J Mater Sci (2007) 42:4390–4397
DOI 10.1007/s10853-006-0606-6

The permeability and stability of microencapsulated epoxy resins

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Received: 12 March 2006 / Accepted: 20 June 2006 / Published online: 28 February 2007

Abstract Microcapsules containing self-healing agents have been introduced into polymer to self-heal the microcracks and toughen the brittle matrix. Poly(urea–formaldehyde) (PUF) microcapsules containing epoxy resins are potential for the self-healing and toughening polymer. The resistance to medium surroundings of microcapsules is required. In the present study, PUF microcapsules containing epoxy resins were prepared by in situ polymerization. The effects of diameter, surface morphology and wall thickness on the permeability and stability of microcapsules in thermal and solvent surroundings were investigated. The morphology of microcapsule was investigated using optical microscope (OM), metalloscope (MS) and scanning electron microscope (SEM), respectively. The composition on the surface of microcapsule was analyzed by using energy dispersive analysis of X-ray (EDAX). The thermal properties of microcapsules were investigated using differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA). The thermal permeability of core increases and the stability of microcapsule decreases with the enhancement of heating temperature mainly due to the expansion of epoxy resins below 251 °C and the decomposition of PUF above 251 °C. At room temperature, the permeability constants of core materials of microcapsules in acetone solvent are small and they are 1.20×10^{-3} m s^{-1}, 1.39×10^{-3} m s^{-1} and 1.60×10^{-3} m s^{-1} corresponding to the microcapsules with diameters of 400 ± 50 μm, 230 ± 40 μm and 120 ± 30 μm. Increasing the surface smoothness, diameter and wall thickness can decrease the permeability and improve the stability of microcapsules in thermal and solvent surroundings.

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Introduction

Microencapsulation is a well-known process in which tiny particles or droplets are covered by a coating or a membrane, which can protect specific functional materials from or to release them into an outer phase in a controlled manner. The microencapsulation concept has been successfully applied for various areas, such as pharmaceuticals [1, 2], agriculture [3, 4], food additives [5], coating and dyes [6], etc. Recently, microcapsules containing polyaniline particle for electrorhological materials [7, 8] and microcapsules containing titanium dioxide (TiO_2) and oil as a microcapsule-based electronic ink display technique [9, 10] have been developed. The microencapsulated self-healing agents applied to polymeric composites is also one of new options for microcapsule applications. The poly (urea–formaldehyde) (PUF) microcapsules containing dicyclopentadiene (DCPD) have been embedded in polymeric composites to achieve the self-healing function of composites and improve the toughness of brittle matrix [11–16]. Due to their promising applications in polymeric composites, the microcapsules containing self-healing agents have been paid more attention. Because polymers can be made by different fabrication methods such as by melt fabrication and by solution

casting at different temperature and pressure, the microcapsules applied to polymeric composites are required specially. They not only store the healing agent during quiescent states, but also withstand the medium surroundings during the processing of composite and rupture when the host polymer is damaged. The final applications of microcapsules are largely depended on their stability in medium surroundings, which can be dominated by many factors such as the properties of materials, the ratio of core to shell material, the agitation rate and so on. Selecting appropriate core and shell materials is important for the improving the stability. Microcapsules have been synthesized with UF [17, 18], melamine–formaldehyde [19], polyurethane [20], nylon [21] and polyurea [22] as shell materials. Owing to the perfection of in situ encapsulation of water-immiscible liquids by the reaction of urea with formaldehyde at acid, PUF materials have been widely used as shell materials and play an important role in the preparation of microcapsules. PUF microcapsules containing liquid epoxy resins are a new series of microcapsules and have been prepared successfully in our laboratory. They are potential for the self-healing and toughness improvement of brittle matrix. Due to the formation of compact PUF wall shell and the high thermal decomposition temperatures of PUF (>200 °C) and epoxy resins (>250 °C), PUF microcapsules containing epoxy resins may possess higher thermal decomposition.

Aiming to understand the stability of PUF microcapsules containing epoxy resins in different medium surroundings and develop their applications in polymers fabricated at different processing conditions, in the present study, a series of microcapsules were synthesized by selecting different weight ratios of core-shell materials, agitation rate and surfactant concentration. The influences of different diameters, wall thickness and surface morphology on the permeability behavior of core and the stability of microcapsules were investigated.

Experimental methods

Materials

Diglycidyl ether of bisphenol A (DGEBPA) used as core material was purchased from Wuxi Resin Plant, China. 1-butyl glycidyl ether (BGE) used as reactive diluent of DGEBPA, was purchased from Shanghai Resin Plant, China. Urea and formaldehyde (37 wt.%) used as shell materials were purchased from Tianjin Chemical Plant, China. Triethanolamine, used to control the pH of solution, and Sodium dodecylbenzene sulphonate (SDBS) (99% purity), used as emulsifier, were purchased from Tianjin Chemical Regents Factory, China. Sulfuric acid solution (10 wt.%) was prepared in our laboratory to control the pH of emulsion.

Preparation of microcapsules

Microcapsules were prepared by in situ polymerization in an oil-in-water (O/W) emulsion. Urea, formaldehyde and deionized water were mixed in a 250 ml three-neck round-bottomed flask and stirred at room temperature. After the urea was dissolved, the pH of solution was adjusted to 8–9 with triethanolamine and the temperature was kept at 60–70 °C for 1 h. The prepolymer solution of urea–formaldehyde was obtained.

Under agitation, aqueous solution of SDBS was added to the as prepared prepolymer solution, and then a slow stream of a prepared mixture of DGEBPA and BGE was added to form an emulsion. After stabilization, the pH of the emulsion was adjusted slowly to 2–3 by addition of sulfuric acid solution while the solution was heated to the target temperature of 60–65 °C. After 3 h, the reaction was ended. The obtained suspension of microcapsules was cooled down to ambient temperature, rinsed with deionized water and acetone, filtered and air-dried for 24 h. The weight of urea, formaldehyde, DGEBA, BGE and some parameters of prepared microcapsules are presented in Table 1 and the property characterizations of prepared microcapsules are presented in Table 2.

Characterization of microcapsules

The surface morphology of microcapsule was observed using optical microscope (OM, XSP-XSZ, Beijing Tech Instrument Co., Ltd, China), metalloscope (MS, PM-T3, OLYMPUS) and scanning electron microscope (SEM, QUANTA200, FEI), respectively. The composition on the surface of microcapsule heat-treated

Table 1 The compositions and parameters of microcapsules

Sample No.	Shell materials		Core materials		Concentration of SDBS (wt.%)	Agitation rate (rpm)
	Urea (g)	Formaldehyde (g)	DGEBPA (g)	BGE (g)		
1	10.00	20.00	31.25	6.25	1.00	280
2	10.00	20.00	25.00	5.00	1.00	400
3	10.00	20.00	25.00	5.00	1.25	450

Table 2 Property characterizations of microcapsules

Sample No.	Mean diameter (μm)	Core content (wt.%)	Wall thickness (μm)	Surface characterization
1	400 ± 50	96.4	56 ± 5	Smoother
2	230 ± 40	81.1	56 ± 5	Smooth
3	120 ± 30	81.2	25 ± 5	Rougher

at different temperatures was evaluated using SEM-energy dispersive analysis of X-ray (EDAX).

The thermal properties of microcapsules were measured using thermogravimetric analysis (TGA-DTA, Q50, TA) and differential scanning calorimetry (DSC, 2910 MDSC, TA) at a heating rate of 10 °C/min in a nitrogen atmosphere.

The permeability of microcapsules in solvent

At room temperature, a certain volume of microcapsules and 200 mL of acetone were added to 250 mL of round-bottom three-neck bottle equipped with magnetic stirrer and a condenser. In order to reduce the volatility of acetone, the top of the condenser was fitted with a stopcock and the join faces of each equipment were covered with thin layer of vaseline to airproof join surface during the experiments. About 3 mL of released acetone was extracted quickly with injector equipped with a filter at intervals and the concentration of core in acetone was analyzed by using ultraviolet-spectrophotometer (722s, Shanghai Precision and Scientific Instrument Cd, Ltd, China) at suitable time intervals. The released acetone was laid back quickly to the bottle after analyzed. Owing to the larger volume of acetone compared with the microcapsules, the volatility of acetone during the experiment may be neglected.

Results and discussion

Thermal permeability of microcapsules

Morphology of microcapsules

The wall shell is composed of PUF nanoparticles. The size of PUF nanoparticle can affect the surface morphology of microcapsule. The smaller the size of PUF nanoparticle, the smoother the surface is. The amount and the size of nanopores existing in wall shell decrease as the surface smoothness improves. Figure 1 shows SEM micrographs of untreated microcapsules, indicating that the surface smoothness of microcapsules from sample No. 1 to sample No. 3 gradually decreases. Figure 2 shows OM micrographs of microcapsule samples heat-treated for 2 h at 50, 100, 120, 140, 160, 180 and

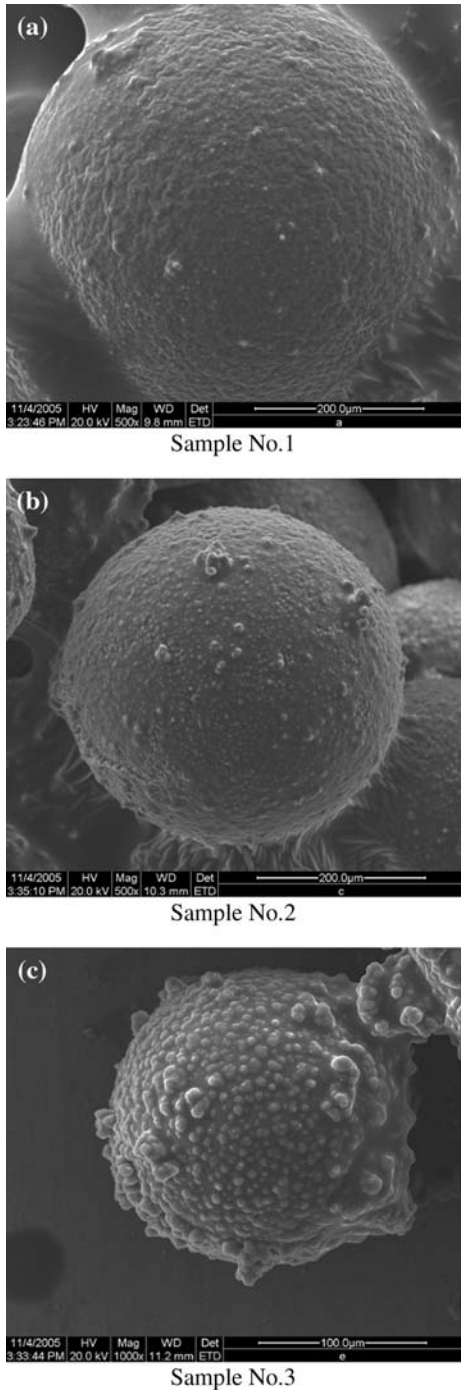

Fig. 1 SEM micrographs of microcapsules. (**a**) Sample No. 1, (**b**) Sample No. 2, (**c**) Sample No. 3

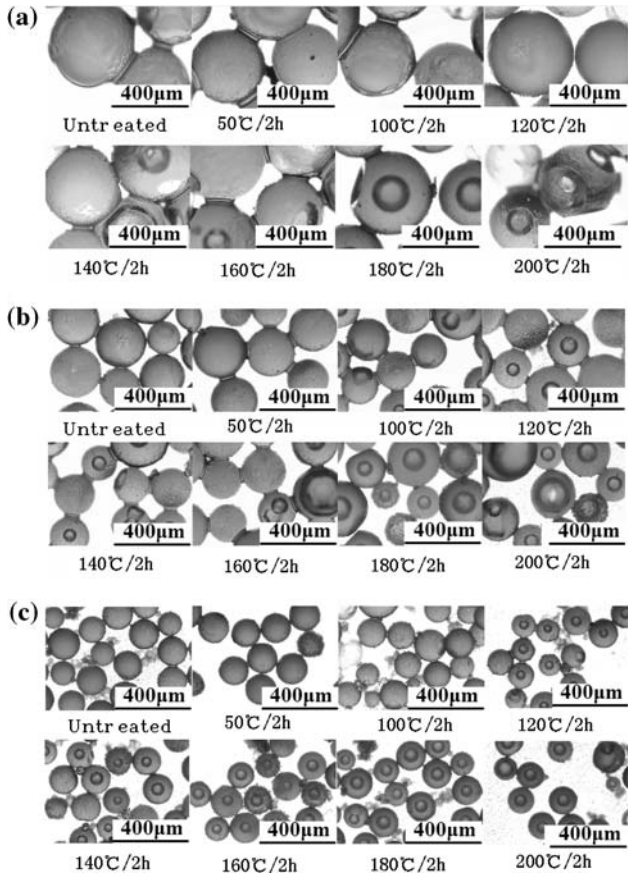

Fig. 2 OM micrographs of microcapsules heat-treated at different temperatures. (**a**) Sample No. 1(magnification: 40), (**b**) Sample No. 2 (magnification: 40), (**c**) Sample No. 3 (magnification: 40)

200 °C, respectively. The intactness of microcapsules can be maintained well below 120 °C, which indicates that the microcapsules exhibit good thermal stability. The deformed microcapsules occur when the temperature is up to approximately 120 °C and they increase with the enhancement of heating temperature. Dimples can be found on the microcapsules. It can be explained by the fact that the expansion of core material causes the diffusion of core material out of the intact wall shell, and the wall shell contracts as it cools to room temperature [23]. When the temperature is below 120 °C, it can be observed from Fig. 2 that microcapsule sample No. 1 maintains better intactness than the microcapsule samples No. 2 and No. 3. The main reason is the fact that the smoother surface and thicker wall shell can reduce the diffusion of core material effectively. When the temperature is above 120 °C, for the microcapsules with the same wall shell thickness (samples No. 1 and No. 2), the microcapsules with higher core content and larger diameter (sample No. 1) are deformed more largely and fractured more easily than the microcapsules with lower core content and smaller diameter (sample No. 2). It may be due to the fact that more core material diffuses out of wall shell for sample No. 1, and thus the contraction degree of wall shell is higher. Although the smoother surface can reduce the diffusion of core material, the improvement of surface smoothness cannot release quickly the expansion of core material when the heating temperature is higher. As a result, the microcapsules with smoother surface are easily fractured. As to the microcapsules with the same core content (samples No. 2 and No. 3), the microcapsules with thicker wall shell and larger diameter (sample No. 2) are deformed more largely than the microcapsules with thinner wall shell and smaller diameter (sample No. 3). It may be explained by the more diffusion of core material and the larger contraction of thicker wall shell for sample No. 2 after cooled to room temperature. Obviously, the increase of wall thickness and smoothness of surface can decrease the permeability of core and enhance the thermal stability of microcapsules at lower temperature (<120 °C). The enhancement of wall thickness and surface smoothness maybe not benefit the intactness maintenance of microcapsules at higher temperature (>120 °C).

Surface element analysis of microcapsules

Figure 3 shows the EDAX spectrum of surface of untreated microcapsule (sample No. 3) and Table 3 represents the surface element analysis data of all microcapsules heat-treated from 120 to 200 °C. C and O element fractions became larger as the heating temperature increases, which indicates that the core material diffuses out of wall shell and the diffusion amount of core material increases with the enhancement of heating temperature.

Figure 4 shows MS micrographs of untreated microcapsules (sample No. 1) and microcapsules

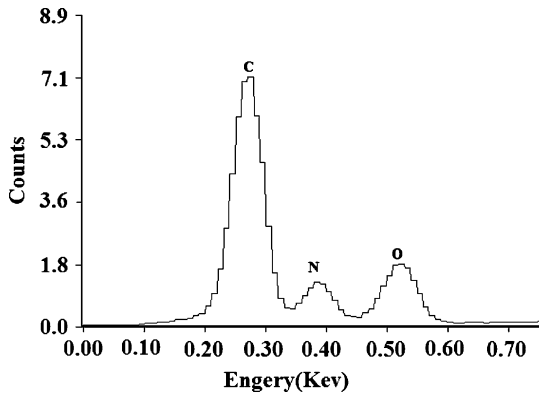

Fig. 3 EDAX spectrum of surface of untreated microcapsule (Sample No. 3)

Table 3 EDAX results of surfaces of microcapsules heat-treated at different temperature

Temperature (°C)	Atomic fraction (%)								
	Sample No. 1			Sample No. 2			Sample No. 3		
	C	N	O	C	N	O	C	N	O
Untreated	54.6	27.5	17.8	54.6	27.5	17.8	54.6	27.5	17.8
50	54.6	27.5	17.9	54.6	27.5	17.8	54.6	27.5	17.8
100	54.6	27.5	17.9	54.6	27.5	17.8	54.6	27.5	17.8
120	54.7	27.4	17.9	54.7	27.4	17.8	54.7	27.4	17.8
140	54.8	27.3	17.9	54.8	27.3	17.9	54.8	27.3	17.9
160	55.0	27.0	18.0	55.0	27.1	17.9	54.9	27.2	17.9
180	55.5	26.5	18.0	55.4	26.7	17.9	55.3	26.8	17.9
200	55.8	26.2	18.0	55.8	26.2	18.0	55.8	26.3	17.9

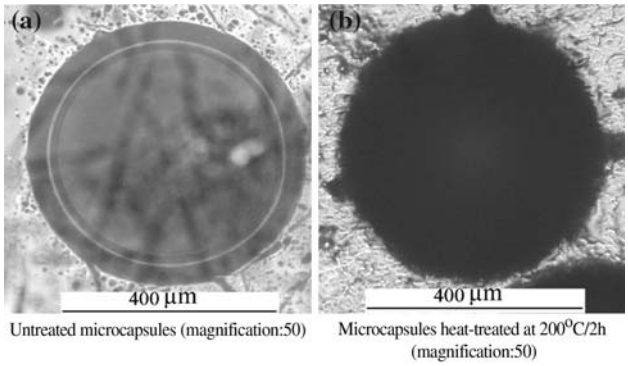

Fig. 4 MS micrographs of microcapsules (Sample No. 1). (**a**) Untreated microcapsules (magnification: 50), (**b**) microcapsules heat-treated at 200 °C/2h (magnification: 50)

(sample No. 1) heat-treated at 200 °C. The diffraction rings can be observed in untreated microcapsules. 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. No diffraction ring can be observed in heat-treated microcapsules, which indicates the interface between the two phases disappears and the core material diffuses through wall shell of microcapsules.

Thermal properties of microcapsules

Figure 5 shows DSC and TGA curves of microcapsules. The endothermic peaks on DSC curves at about 251 °C are mainly due to the thermal decomposition of a partial shell material. The distinctly exothermic peaks appear on DSC curves at about 261 °C owing to the polymerization reaction of between partial epoxy resins and amino-derivatives produced by the decomposition of shell material [24]. The weight loss of microcapsules on TGA curves below 251 °C is mainly attributed to the diffusion of core material. When the temperature is approximately up to 251 °C, the wall shell material begins to decompose. As a result, the diffusion of core material and weight loss increases significantly at temperatures between 235 and 284 °C. Due to the formation of cross-linked polymer of epoxy resins, the weight loss rates and the slopes of weight loss curves decrease at temperatures between 284 and 320 °C. The residual materials are decomposed further above

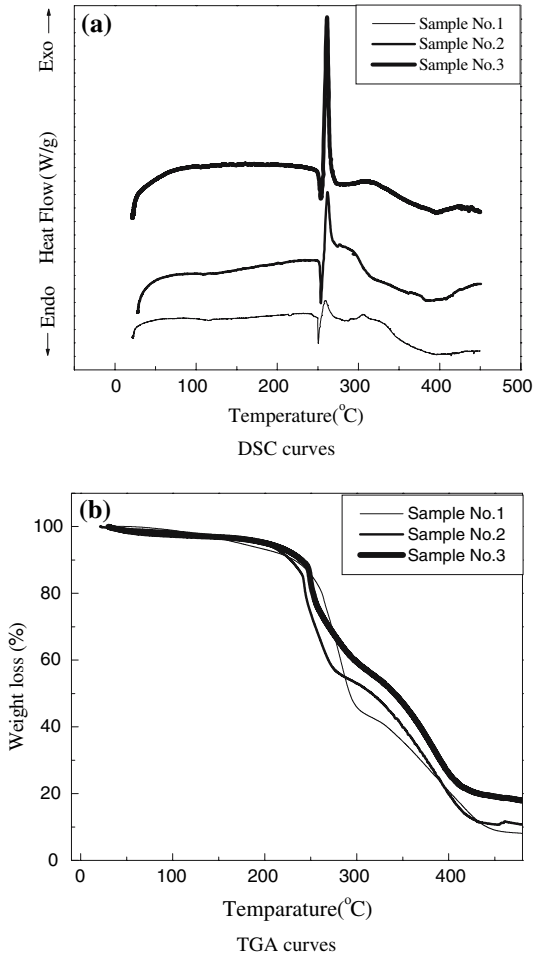

Fig. 5 DSC and TGA curves of microcapsules

320 °C, the weight loss rates increase and the weak exothermic peaks appear on DSC curves. Obviously, the diameter, the wall thickness and the surface smoothness have no influence on the initial thermal decomposition temperature of microcapsules (251 °C), which depend on the wall shell materials. Table 4 represents the thermal weight loss temperature at different weight loss percentage of microcapsules below 251 °C. For the microcapsules with same wall thickness (samples No. 1 and No. 2), the T^1_d of sample No. 1 are higher than that of sample No. 2. It can be explained by the fact that the smoother surface and thicker wall shell of microcapsules can reduce the diffusion of core material. The T^3_d and T^4_d of sample No. 1 are lower than that of sample No. 2 possibly due to the higher core content of sample No. 1. For the microcapsules with same core content (samples No. 2 and No. 3), the T^1_d, T^2_d, T^3_d and T^4_d of sample No. 2 are higher than that of sample No. 3 due to the thicker wall shell and smoother surface. When the temperature is approximately up to 251 °C, the wall shell material begins to decompose. The mixed weight losses of wall shell and core material cause the erratic weight loss of microcapsules, which can be implied by the T^5_d and T^6_d of each microcapsule sample. Obviously, increasing the wall thickness, the surface smoothness and diameter can decrease the thermal permeability and enhance the thermal stability.

The permeability and stability of microcapsules in solvent

The wall thickness, mean diameter and surface morphology affect significantly the permeability and stability of microcapsules in solvent. The permeability behavior of microcapsules in solvent can be characterized by the permeability distance of core material through wall shell in unit time (shown in Fig. 6), i.e., the permeability constant P(m s^{-1}). According to Fick's first law of diffusion and the results reported by the reference [25], the rate of change in concentration of core material in the outside of microcapsules (Eq. 1) can be obtained

$$\frac{dC_t}{dt} = -\frac{DA}{V_s} \cdot \frac{\Delta C}{\Delta X}, \tag{1}$$

where C_t is the concentration of core material of outside of microcapsules (i.e. acetone surrounding) at time t, A is total surface area of microcapsules, the proportionality constant D is the diffusion coefficient, ΔC implies the difference in core material concentration between the outside and inside of the microcapsules, ΔX is the wall shell thickness, V_s is the volume of outside of microcapsules.

Since the total amount of core material in the system always remains unchanged, the following equation should hold

$$C_{i,0}V_i + C_0V_s = C_tV_s + C_{i,t}V_i = C_f(V_s + V_i), \tag{2}$$

where $C_{i,0}$ ($C_{i,0}$=1), and C_0 ($C_0 = 0$) are the initial concentrations of core material of the inside of microcapsules and the outside of microcapsules, respectively. $C_{i,0}$ is the concentration of core material of the inside of microcapsule at time t. C_f is the final concentration of core material of the outside and inside of the microcapsules, i.e. the balance concentration. V_i is the volume of microcapsules.

Transforming Eq. 1 using the following relation

$$\Delta C = \left(1 + \frac{V_s}{V_i}\right)(C_t - C_f) \tag{3}$$

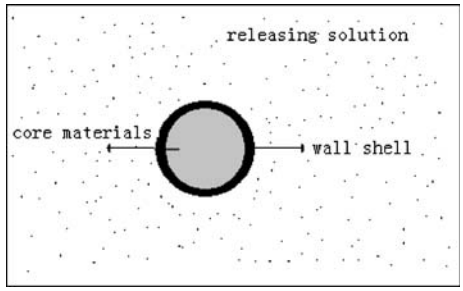

Fig. 6 The permeating of core material of microcapsule in solvent

Table 4 Weight loss temperature of microcapsules at different weight loss percentage

Sample No.	Endothermic peaks value (°C)	Exothermic peak value (°C)	T^1_d (°C)	T^2_d (°C)	T^3_d (°C)	T^4_d (°C)	T^5_d (°C)	T^6_d (°C)
1	251	261	97	120	140	153	232	251
2	251	261	71	121	161	199	228	241
3	251	261	44	71	140	202	239	248

[1,2,3,4,5 and 6] The temperature when the weight loss percentage of microcapsule sample is 1, 2, 3, 5, 10 and 15 wt.%, respectively

which can be obtained from Eq. 2, and then

$$\frac{dC_t}{dt} = -\frac{DA}{V_s V_i \Delta X}(V_i + V_s)(C_t - C_f). \quad (4)$$

Integration of Eq. 4 leads to

$$\ln\frac{C_f - C_t}{C_f - C_0} = -\frac{DA}{\Delta X}\cdot\frac{V_i + V_s}{V_i V_s}\cdot t. \quad (5)$$

Due to $V_s >> V_i$, Eq. 6 can be obtained:

$$\ln(C_f - C_t) = -\frac{DA}{\Delta X V_i}\cdot t + \ln(C_f - C_0). \quad (6)$$

Therefore, a liner relation is expected when $\ln(C_f - C_i)$ is plotted against t. From the slope of the line, we obtain:

$$P = \frac{D}{\Delta X} = -\frac{V_i}{A}S \quad (7)$$

where S is the slope.

For the spherical microcapsules, it is assumed that d is the diameter of microcapsule and the number of microcapsules is N, then

$$A = N\pi d^2 \quad (8)$$

$$V_i = N\pi d^3/6 \quad (9)$$

The Eqs. 8 and 9 are introduced to Eq. 7, and then

$$P = -dS/6. \quad (10)$$

Knowing the concentration of core material, we can calculate the P according to Eqs. 6 and 7.

Table 5 represents the P value of microcapsules. When the wall shell thickness is kept at constant (samples No. 1 and No. 2), the S value of microcapsule sample No. 1 with larger diameter and higher core content is larger, whereas the P value is smaller. It can be explain by the fact that microcapsule sample No. 1 have smoother surface and smaller surface areas, which can reduce the permeability of core. When the core content is kept at constant (samples No. 2 and No. 3), the S value of microcapsule sample No. 2 with larger diameter is larger, whereas the P value is smaller. The main reason is the fact that the microcapsule sample No. 2 has smoother surface, smaller surface areas and thicker wall thickness, which can effectively restrain the permeability of core because the smoother surface and smaller areas can decrease the diffusion of core material and the thicker wall shell can increase the diffusion distance of core material.

Table 5 The core permeability constant P of microcapsules (it is assumed that the molecular weight average of the mixture of DGEBPA and BGE is 352.87.)

Sample No.	S	10^{-3} P (m s^{-1})
1	–0.0018	1.20
2	–0.0036	1.39
3	–0.0086	1.60

S: the slope of $\ln(C_f - C_t)$ to t

Figure 7 shows the relationship between C_t and t of different microcapsules in acetone. When the wall thickness of microcapsules is kept at constant, the initial core concentration of microcapsule sample No. 1 is smaller than that of microcapsule sample No. 2. The reason is the smaller P value of sample No. 1. The balance core concentration of sample No. 1 is larger and its balance core concentration time is longer than that of sample No. 2. It can be explained by the fact that the smaller surface areas slower the diffusion rate of core material and the higher core content need more time to achieve balance core concentration of microcapsule sample No. 1. When the core content of microcapsules is kept at constant, the initial core concentration of microcapsule sample No. 2 is smaller than that of sample No. 3 due to the smaller P value of sample No. 2. The balance core concentration time of sample No. 2 is longer than that of microcapsule sample No. 3. It is mainly due to the thicker wall shell and smoother surface of sample No. 2 reduce the diffusion rate of core material.

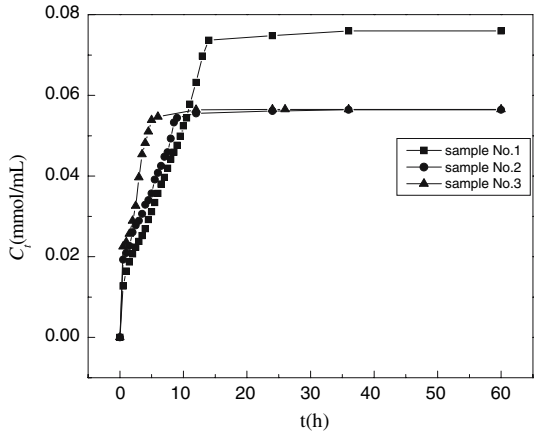

Fig. 7 The relationship between C_t and t. It is assumed that the initial concentrations (C_0) of core materials of three microcapsules in acetone are 0 mmol/ml

Conclusions

The applications of PUF microcapsules containing epoxy resins depend on their stability in environment. The prepared microcapsules maintain intact below 120 °C. Owing to the diffusion of core material, the deformed microcapsules occur when the temperature is up to 120 °C and the thermal stability of microcapsules decreases with the increase of heating temperature. For the microcapsules with same wall thickness, the microcapsules with smoother surface and larger diameter maintain better intactness and have higher thermal stability when the heating temperature is below 120 °C, but they are deformed more largely due to the more diffusion of core material when the heating temperature is above 120 °C. For the microcapsules with same core constant, the microcapsules with thicker wall shell, smoother surface and larger diameter have higher thermal stability when the heating temperature is below 120 °C, and they are deformed more largely when the heating temperature is above 120 °C due to the larger contraction degree of wall shell. When the heating temperature is above 251 °C, the microcapsules are damaged largely for the decomposition of wall shell material. For the microcapsules have the same wall thickness, the microcapsules with larger diameter and smoother surface have smaller core permeability constant P and higher stability in solvent due to the smaller surface areas restraining the core diffusion. For the microcapsules have the same core content, the microcapsules with thicker wall thickness and smoother surface have smaller core permeability constant P and higher stability due to the thicker wall and smaller areas effectively reducing the core diffusion. Obviously, the permeability and stability of microcapsules can be controlled by wall thickness, surface morphology and diameter. Among the prepared microcapsules, the microcapsules with diameter of 400 ± 50 μm, wall thickness of 56 ± 5 μm may be optimal because of the lowest permeability and highest stability in medium surroundings. Due to the lower permeability in solvent and higher thermal stability, the PUF microcapsules containing epoxy resins may be applied to the polymer fabricated at higher temperature (<251 °C) or by solution casting.

Acknowledgements The work was supported by the special research foundation of doctoral subject from the education department of high school (20050699034) and the graduate staring seed fund of Northwestern Polytechnical University (Z200584).

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