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ORIGINAL CONTRIBUTION

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Structure and thermal stability of microencapsulated phase-change materials

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Abstract A series of microcapsules containing n-octadecane with a urea-melamine-formaldehyde copolymer shell were synthesized by in-situ polymerization. The surface morphology, diameter, melting and crystallization properties, and thermal stability of the microcapsules were investigated by using FTIR, SEM, DSC, TGA and DTA. The diameters of the microcapsules are in the range of 0.2–5.6 μm. The n-octadecane contents in the microcapsules are in the range of 65–78wt%. The mole ratio of urea-melamine has been found to have no effect on the melting temperature of the microcapsules. Two crystallization peaks on the DSC cooling curve have been observed. The thermal damage mechanisms are the liquefied n-octadecane leaking from the microcapsule and breakage of the shell due to the mismatch of thermal expansion of the core and shell materials at high temperatures. The thermal stability of materials can be enhanced up to 10 °C by the copolymerization of urea, melamine and formaldehyde in a mole ratio 0.2:0.8:3. The thermal stability of 160 °C heat-treated microcapsules containing 8.8% cyclohexane can be further enhanced up to approximately 37 °C.

Keywords Microcapsule · n-Octadecane · Thermal stability · In-situ polymerization

Introduction

Microcapsules are tiny particles that contain active agent or core material surrounded by a coating or shell [1]. The diameters of microcapsules are usually in the range of 1 to 1000 μm. The core materials of the microcapsules can be drugs, paper coatings, enzymes, dyes, fragrant oils, water, or salts, etc. The core material can also be microparticles as used in electronic ink [2]. Microencapsulated phase change materials (MicroPCMs) have attracted more and more attention since the 1990s. MicroPCMs have been widely studied as an active or pumped coolants [3, 4, 5, 6], solar and nuclear heat storage systems [7] and in a packed bed as a heat exchanger [8]. MicroPCMs have also been used in the manufacture of thermo-regulated fibers, fabrics, and foams [9].

Thermal stability of MicroPCMs is crucial for manufacturing thermo-regulated fibers and fabrics. Selecting appropriate shell and core materials is important for improving thermal stability. MicroPCMs have been synthesized with urea-formaldehyde [3, 4], cross-linked nylon [4], melamine-formaldehyde [6], gelatin-formaldehyde [8], and polyurethane [10] as shell materials and were usually used at a temperature lower than 150 °C. Calcium silicate [11] and aromatic polyamide were used as shell materials to fabricate stable microcapsules [12]. Bryant studied the effects of the diameter of microcapsules on their thermal stability in the range of 3–50 μm. The weight loss at temperatures > 200 °C was found to

be more significant for microcapsules with smaller diameters than for those with larger diameters, however, the shell compositions were not disclosed [13]. Furthermore, the microcapsules expand during the melting process of the core and contract during the core crystallization process with an order of magnitude of 10% [5]. Dimples were found on microcapsules after solidification of the core, this was attributed to the fact that the contraction of the shell is less than that of the core. Moreover, thermogravimetric analysis and DSC experiments indicated that diffusion through the intact microcapsule wall at higher temperatures was the major mode by which the capsules lost their core materials [13].

In this study, the factors influencing thermal stability were investigated in relationship with the structures of MicroPCMs. Microcapsules were prepared using in-situ polymerization with various mole ratios of urea, melamine and formaldehyde as shell, or synthesized with urea-melamine-formaldehyde shell, 8.8v% cyclohexane and 91.2v% n-octadecane as the core. The diameters, phase change properties, and thermal stability were investigated by using FTIR, LM, SEM, DSC, TGA and DTA.

Materials

N-octadecane (95 wt%) was purchased from Union Lab. Supplies Limited, Hong Kong. Urea (95 wt%), Citric Acid (98 wt%), cyclohexane and Triethanolamine (95 wt%) were purchased from Tianjin Chemical Regents Inc. and used without further purification. Melamine (98 wt%) was purchased from Tianjin Resins Material Factory. Formaldehyde (37 wt%) was purchased from Jinan Organic Chemical Plant. Emulsion of Na Salt of styrene-maleic anhydride copolymer (TA, content 19 wt%) was a product of Shanghai Leather Chemical works.

Preparation of microcapsules

Microcapsules with Different Shell Structures

A mixture was prepared by mixing 4.76 g of urea, 19.50 ml of formaldehyde and 20 ml of distilled water. The mixture was adjusted to pH 8 to 8.5 with triethanolamine and stirred at 65 °C till the suspension became transparent. The prepolymer was synthesized.

A mixture 34.06 g of n-octadecane, 10 g of TA and 250 ml of distilled water was produced with a homomixer (Shanghai Xinrui Mechanical and Electrical Equipments Inc., MBE-100L) at a speed of 9500 rpm. TA was used as emulsifier in the aqueous dispersant solution. The stirring speed was decreased to 2000 rpm after the diameters of most oily droplets were smaller than 4 μm. The diameters were measured with a light microscope (Nikon, SE102). Then the pH of the emulsion was adjusted to 5.5 with 10 wt% solution of citric acid.

The prepolymer was added to the emulsion in droplets while the emulsion was stirred at a speed of 2000rpm. After all of the prepolymer had been added to the emulsion, the emulsion was stirred for a further 2hr. Then the pH of the emulsion was adjusted with 50 wt% triethanolamine solution to 9, which terminated the reaction. The emulsion was cooled down to 25 °C, filtered and the microcapsules were washed with distilled water 3 times. Sample 1 was synthesized. Samples 2–5 were synthesized with the same procedure as for sample 1, the weight and mole ratio of urea, melamine, formaldehyde, TA, n-octadecane and theoretical n-octadecane content are presented in Table 1.

Microcapsules containing n-octadecane and cyclohexane

A mixture of 39.98 g of melted n-octadecane (density 0.777 g/cm^3) and 3.86 g (4.96 ml) of cyclohexane (density 0.777 g/cm^3) with a volume ratio of 91.2:8.8 was used as the oil phase. A copolymer of urea-melamine-formaldehyde with a mole ratio of 0.2:0.8:3 was used as the shell material. The other steps were the same as in the previous section. The cyclohexane inside the microcapsules was removed after drying the microcapsules in a vacuum oven till the weight of microcapsules was constant. Sample 6 was synthesized (Table 1). These microcapsules then were heat-treated in an oven at 120, 140, 160 and 180 °C for 30 min, respectively (sample 6–1 to sample 6–4 in Table 1).

Table 1 Reactants and n-octadecane (PCM) contents

Sample No	Melamine		Urea		Formaldehyde		TA[1] g	PCM[2] g	PCM[2] wt%	CH[3] g	CH[3] v%
	g	mole	g	mole	ml	mole					
1	0	0	4.76	0.079	19.50	0.264	10.00	34.06	70.00	0	0
2	7.00	0.056	1.42	0.024	19.50	0.264	10.00	42.59	70.00	0	0
3	8.00	0.063	0.95	0.016	19.50	0.264	10.00	43.84	70.00	0	0
4	9.00	0.071	0.48	0.008	19.50	0.264	10.00	45.06	70.00	0	0
5	10.00	0.079	0	0	19.50	0.264	10.00	46.28	70.00	0	0
6	8.00	0.063	0.95	0.016	19.50	0.264	10.00	39.98	63.84	3.86	8.80

[1]Na Salt of styrene-maleic anhydride copolymer (emulsifier)
[2]n-Octadecane
[3]Cyclohexane

Characterization of microcapsules

FT-IR transmittance of n-octadecane, microcapsules and the shell were obtained by using a Perkin Elmer 2000 spectrophotometer (wave-numbers 400-4000 cm^{-1}).

The surface morphology and diameter were obtained by using a scanning electronic microscope (SEM, China Zhongke Scientific Instrument Inc., KYKY-2800). One drop of the microcapsule dispersion was placed on a stainless steel SEM stub and allowed to air-dry overnight. The samples were silver-coated.

The phase change properties of the dry microcapsules were observed by using a differential scanning calorimeter (DSC, Perkin-Elmer, DSC7) at a rate of ± 10 °C/min in a nitrogen atmosphere.

One drop of the microcapsule dispersion was placed on a glass plate and air-dried overnight. The samples were heat treated on a heating stage with the temperature being increased at a rate of 10 °C/min. The samples were removed from the heating stage and subsequently cooled to room temperature when the temperature reached 140, 160, 200 and 220 °C, respectively. The surface morphology of the heat-treated samples was measured by using SEM.

Air-dried microcapsules, sample 1 to sample 5, were heat treated for 90 min at 100 °C. The weight loss temperature of the microcapsules was investigated by using a thermogravimetric analyzer (TGA, Japan Regaku Standard TG-DTA) at a rate of 10 °C/min in an atmosphere of air.

TGA curves and SEM micrographs of sample 6 and heat-treated sample 6 at 120, 140, 160 and 180 °C for 30 min, respectively, were obtained.

Results and discussion

FT-IR spectra of the n-octadecane, urea-melamine-formaldehyde (mole ratio 0.2:0.8:3) copolymer and microencapsulated n-octadecane are shown in Fig. 1. The strong adsorption peaks of the microencapsulated

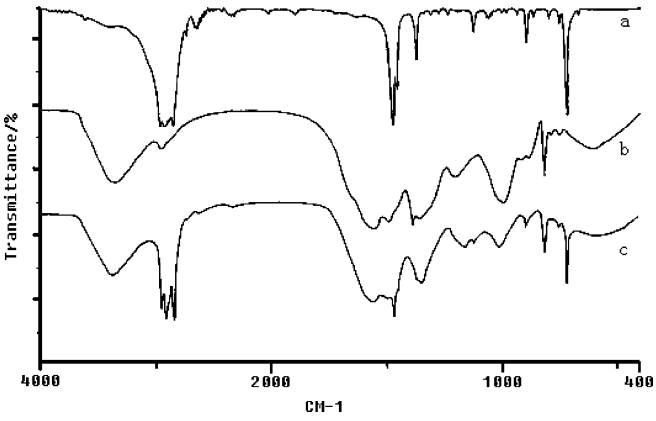


Fig. 1 FT-IR spectra of n-octadecane microcapsule (sample 3) and shell polymer (*a* n-octadecane; *b* shell polymer; *c* microcapsule)

n-octadecane at 2916–2848 cm^{-1} are associated with the aliphatic C-H stretching vibration. The adsorption peak at 717 cm^{-1} is associated with the in-plane rocking vibration of the CH_2 group.

Figure 2 shows SEM micrographs of sample 3 and sample 6. Most of the microcapsules have smooth surfaces. However, dimples exist on some of the microcapsules, these being caused by the volume contracting as n-octadecane crystallized or/and the removal of cyclohexane. The SEM micrographs show that, the diameters of sample 3 are in the range of 0.4–5.6 μm and the diameters of sample 6 are in the range of 0.2–3.3 μm.

The thermal properties of n-octadecane and microcapsules with different compositions are listed in Table 2. The n-octadecane contents in the microcapsules according to DSC measurement are in the range of 71.4–78.8 wt% which are slightly higher than the theoretical contents in Table 1. The differences between the measured and theoretical contents are caused by the elimination of water and formaldehyde from the reaction of hydroxymethyl groups and the partially removal of TA after washing the microcapsules with distilled water. The experimental results show that the shell composition of

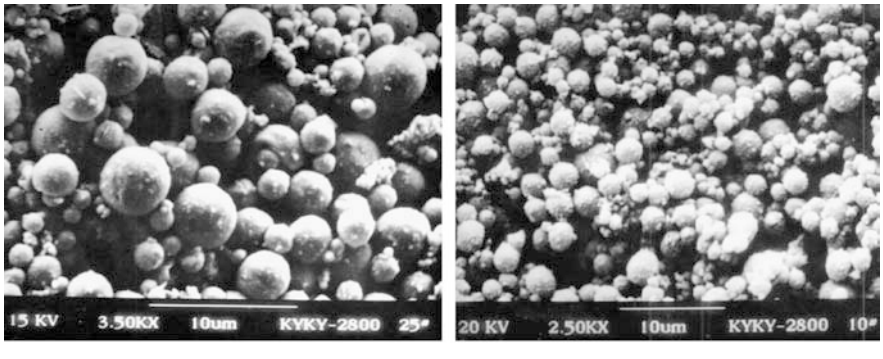


Fig. 2 SEM micrographs of MicroPCMs, **a** sample 3; **b** sample 6

Table 2 Thermal properties of n-octadecane and microencapsulated N-octadecane

No	Shell composition (mole ratio)			Th[4]/°C	Tm[5]/°C	Tc[6]/°C		ΔHm[8]/J	PCM[9]	Td[10]
	U[1]	M[2]	F[3]			α[6]	β[7]	g	%	°C
0	0	0	0	100	33.88	26.16	Not detectable	241.68	100	138
1	1.0	0	3	100	35.67	25.94	9.95	187.86	77.6	145
2	0.3	0.7	3	100	34.42	26.47	10.01	189.68	78.4	157
3	0.2	0.8	3	100	34.77	24.32	10.04	190.62	78.8	163
4	0.1	0.9	3	100	35.13	25.32	9.98	188.76	78.1	160
5	0	1.0	3	100	33.23	26.03	10.11	172.74	71.4	152
6	0.2	0.8	3	Untreated	34.58	26.70	12.30	158.63	65.6	156
6–1	0.2	0.8	3	120	34.22	25.45	11.45	159.76	66.1	167
6–2	0.2	0.8	3	140	34.87	24.88	9.91	150.54	62.2	170
6–3	0.2	0.8	3	160	34.78	24.37	11.13	150.46	62.2	200
6–4	0.2	0.8	3	180	32.77	21.43	4.32	91.10	37.6	175

[1]Urea
[2]Melamine
[3]Formaldehyde
[4]Heat treatment temperature
[5]The peak value on the DSC heating curve
[6]The peak value at the higher temperature on the DSC cooling curve
[7]The peak value at the lower temperature on the DSC cooling curve
[8]The enthalpy obtained from DSC heating curve
[9]Mesured n-octadecane content in the microcapsules
[10]The temperature when weight loss percentage of the sample was 5 wt%

the microcapsules has no effect on the melting temperature. Two crystallization peaks appear in the DSC cooling curve of the microcapsule (Fig. 3), however, only one peak in that of the bulk n-octadecane. The first peak (α) at the range of 24.32–26.47 °C is almost the same as the crystallization temperature of n-octadecane (26.16 °C), while the second peak (β) is at approximately 10 °C. The results are different from those of the previous study [11] where supercooling crystallization phenomena of microencapsulated n-dodecane and n-tetradecane occurred when the diameters of microcapsules were smaller than 100 μm. The smaller the diameter, the lower is the crystallization temperature. Yamagishi stated that the supercooling crystallization was caused by the decrease in the number of nuclei in each microcapsule due to the reduced diameter. The discrepancy in effects of diameters on the crystallization temperature needs to be studied further.

Figure 4 shows the weight loss percentage of Micro-PCMs with different mole ratios of urea-melamine-formaldehyde copolymers (sample 1–5) and that of n-octadecane (sample 0) as a function of temperature. The weight loss temperature (Td-5 wt% weight loss) of bulk n-octadecane in the air is 138 °C due to the evaporation of n-octadecane (Td, Table 2). The evaporation therefore leads to a broad and gradual endothermic process in the DTA curve. And the n-octadecane caught fire at approximately 232 °C this is shown in the DTA curve as an exothermic peak. The combustion process was observed under a heating stage microscope.

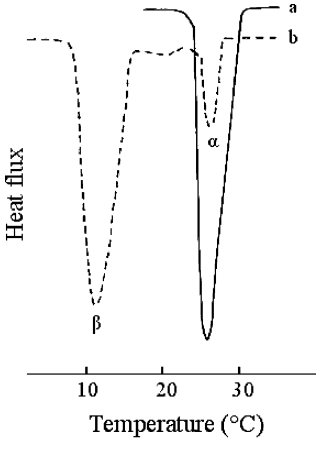


Fig. 3 DSC cooling curves (*a* n-octadecane; *b* sample 3)

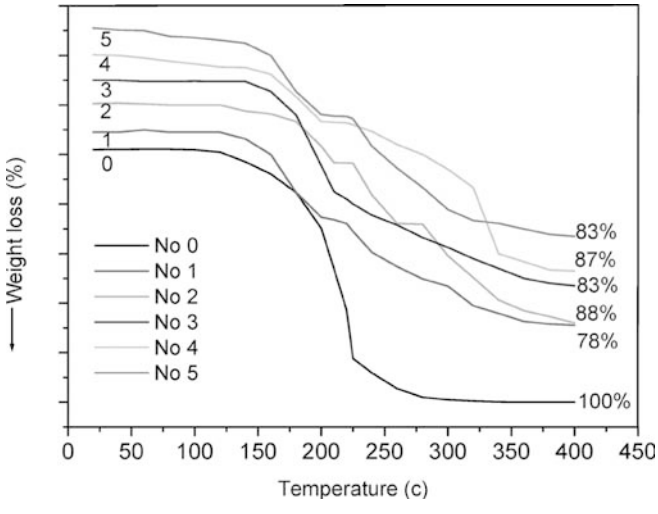


Fig. 4 TGA curves of microcapsules with different composition

Comparatively, the weight loss temperature of microencapsulated n-octadecane is higher than that of the bulk. Both the shell monomer types and their mole ratios in the copolymer have effects on the thermal stability of the microcapsule. The results also indicate that, microcapsules with a urea-formaldehyde shell and melamine-formaldehyde shell have relatively lower weight loss temperature than that of the microcapsules with a urea-melamine-formaldehyde copolymers shell. The weight loss temperature of microcapsules is approximately 163 °C when the urea-melamine mole ratio is 2:8 (sample 3). Adding urea in the melamine-formaldehyde polymerization would probably reduce the interaction force inside the molecular chains and therefore improve the thermal stability. In the meantime, adding urea to the melamine-formaldehyde system would decrease the release rate of formaldehyde [15].

The SEM micrographs in Fig. 5 show the microcapsule damage processes when heating sample 3 to different temperatures, i.e. 140, 160, 200 and 220 °C, respectively. After heating to 140 °C, core materials of a small number of microcapsules diffuse out of the shell due to the expansion of n-octadecane as the temperature increases [13]. Strumae can be found on the surface of these microcapsules and the shells shrink to form flakes. The microcapsules are broken by the expansion of the core material at high temperature [5]. The results also reveal that the higher the heating temperature, the more broken microcapsules there are.

The phase change properties, heat treatment temperature and weight loss temperature of sample 6 are presented in Table 2 and Fig. 6. The melting and crystallization temperatures of sample 6 are similar to those of sample 3. The measured n-octadecane content in sample 6 is also slightly higher than the theoretical value. It can be explained by the elimination of water, formaldehyde and the partially removal of TA. As the heat treatment temperature increases from 120 °C to 160 °C, the melting enthalpy remains almost constant, however, the melting enthalpy of 180 °C treated microcapsules (sample 6–4) decreases significantly. Some yellowish substances on the surface of microcapsules after 180 °C heat treatment, which are supposed to be partially oxidized n-octadecane, can be removed by alcohol.

The weight loss temperature is enhanced as the heat-treated temperature increases from 120 °C to 160 °C. The results also show that, the higher the heat-treatment temperature, the higher the weight loss temperature. This may be explained by the cross-linking formed during the heat-treatment process with the elimination of water and formaldehyde from the reaction of hydroxymethyl groups. The formation of

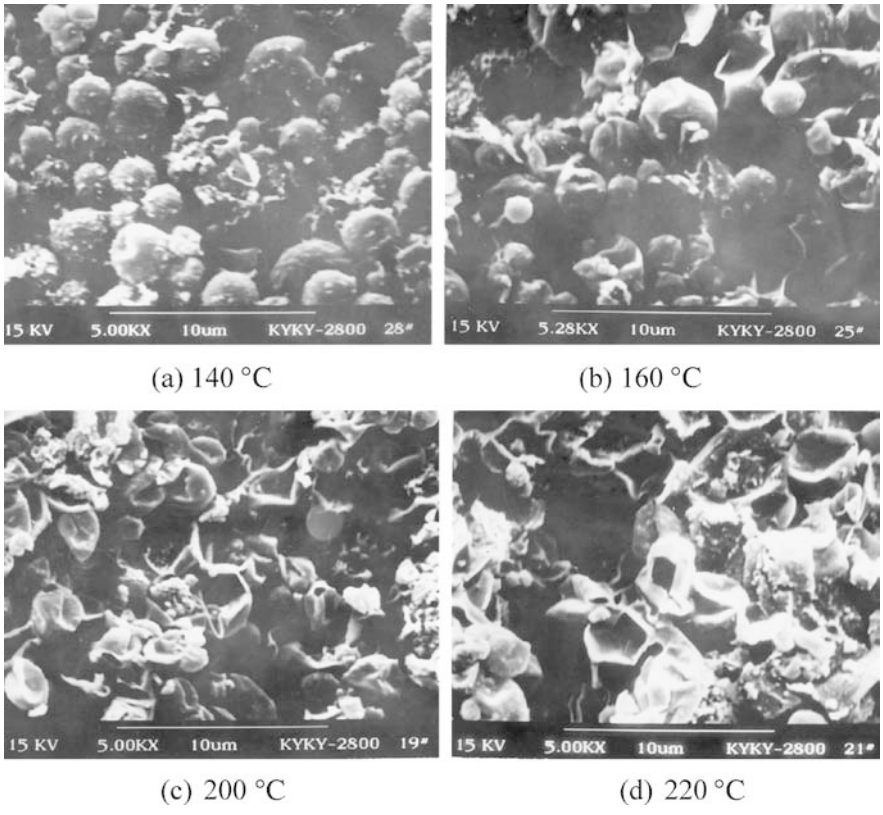


Fig. 5 SEM micrographs of heat-treated microcapsules (sample 3)

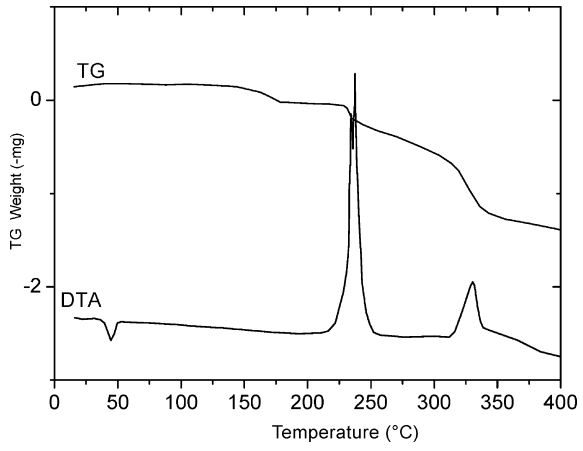
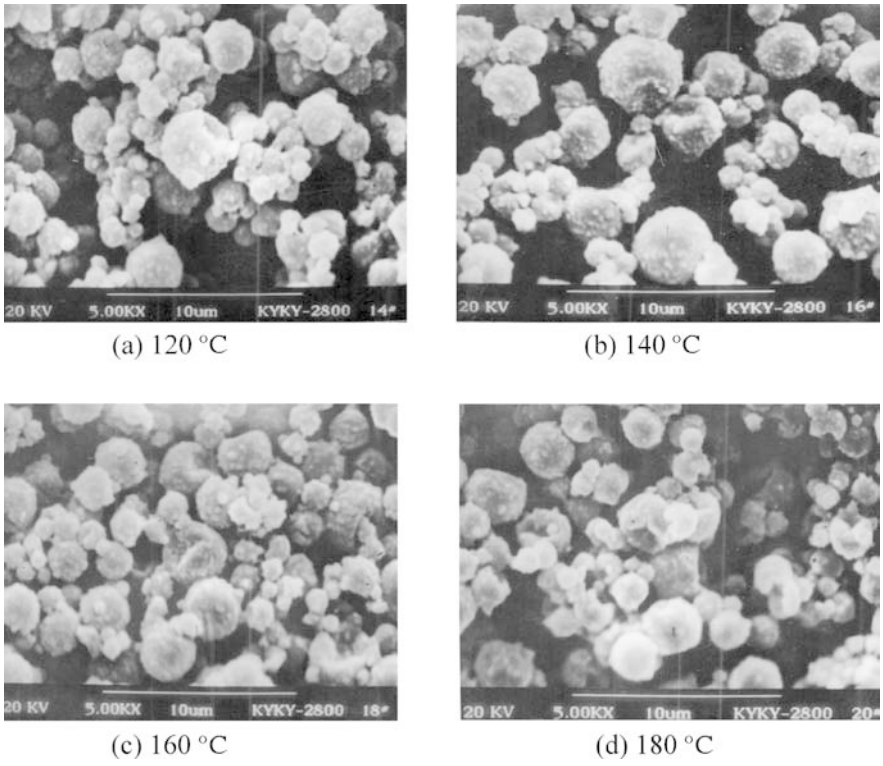


Fig. 6 TG and DTA curves of sample 6–3

"methylene" cross-links strengthens the shell and reduces the content of volatile component. As the temperature rises to 180 °C, the percentage of weight loss increases slightly. As a result, the preferable heat-treatment temperature is 160 °C that is equivalent to the molding temperature of melamine-formaldehyde resin [16]. The weight loss temperature of heat-treated sample 6 is higher than that of sample 3, although the reduced diameters may decrease the thermal stability [13]. It cannot be explained by the slightly lower n-octadecane content in sample 6 that the approximately 37 °C difference of weight loss temperature between sample 6 and sample 3. It implies that adding solvent inside the microcapsules and removing the solvent after their formation can make them more stable during the heating process. The combustion of microcapsules at 231 °C, as indicated by their DTA curve, shows that some of the n-octadecane diffused out of the shell at that temperature. Therefore, adding 8.8v% of cyclohexane is not enough for the expansion of n-octadecane when the temperature is as high as 230 °C since the density of the n-alkanes decreases gradually as the temperature increases [17]. Increasing the volume ratio of cyclohexane inside the core of microcapsule would probably further enhance their thermal stability.

Figure 7 shows SEM micrographs of microcapsules heat-treated at different temperatures. Microcapsules are intact for 160 °C heat-treated sample (sample 6–3), and most of the microcapsules are intact for 180 °C heat-treated sample (sample 6–4), however, the breakage of 140 °C heat-treated sample 3 is obvious (Fig. 5). The contraction of shell after the removal of cyclohexane allows the microcapsules to be heat-treated and form the cross-link before the core diffuses out of the shell. The elimination of water and formaldehyde during cross-linking process enhances the weight loss temperature.



(a) 120 °C (b) 140 °C

(c) 160 °C (d) 180 °C

Fig. 7 SEM micrographs of sample 6 heat-treated at different temperatures for 30 min

Conclusions

This study has demonstrated that the thermal stability of microencapsulated n-octadecane can be improved by using different mole ratios of urea-melamine-formaldehyde copolymers as shells. The highest thermal stable temperature of microcapsules with diameters in the range of 0.4–5.6μm is approximately 163 °C and the urea-melamine-formaldehyde mole ratio is 0.2:0.8:3. The core material diffuses out of the shell due to the expansion of n-octadecane as the temperature continuously increases. The thermal stability of microencapsulated n-octadecane can be further enhanced by adding cyclohexane in the oil phase and heating them at 160 °C for 30 min. Such microcapsules are thermally stable up to approximately 200 °C.

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