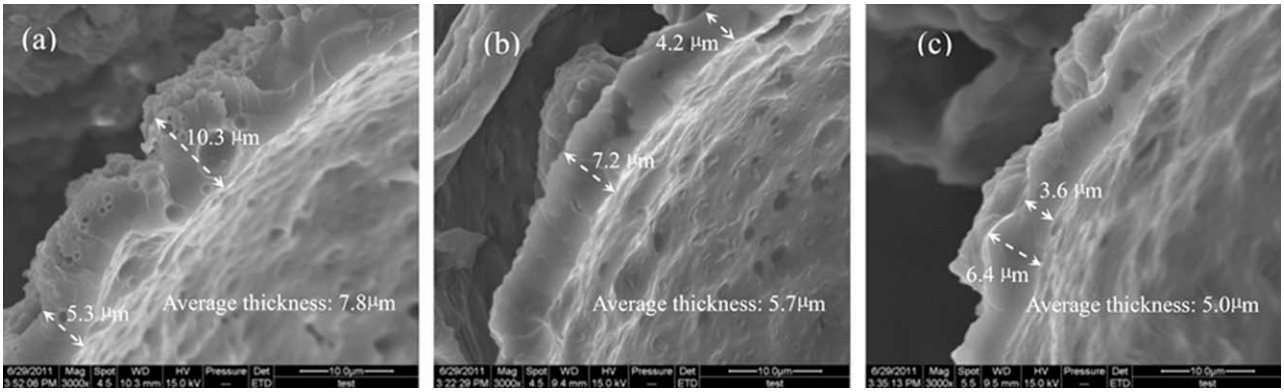

Figure 4 The average shell thickness of microcapsule at different weight ratio of core/shell material with (a) 1.2 : 1 (average diameter: 203 μm); (b) 1.4 : 1 (average diameter: 216 μm); (c) 1.6 : 1 (average diameter: 238 μm). Synthesis condition: 250 rpm for the agitation rate, 3 h for the reaction time, and emulsifier SDBS.

processing parameters are kept constant. Although the shell thickness may decrease due to the increase of core material, it slightly influences the diameter of microcapsule when the core material changes largely. But the microcapsules with thinner shell prepared by choosing higher weight ratio of core/shell material are easily fractured during the preparation of self-healing material. Increasing the core material can form larger size core droplet, and accordingly, the microcapsule size becomes larger. However, excess core materials would cause poor dispersion, promoting aggregation of core droplets, resulting in wider size distribution of microcapsule.

The weight ratio of core/shell material effect on the core content of microcapsules is relative to the microcapsules' size because the core content is proportional to the microcapsules' size. As discussed above, the microcapsules' size increases with the enhancement of core/shell ratio. Therefore, raising the weight ratio of core/shell material increases the core content, which is consistent with the result of orthographic experiment (Table III).

The average shell thickness of microcapsules influenced by weight ratio of core/shell is estimated through SEM photographs of fractured microcapsules (Fig. 4). As the increase of weight ratio of core/shell material, the average shell thickness of microcapsules decreases obviously. The main reason is that raising the weight ratio of core/shell would lead to the larger size oil droplets, which increases the specific surface area of encapsulated oil droplets when the other processing parameters are kept constant. Additionally, compared with core material, stoichiometric composition of shell material former decreases. As a result, the shell thickness of microcapsule becomes thinner.

Adhesion is an important property for the resultant microcapsules, which largely influences on the dispersion of microcapsules mixed into the resin matrix to fabricate self-healing polymeric materials. The less adhesion microcapsules have the better dispersion property will the microcapsules have. From Figure 5, as the weight ratio of core/shell material increases, the adhesion among microcapsules obviously tends to decrease. For the reason, lower weight ratio of core/shell material results in redundant shell formers forming on the surface of microcapsules via *in-situ* polymerization. As a result, the surface of microcapsules becomes roughness which is benefit for interfacial performance between microcapsules and matrix, but the ratio of microcapsules adhered together with each other increases which is disadvantage for the microcapsule's dispersion property [as is shown in Fig. 5(a,b)]. It is worth of notice that the unencapsulated shell material and semiencapsulated microcapsules raises with the increase of weight ratio of core/shell material from Figure 5(c). The main reason is that wall shell former is not adequate for encapsulating the whole core material. Therefore, considering the adhesion and microcapsule's quality, the optimum synthesis condition for weight ratio of core/shell material is concluded to 1.4 : 1.

The effect of agitation rate on microcapsules' properties

According to the orthographic experiment results discussed above, the microcapsules' properties i.e., size distribution and average diameter is greatly influenced by the agitation rate. In this section, the agitation rate effecting on size distribution and average diameter, average shell thickness of microcapsules was investigated.

Figure 6 shows the size distribution of epoxy-containing microcapsules at different agitation rate on the condition of 1.4 : 1 for weight ratio of core/shell material, 3 h for the reaction time, and emulsifier SDBS. Obviously, as the agitation rate decreases, the microcapsule size distribution becomes wide, the

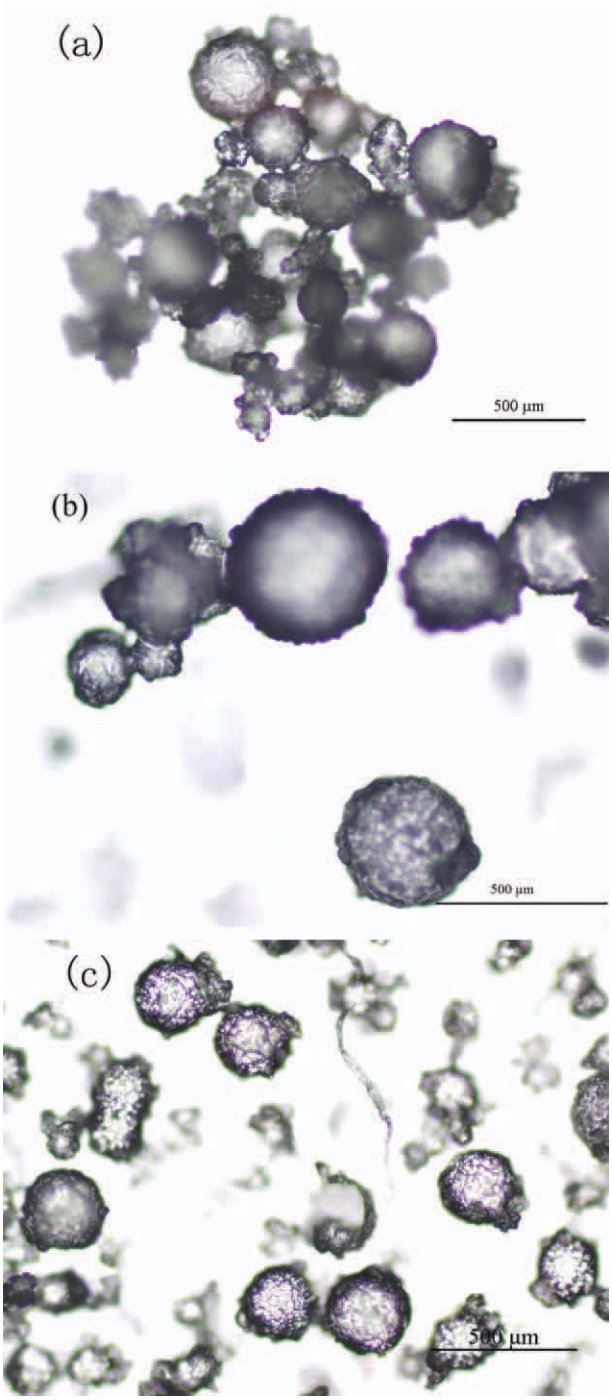

Figure 5 The OM images of microcapsules at different weight ratio of core/shell material with (a) 1.2 : 1; (b) 1.4 : 1; (c) 1.6 : 1. Synthesis condition: 250 rpm for the agitation rate, 3 h for the reaction time, and emulsifier SDBS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

microcapsules' average diameter increases and the bigger microcapsules become dominant. The inset of Figure 6 gives the plots of average diameter of the microcapsules. Linear relationships are observed, which coincides with the results of other researchers.[9,11] These results are likely the reflection of the fact that the colloid size increases along with decreasing agitation rate. The reason is that the oil droplets suffer smaller shear stress and their sizes become bigger when the agitation rate decreases. Consequently, the diameter of resultant microcapsules becomes larger and their size distribution is broadened. Additionally, the fluid flow around the propeller is turbulent, larger microcapsules exist in the region of flow away from the propeller and many smaller microcapsules exist in the vicinity of the propeller blades.

Figure 7 shows the average shell thickness of microcapsule at different agitation rate. Apparently, the average shell thickness decreases with the enhancement of agitation rate. The main reason is that the size of oil droplets in an emulsion becomes smaller due to the larger shear stress when the agitation rate increases, which results in the enhancement of specific surface area of core material phase. This is equal to reduce the stoichiometric composition of shell material former when the weight ratio of core/shell material and other processing parameters are kept constant. As a consequence, the average shell thickness of microcapsule decreases. Considering the average yield of microcapsules in Figure 2 and Table II, the optimum synthesis condition for agitation rate is concluded to 250 rpm.

The effect of reaction time on microcapsules' properties

The effect of reaction time on microcapsules' properties including surface morphology and core material permeability were investigated in this section.

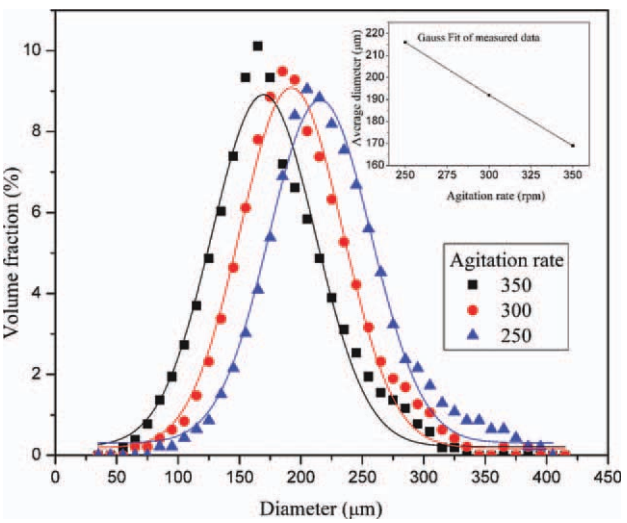

Figure 6 Size distribution of epoxy-containing microcapsules at different agitation rate. Synthesis condition: 1.4 : 1 for weight ratio of core/shell material, 3 h for the reaction time, and emulsifier SDBS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

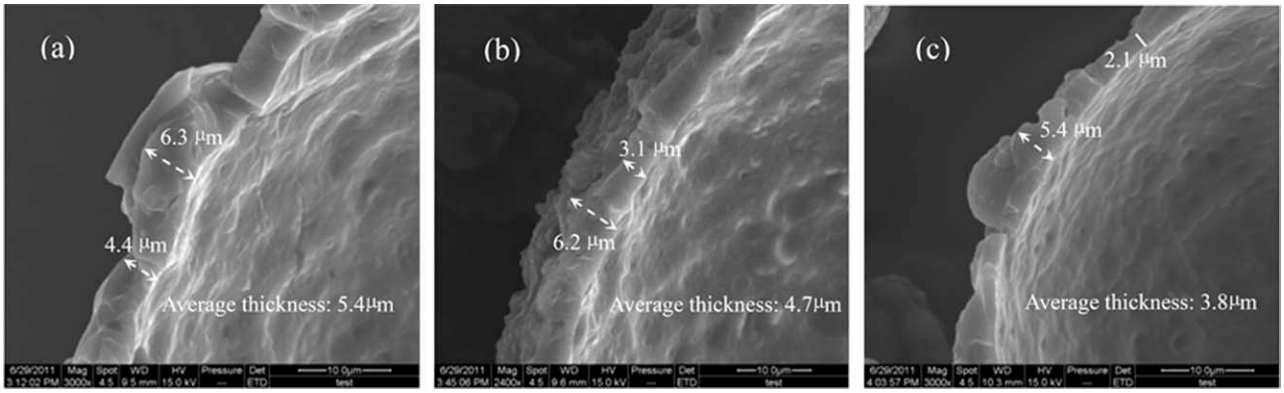

Figure 7 The average thickness of microcapsule at different agitation rate with (a) 250 rpm (average diameter: 216 μm); (b) 300 rpm (average diameter: 192 μm); (c) 350 rpm (average diameter: 169 μm). Synthesis condition: 1.4:1 for weight ratio of core/shell material, 3 h for the reaction time, and emulsifier SDBS.

Figure 8 shows the surface morphology of microcapsules at different reaction time. Evidently, as the reaction time increases, the surface morphology of microcapsules become rough, which is an advantage for the interfacial join between microcapsules and matrix due to the mechanical engagement according to the research of Blaiszik et al..[28] It is worth noting that reaction time is less significant importance for

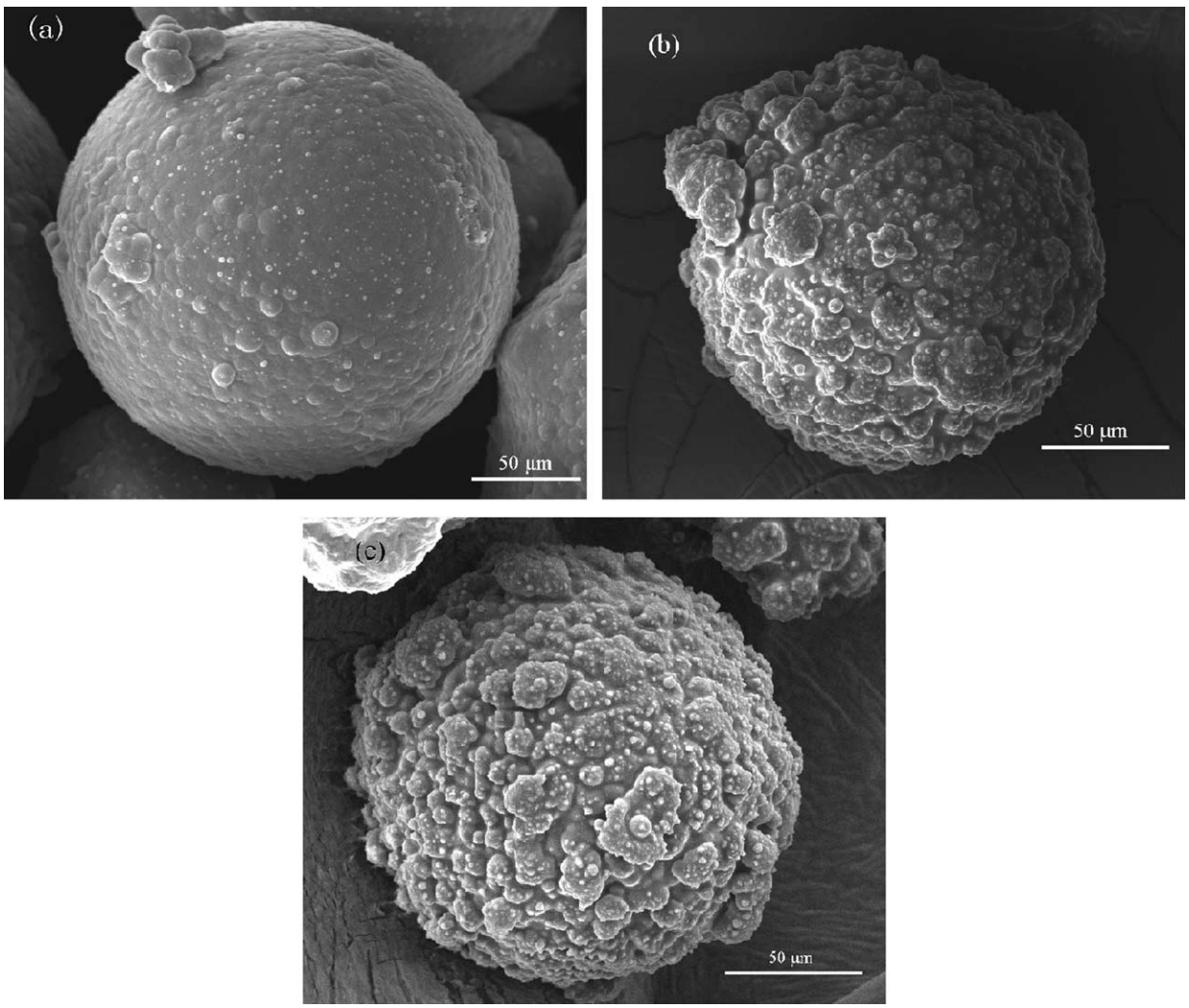

Figure 8 Surface morphology of epoxy-containing microcapsules at reaction time (a) 1 h; (b) 2 h; (c) 3 h. Synthesis condition: 1.4 : 1 for weight ratio of core/shell material, 250 rpm for the agitation rate, and emulsifier SDBS.

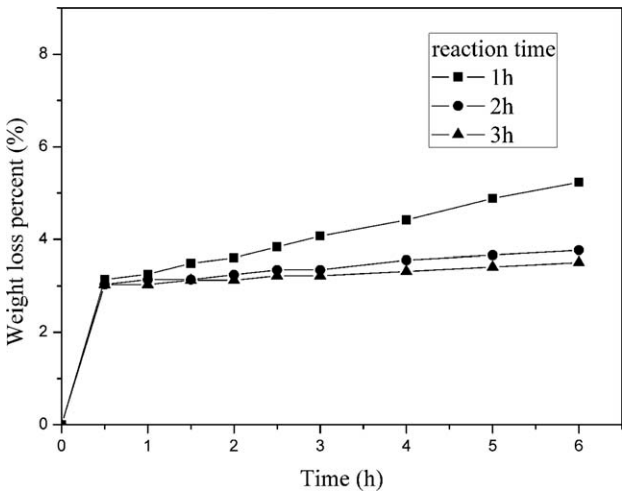

Figure 9 The core material permeability of microcapsules in the solvent at different reaction time. Synthesis condition: 1.4 : 1 for weight ratio of core/shell material, 250 rpm for the agitation rate, and emulsifier SDBS.

the surface roughness after 2 h [Fig. 8(b,c)], compared with 1 h for reaction time [Fig. 8(a)]. Presumably, the polycondensation of urea–formaldehyde derivative prepolymers is basically completed after 2-h reaction time. Therefore, the optimum synthesis condition for reaction time is considered to 2 or 3 h.

To evaluate the core material permeability of microcapsule influenced by the reaction time, the weight loss of microcapsules in the solvent were investigated at different time. From Figure 9, it is worth noting that the weight loss of microcapsules immersed into solvent for 0.5 h is almost 3 wt %, and as the immersed time increases further, the weight loss of microcapsules obviously tends to decrease and the slope of curve becomes small, indicating that the microcapsules immersed into solvent can all maintain well in 6 h. The weight loss before 0.5 h is mainly due to the dissolution of entrapped residual water and small molecule such as low molecular weight urea–formaldehyde derivatives, and the weight loss of microcapsules after 0.5 h is mainly owing to slow diffusion of little core material throughout the wall shell. The weight loss of microcapsules solvent-treated increases with the enhancement of time, indicating that the microcapsules cannot be immersed into solvent surrounding timelessly, which cause the larger weight loss of microcapsules. The permeability of microcapsules increases with the enhancement of slope of curve when the sample is immersed into solvent after 0.5 h. Therefore, the permeability of microcapsules from high to low in turn is microcapsules prepared at the reaction time 1, 2, and 3 h, respectively. The results can be easily concluded that raising reaction time would obviously decrease the permeability of microcapsule to some extent. As a result, the optimum synthesis condition for reaction time is concluded to 3 h.

The effect of emulsifier on microcapsules' properties

As discussed above, the varieties of emulsifier largely influence on the microcapsule's yield because suitable emulsifier decreases the Gibbs free energy at the interface of oil-in-water emulsion and keeps stabilization of the emulsion. Therefore, the microcapsule yield increases. The adhesion, size distribution and average diameter affected by emulsifier varieties and content, were investigated in this section.

To assess the effect of the presence or absence of emulsifier on adhesion and microcapsules' quality, the comparative experiments were carried out. The core content of microcapsule samples prepared by emulsifier SDBS and no emulsifier are 77.4% and $<$14.2%, respectively, (other synthesis condition: 1.4 : 1 for weight ratio of core/shell material, 250 rpm for the agitation rate, 3 h for the reaction time). The lower core content of microcapsule synthesized by no emulsifier is owing to the existence of semiencapsulated and unencapsulated microcapsules. Similar results can be obtained from other specimens of orthographic factorial experiments (Table II). According to optical theory, two different refractive index media microencapsulate each other, the diffraction ring will occur at the interface between the two different media. If the shell materials only exist, the diffraction ring would not be observed from OM photos. Compared to the microcapsules prepared by emulsifier SDBS, microcapsules prepared by no emulsifier increasingly adhere together with each other and the quantity of semiencapsulated and unencapsulated microcapsules increases obviously which can be observed from Figure 10(a,c)]. The reason is that interfacial tension between the oil droplets and water phase decreases greatly as a result of the emulsification so as to keep the stable emulsion. As a consequence, mutually exclusive oil colloids tend to increase, which brings about the decrease of adhesion among the resultant microcapsules [Fig. 10(b,d)]. Contrarily, the oil droplets tend to get together in an oil-in-water emulsion within no emulsifier due to unstable oil-water interface resulted by larger interfacial tension. As a result, the weight ratio of semiencapsulated or unencapsulated microcapsules and adhesion among microcapsules increases.

To value the effect of different emulsifier on microcapsule's property, microcapsules were synthesized by emulsifier SDS and SDBS, respectively. Hydrophilic–lipophilic balance value (HLB) is an important constant for helping match the oils used

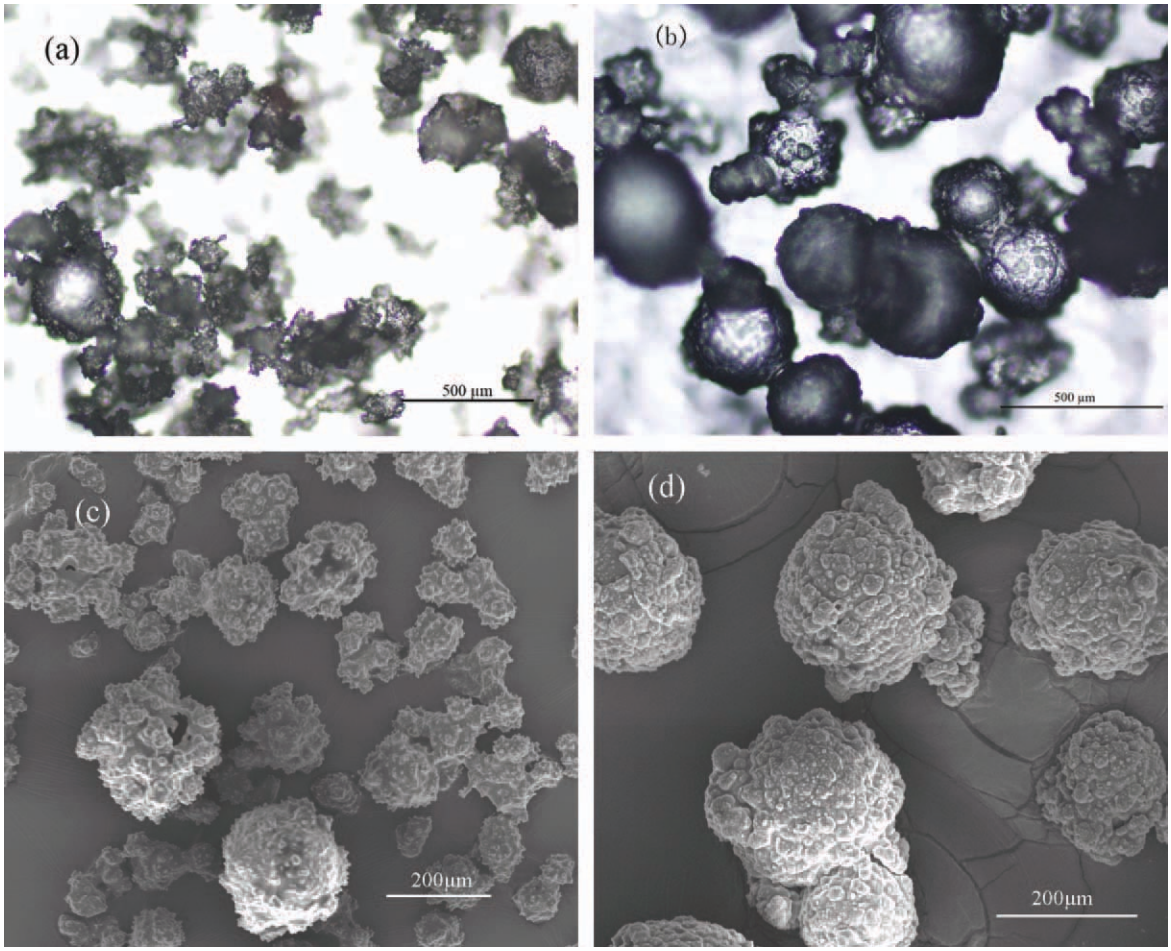

Figure 10 Images of microcapsules. (a) OM photos of no emulsifier; (b) OM photos of emulsifier DBS; (c) SEM photos of no emulsifier; (d) SEM photos of emulsifier DBS. Synthesis condition: 1.4 : 1 for weight ratio of core/shell material, 250 rpm for the agitation rate, 3 h for the reaction time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with appropriate emulsifiers because an emulsifier can provide a stable system for combination of oil and water that has a hydrophilic and a lipophilic end. HLB value of a surfactant is determined by calculating values for the different regions of the molecule.[29] In our work, HLB value of SDS and SDBS is 40 and 10.638, respectively. The surfactants used in this work are all anion emulsifier which is adapting for oil-in-water emulsion. From Figure 11(a), microcapsules prepared by SDS obviously assemble together, and are abnormity, many adhesions, weaker shell wall. Compared to the microcapsules prepared by SDS, microcapsules prepared by SDBS are spherical, few adhesions [Fig. 11(b)]. This infers that the surfactant SDBS provides a stabler oil-in-water emulsion system for the microencapsulation as result of appropriate HLB value which is in the range of 8–18. Similarly, emulsifier SDS fails to keep the balance of oil–water emulsion so that core material fails to be encapsulated and abnormal capsules are formed.

The influence of emulsifier content on the average diameter and size distribution is shown in Figure 12. As the emulsifier content decreases, the microcapsule's average diameter increases and the size distribution broadens. For the reason, the size of resultant microcapsules is definitely decided by the size of oil colloids in the emulsion. With the decrease of the content of surfactant, oil droplets tend to get together and become bigger in an emulsion so as to keep the stabilization as result of larger surface tension. Similarly, a finer emulsion can be obtained with the increase of the content of emulsifier so that the microcapsule's size becomes small and size distribution is narrowed down. The property for microcapsule's average diameter while the maximum healing efficiency occurs at low microcapsule concentrations ($\sim$ 5 vol %) is $\sim$ 180 μm, which has been reported in the literature.[30] Therefore, considering microcapsule's size and quality, the optimum synthesis condition for emulsifier SDBS content is concluded to 1.5%.

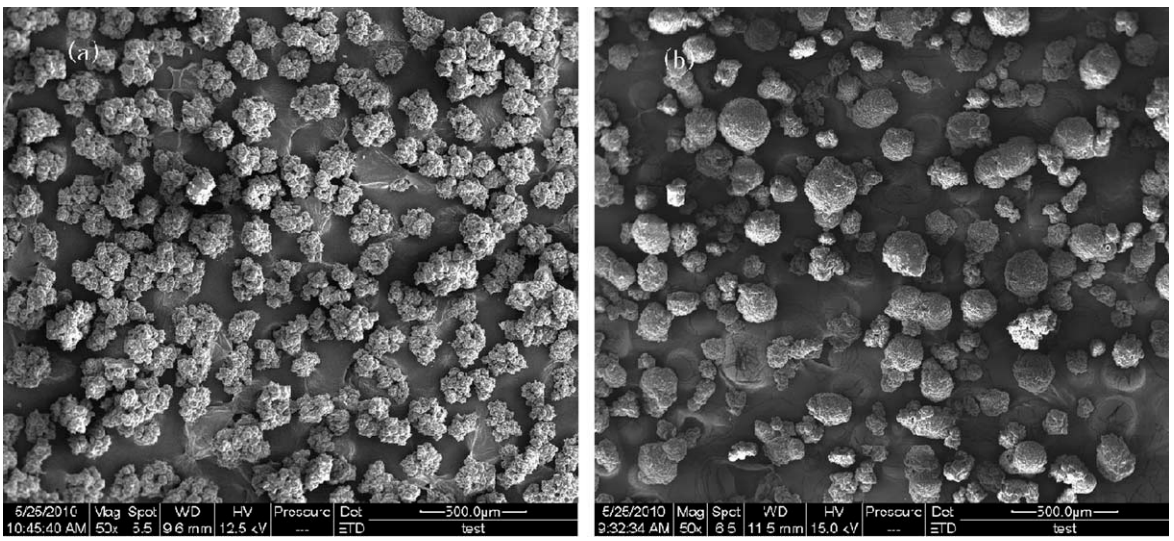

Figure 11 SEM photographs of epoxy-containing microcapsules with different emulsifier. (a) SDS; (b) SDBS. Synthesis condition: 1.4 : 1 for weight ratio of core/shell material, 250 rpm for the agitation rate, 3 h for the reaction time.

Chemical structure of microcapsule

Figure 13 shows the FTIR spectra of mixture of DGEBPA and TMPEG, microcapsules, PUF shell material. Table VI lists the detailed peak assignments of mixture of DGEBPA and TMPEG, PUF shell material. Obviously, the FTIR spectrum of PUF microcapsules containing the core material presents absorption peaks of epoxy group at 915 and 830 cm^{-1}, which indicates that the mixture of DGEBPA and TMPEG are successfully encapsulated by PUF.

The reactivity of core material of microcapsules is further evaluated by DSC (Fig. 14). For the curve of mixture of core material and TETA, an obvious exothermic reaction is detected at temperature 87.91°C with the heat of reaction 332.6472 J g^{-1}. When core material was replaced by the ground microcapsules containing the mixture of DGEBPA and TMPEG, similar exothermic peak with a heat of reaction of 145.4426 J g^{-1} appears at 73.05°C. This infers that the core material of microcapsules presents the reaction activity. Compared with the DSC curve of PUF shell material/TETA, an endothermic reaction peak appears at 130.26°C with 724.0572 J g^{-1}. Similar reaction peak can be found from the curve of ground microcapsules/TETA.

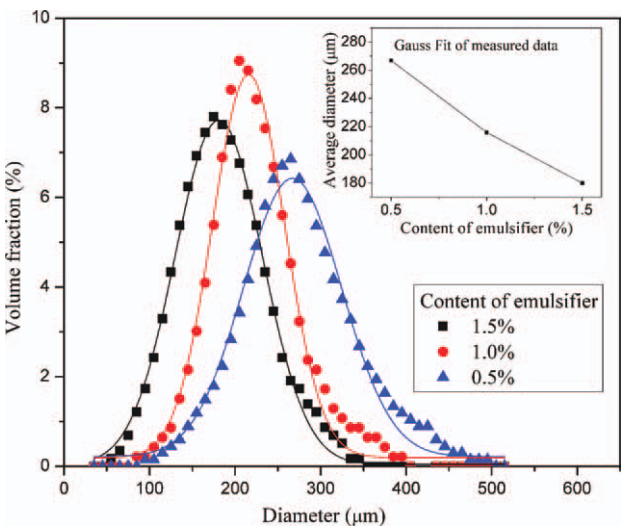

Figure 12 Size distribution of epoxy-containing microcapsules at different emulsifier content. Synthesis condition: 1.4 : 1 for weight ratio of core/shell material, 250 rpm for the agitation rate, 3 h for the reaction time, and emulsifier SDBS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

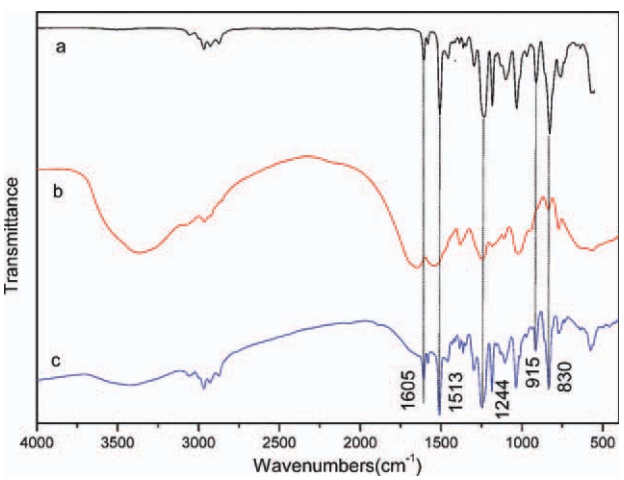

Figure 13 FTIR spectra of (a) mixture of DGEBPA and TMPEG, (b) PUF shell material, (c) microcapsules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE VI
Wavenumbers (cm^{-1}) and Assignments of the FTIR Spectra of Mixture of DGEBPA and TMPEG, PUF Shell Material

DGEBPA	Approximate assignment	TMPEG	Approximate assignment	PUF	Approximate assignment
3490	νO—H	2870–2970	νC—H (methyl group)	3420	νN—H, νO—H
1605	νC=C (phenyl ring)	1033	C—O—C	2920–3000	νC—H
1382	—$C(CH_3)_2$	915 830	—CH—CH_2 (epoxy)	1651	—C=O
1513	C—O—C			1556	—C—N
1244 915 830	—CH—CH_2 (epoxy)				

Physical properties of microcapsule

The synthesis parameters when the microcapsules exhibit the most optimum properties are concluded: 1.4 : 1 for weight ratio of core/shell material, 250 rpm for the agitation rate, 3 h for the reaction time, and 1.5% for the content of emulsifier SDBS. The physical properties of microcapsules including physical structure, surface morphology, shell thickness, adhesion, the compatibility, and interfacial performance of microcapsules and epoxy matrix were investigated in this section.

Figure 15 shows the OM photo of microcapsule. According to optical theory, two different refractive index media microencapsulate each other, the diffraction ring will occur at the interface between the two different media. The diffraction ring can be observed evidently, which indicates that the PUF successfully microencapsulates core material.

Figure 16 shows the SEM micrograph of microcapsules sample. The microcapsules observed are spherical and few adhesions [Fig. 16(a)]. The outside surface of microcapsules is rough which can increase the surface areas of microcapsules and enhance interface adhesion [Fig. 16(b,c)]. It is strong evidence that epoxy-containing microcapsules are synthesized successfully from Figure 16(d) which shows single cracked microcapsule. Shell thickness determines the mechanical properties of microcapsules and the release model of core materials, which is measured directly from the SEM images of the fracture surfaces. Here, the average shell thickness of the microcapsules sample is ~ 7 μm from Figure 16(e,f).

To value the compatibility of microcapsules and epoxy matrix, contact angle between core material and PUF shell material was carried out so as to assure the core materials flowing out as result of capillary effect while microcapsules are embedded in the epoxy matrix (Fig. 17). The average contact angle is 65.9°, which indicates that core material is

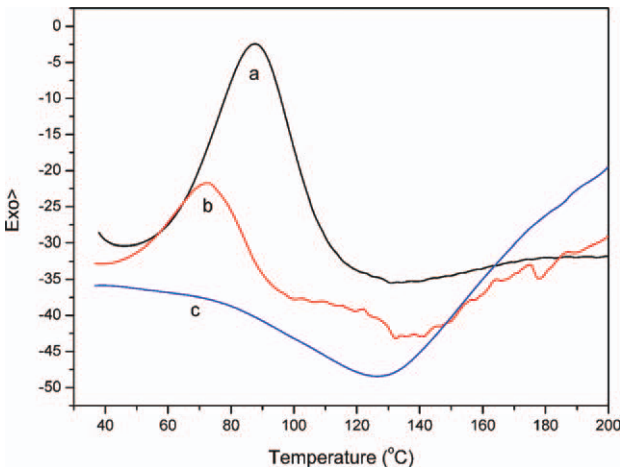

Figure 14 DSC curves of (a) core material/TETA = 10 : 1.3, (b) ground PUF-walled microcapsules/TETA = 14.2 : 1.3, (c) PUF shell material/TETA = 4.2 : 1.3 The compositions are expressed in terms of weight ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

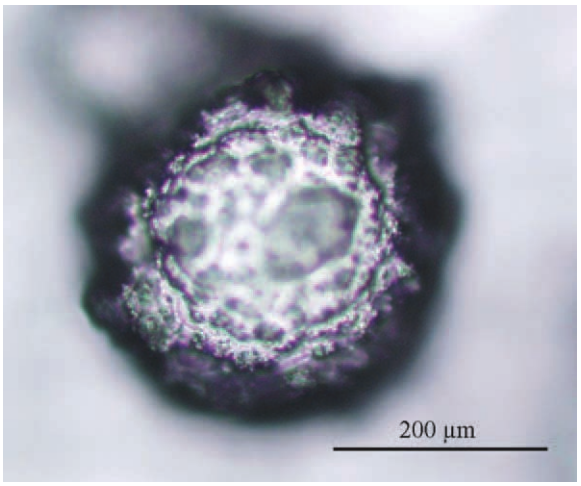

Figure 15 OM micrograph of prepared microcapsule. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

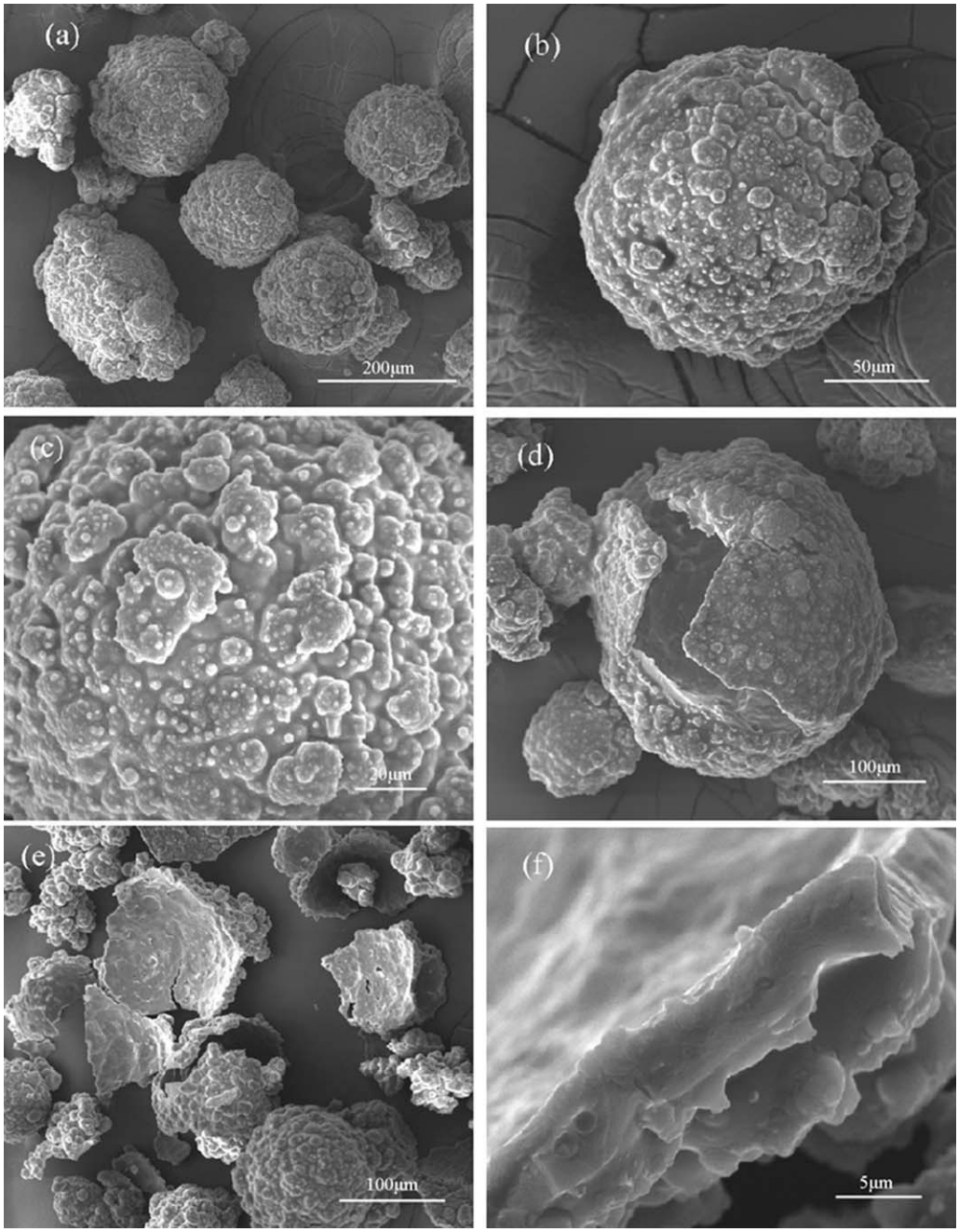

Figure 16 SEM micrographs of microcapsules. (a) Overview; (b) Single microcapsule; (c) Microcapsule's surface; (d) Single cracked microcapsule; (e) Crushed microcapsules; (f) Shell thickness.

wettable with shell material. Therefore, the core material can flow out through shell material when the microcapsules are cracked in the matrix.

Figure 18 shows the SEM photograph of fractured microcapsule embedded in epoxy matrix. The strong interface bond between microcapsule and matrix can be observed obviously, which infers that the microcapsules could be fractured when cracks propagate through self-healing material. At the same time, it is also proved that the core material is successfully microencapsulated via *in-situ* polymerization.

CONCLUSIONS

The PUF microcapsules containing DGEBPA and TMPEG were successfully prepared via *in-situ* polymerization in an oil-in-water emulsion. The properties of microcapsules influenced by the synthesis conditions were investigated systematically in this article. Finally, the synthesis parameters when the epoxy-containing microcapsules exhibit the most optimum properties are concluded: 1.4 : 1 for the weight ratio of core/shell material, 250 rpm for the agitation rate, 3 h for the reaction time and 1.5%

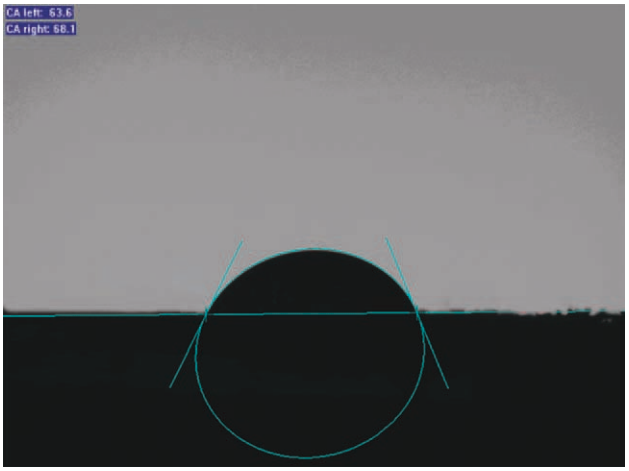

Figure 17 Contact angle between core material and PUF shell material. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

emulsifier content for the emulsifier SDBS. The chemical structure of microcapsules is confirmed and the core material exhibits reaction activity. To provide physical parameters of microcapsule's properties for making binary self-healing composites in the subsequent works, the resultant microcapsules are characterized by SEM, OM, and contact angle experiment. As a consequence, the resultant microcapsules are suitable for fabricating self-healing composites.

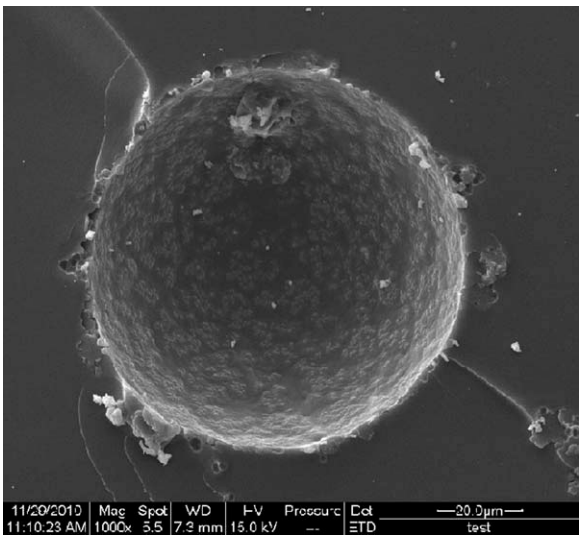

Figure 18 SEM photograph of fractured microcapsule embedded in epoxy matrix.

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