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ORIGINAL PAPER

Effect of different amounts of surfactant on characteristics of nanoencapsulated phase-change materials

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Abstract Phase-change nanocapsule particles are successfully synthesized by the two-step miniemulsion polymerization method. Urea–formaldehyde resin is used as the shell material. Hexadecane is used as the core material. The particle size distribution and the surface morphology of nanocapsules are characterized by laser particle size analyzer, optical and scanning electron microscopy. The thermal properties are investigated by differential scanning calorimeter. The effects of the amounts of surfactant (AS) on the properties of prepared nanocapsules are also investigated. The results indicated that the nanocapsules have smooth surface and the mean particle size is about 270 nm; nano-structure of capsules has not changed dramatically after being heated at 100 °C for 72 h; The phase-change enthalpy of nanocapsules increases from 114.6 to 143.7 J/g with the increasing of the AS, but the mean particle diameter decreases from 285 to 253 nm; The degree of undercooling of hexadecane decreases about average 94% after being encapsulated in capsules.

Keywords Nanocapsules · Phase-change materials · Urea–formaldehyde resin · Miniemulsion polymerization

Introduction

Phase-change materials (PCMs) can absorb and release large amounts of latent heat over a defined temperature range as their physical state changes. The PCMs have high energy density and isothermal behavior during charging and discharging, and

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can avoid the contradiction of the energy supply and demand mismatching in time and space [1].

Micro- or nano-encapsulated PCMs are tiny particles that PCMs as core are surrounded by a polymer or inorganic shell. Encapsulation of PCM has recently attracted considerable attention because it can increase heat transfer area, prevent PCMs from the influences of the outside environment, and enable the core material to withstand frequent changes in the volume of the storage material during phase change [2]. The encapsulation can expand application fields of the PCMs technology greatly, such as in thermal energy storage system [3, 4], thermal insulation [5], thermoregulation textile [6–10], and energy-saving buildings [11–14].

Several methods have been used for preparing encapsulated PCMs, such as spray drying, complex coacervation [15–17], interfacial polymerization [18, 19], in situ polymerization [20, 21] and miniemulsion polymerization methods [22], and so on. The properties of the particle after PCMs was encapsulated are also characterized. Hawlader et al. [15] reported microencapsulated PCMs kept its geometrical profile and energy storage capacity after 1000 cycles operation, and the phase-change enthalpy was about 145–240 J/g. Zou et al. [18] reported that the encapsulation efficiency of PCMs increased as the core content decreasing. Wei et al. [21] reported the average diameter of the capsules was about 2.2 μm and the enthalpy was 144 J/g when containing 59 wt% *n*-octadecane. Park et al. [22] reported the average diameter of nanocapsules was about 100 nm and the latent heat was the maximum 145 J/g. They also investigated the polymer particles prepared with different parameters in terms of average particle size, particle distribution, and latent heat storage. However, there have been relatively few reports concerning the effect of amounts of surfactant (AS) on the characteristics of encapsulated PCMs. In our study, the objective is to prepare nanoencapsulated PCMs with hexadecane as core and urea–formaldehyde resin as shell material by miniemulsion polymerization [23–25], and investigate effects of surfactant on properties.

Experimental

Materials

Urea (AR, 99%) and formaldehyde (AR, 7%) were used as shell-forming monomers. Hexadecane was used as core material. Sodium dodecyl sulfate (SDS, AR, 99%) was used as surfactant. Cetyl alcohol (CA, AR, 99%) was used as stabilizer. Triethanolamine (10%) was used to control the pH during polymerization. Deionized water was used as solvent. All the experimental materials were purchased from Sinoharm Chemical Reagent Co.

Preparation

The different formulas of urea, formaldehyde, hexadecane, and sodium dodecyl sulfate (SDS) are shown in Table 1. Dodecyl sulfate (SDS) was 0.05, 0.10, 0.15, and 0.20 g, respectively, when other parameters are the same.

Table 1 Formula of raw material

	Formaldehyde solution (37%, g)	Urea (g)	Hexadecane (g)	SDS (g)	CA (g)
AS5	4.054	1.5	3.0	0.05	0.06
AS10	4.054	1.5	3.0	0.10	0.06
AS15	4.054	1.5	3.0	0.15	0.06
AS20	4.054	1.5	3.0	0.20	0.06

(a) Synthesis of UF prepolymer
A certain amount of urea, formaldehyde aqueous solution, and 20 mL of deionized water were mixed together and adjusted to pH 7–10 with 10% triethanolamine. Then the mixture was stirred at 70 °C for 3 h to prepare urea–formaldehyde prepolymer aqueous solution.

(b) Preparation of PCM miniemulsion
3.0 g of PCM (hexadecane) and 30 mL of deionized water were emulsified mechanically with stabilizer (CA) and different AS (SDS) and stirred until the mixture was uniform at 50 °C. The mixture was ultrasonicated for 10–15 min to prepare stable PCM miniemulsion.

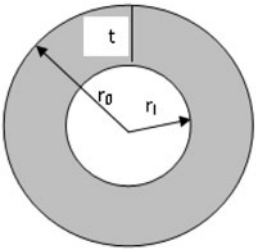
(c) Fabrication of nanoencapsulated PCMs
The urea–formaldehyde prepolymer solution was added into the PCM miniemulsion with stirring and adjusted to pH 3–5 with 10% triethanolamine. The mixture was slowly drained to three-neck flask to start polymerization at 60–80 °C under magnetic stirring. Three hours later, the pH was adjusted to 7 to stop the polymerization. The resultant capsules in the slurry were filtered, washed by the deionized water, and dried at the room temperature to obtain nanocapsule particles.

Thermal stability

The certain weight of capsule was dispersed in the central area of the filter paper uniformly, baked at 100 °C for 12 h. Then the exudative situation of PCM in filter paper was observed, the thermal stability of the composite was determined based on the patent by Jinsheng Liang et al. [26].

Morphology and chemical structures

The surface morphology of nanocapsules was observed by scanning electron microscopy (SEM, Quanta 200 FEG) at an accelerated voltage of 15 kV. The samples were coated with a layer of gold in vacuum conditions. The chemical structures of nanoencapsulated PCMs was analyzed by the Fourier transform infrared spectroscopy (FTIR) at room temperature. The samples were applied on dry KBr pellets prepared using a manual hydraulic press and were scanned among the range of 450–4,000 cm^{-1}.



$$r_I = r_0 \cdot (\Delta H / \Delta H_h)^{1/3} \quad (1)$$

$$t = r_0 - r_I \quad (2)$$

Fig. 1 Schematic of nanocapsules

Phase-change behavior

Thermal behavior of nanocapsules was measured by differential scanning calorimeter (DSC, MDSC-Q100) equipped with a refrigerated cooling system and nitrogen as the purge gas. These measurements were performed at a heating rate of 10 °C/min among the range of −10 to 80 °C under nitrogen atmosphere.

Particle diameter

The particle size distribution of nanocapsules was measured using laser particle analyzer (LS-230) with 0.01 wt% nanocapsules in ethanol. Combined with the DSC test results, the radius of the core and the thickness of the shell of nanocapsules can be calculated. Schematic of nanocapsules is shown in Fig. 1. According to phase-change enthalpy of hexadecane (ΔH_h) and nanocapsules (ΔH) and the particle diameter (D_0) of nanocapsules, the radius of the core (r_I), and the thickness of the shell (t) can been calculated from formulas 1, 2.

Results and discussion

Morphology and thermal stability of the nanoencapsulated PCMs

From the photographs in Fig. 2, it can be seen that the prepared nanocapsules appear homogeneous white powders (Fig. 2a), and no hexadecane exuded in test strip after being heated at 100 °C for 12 h (Fig. 2b), but hexadecane melted in test strip with a spread circle after being heated at 100 °C for 12 h (Fig. 2c, d). Based on no hexadecane exuded from nanocapsules, the thermal stability can be determined well.

Particle size and shape can dramatically alter the physical and therapeutic properties of a substance. The solubility, material strength, opacity, stability, flowability, and chemical reactivity of many materials are affected by the size and characteristics of the particles within them. From the SEM micrographs in Fig. 3, it is clear that the nanocapsules are spherical particles basically; the interface is clear and smooth and the particle size is about 230 nm (Fig. 3a, b). The morphology of

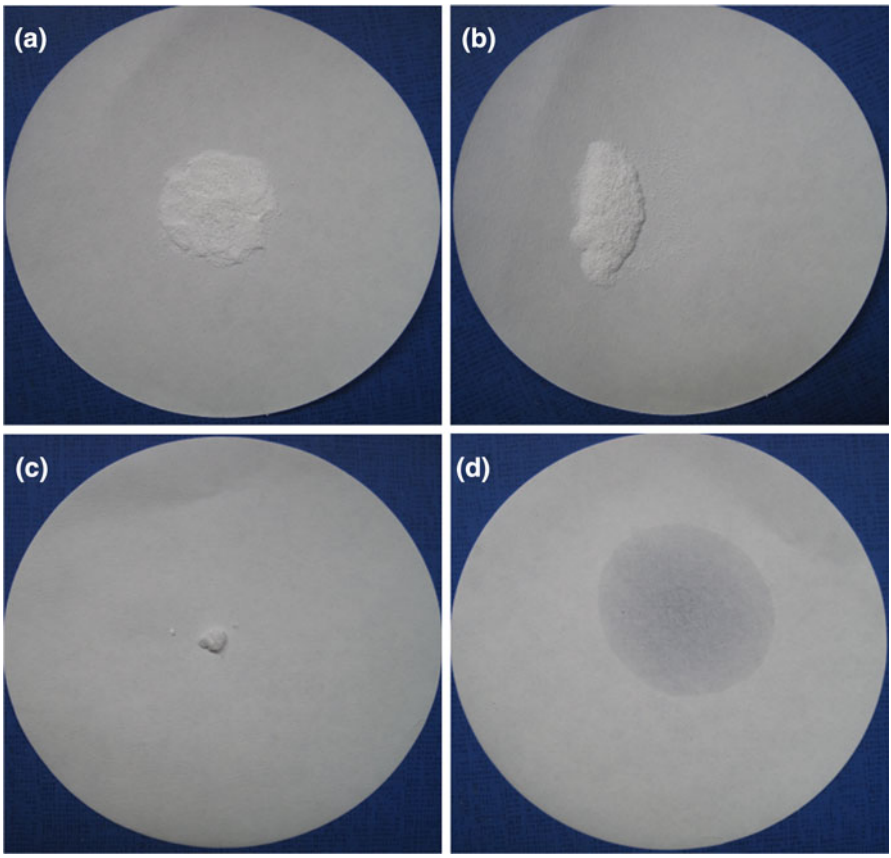


Fig. 2 Photos of nanocapsules and hexadecane heated at 100 °C. **a** Nanocapsules for 0 h; **b** nanocapsules for 12 h; **c** hexadecane for 0 h; and **d** hexadecane for 12 h

the nanocapsules has not changed basically after being heated at 100 °C for 24 and 72 h, respectively, the interfaces are still clear (Fig. 3c, d). It also indicated that prepared nanocapsules have good thermal stability.

FTIR of the nanoencapsulated PCMs

The FTIR spectra of urea–formaldehyde resin and the nanocapsules are presented in Fig. 4. It can be seen that the FTIR spectra of urea–formaldehyde resin (Fig. 4a) is identical with the nanocapsules (Fig. 4b) basically. The wide absorption peak at approximately 3333 cm^{-1} is attributed to the –OH stretching vibrations. The absorption peak at approximately 1634 cm^{-1} is assigned to the $–NH_2$ deforming vibrations. The peaks at 1134 and 1022 cm^{-1} are corresponding to the –C–O–C– asymmetric stretching vibrations and –C–O– deforming vibrations, respectively. However, the nanocapsules appeared the $–CH_3$ stretching absorption peaks at approximately 2953 cm^{-1}, the $–CH_2–$ absorption peaks at approximately 2917 and

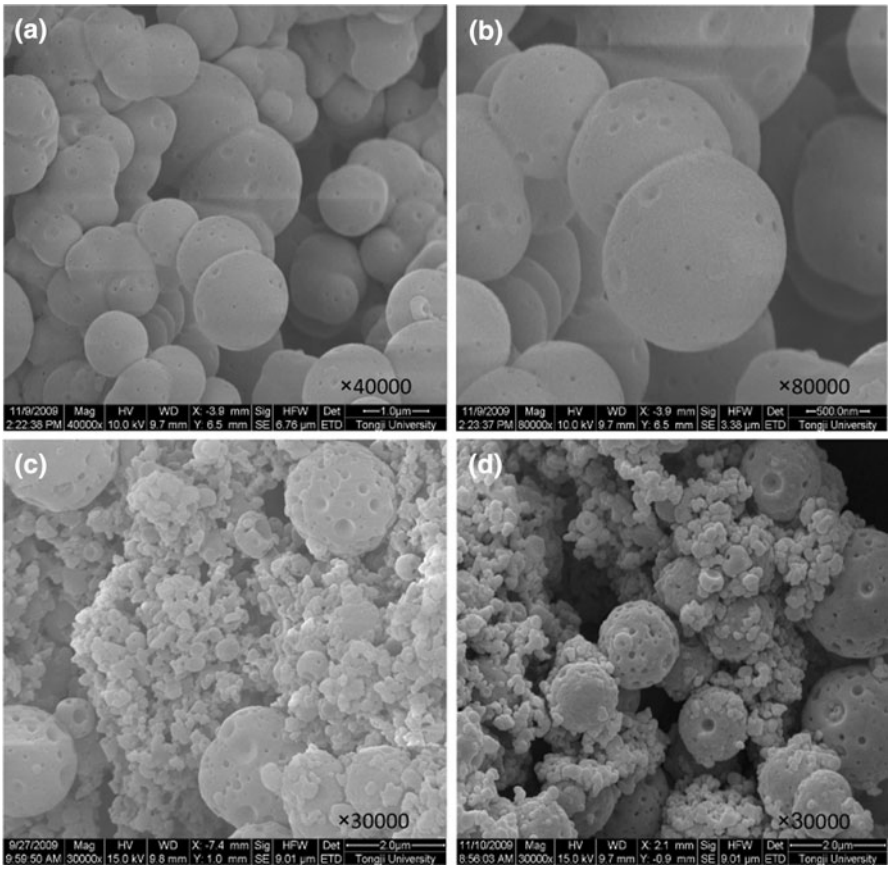


Fig. 3 SEM micrographs of the nanocapsules after being heated for **a** 0 h; **b** 0 h; **c** 24 h; and **d** 72 h

2843 cm^{-1}. It indicates that the hexadecane was contained in the nanocapsules with urea–formaldehyde resin as shell materials.

Effect of the AS on the nanocapsules

Surfactant plays an important role in the process of preparing the miniemulsion. A series of nanoencapsulated PCMs were prepared with different AS by miniemulsion polymerization, which is to study the effect of the AS on the properties of nanocapsules. The DSC curves and the diameter distributions are shown in Figs. 5 and 6. The parameters of phase-change behavior and particle size of nanocapsules are listed in Table 2.

Phase-change behavior

During the heating and cooling process, the phase-change temperatures (T_c, T_m) of nanocapsules are different from pure hexadecane, which can be observed from

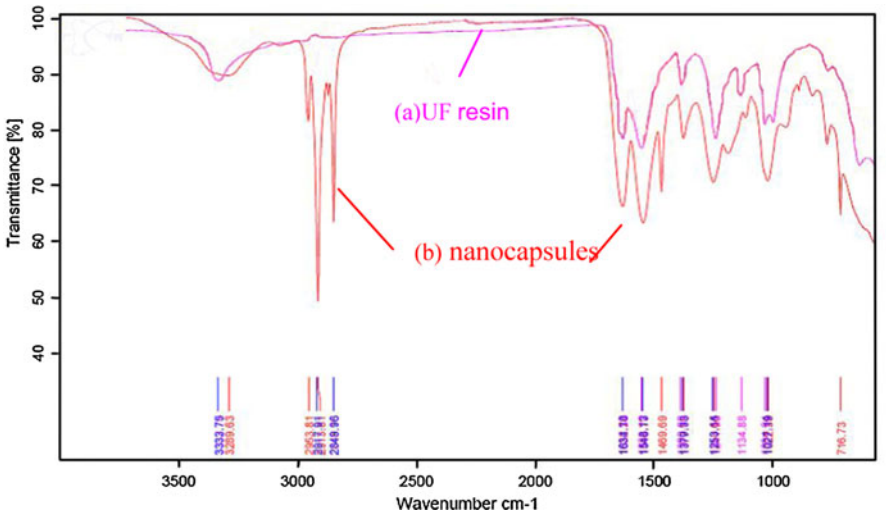


Fig. 4 FTIR spectra of urea–formaldehyde resin and nanocapsules

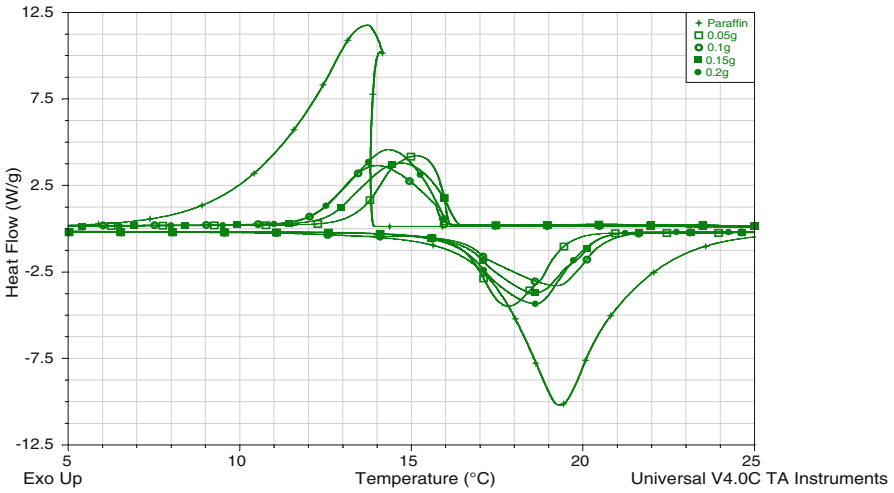


Fig. 5 DSC curves of nanocapsules prepared with different AS

Fig. 5 and Table 2, but the largest difference is only 2.51 °C. It is mainly because the thermal physical properties such as thermal conductivity of the nanocapsules are different from pure hexadecane. The phase-change enthalpy is very different mainly because the unit mass proportion of hexadecane decreases after the hexadecane is encapsulated.

Effect of the AS on phase-change enthalpy is shown in Fig. 7. It illustrates that the phase-change enthalpy, in a certain range, increases from 114.6 to 143.7 J/g with the AS increasing in heating process and 99.0 to 143.3 J/g in cooling process

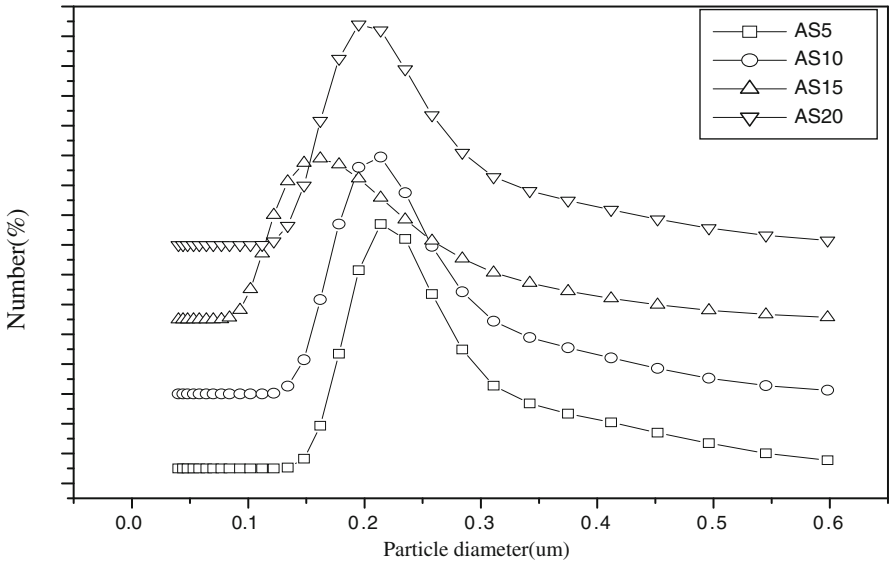


Fig. 6 Diameter distribution of nanocapsules prepared with different AS

Table 2 Parameters of phase-change behavior and particle size

	ΔH (J/g)		T_c (°C)	T_m (°C)	ΔT (°C)	D_0 (nm)	r_0 (nm)	r_I (nm)	t (nm)	CV (%)
	Heating	Cooling								
Hexadecane	208.4	213.5	13.81	17.02	3.21					
AS5	114.6	98.99	16.07	16.36	0.29	285	142.5	116.7	25.8	47.9
AS10	119.4	112.3	15.88	16.27	0.39	268	134.0	111.3	22.7	43.5
AS15	121.0	112.5	16.32	16.26	−0.06	259	129.5	108.0	21.5	44.2
AS20	143.7	134.3	16.04	16.15	0.11	253	126.5	111.8	14.7	39.6

(Fig. 7). The reason is probably that a part of the oily PCMs can not form a small oil-core but suspend above the miniemulsion when the AS is small so that less hexadecane is contained by urea–formaldehyde resin in the polymerization. As a result, the enthalpy is smaller. However, the phase-change enthalpy in AS15 is basically the same with AS10, which may because the AS in the range of 0.10–0.15 g has identical effect in the preparation process, or caused by operating error.

Particle size of nanocapsules

It can be seen from Fig. 6 and Table 2 that the diameter distribution of nanocapsules is in the range of 30–600 nm and concentrated in about 230 nm when using different AS. The mean particle diameter (D_0) and the coefficient of variation (CV) can be obtained by testing results of the LS-230. Figure 8 shows the effect of the AS

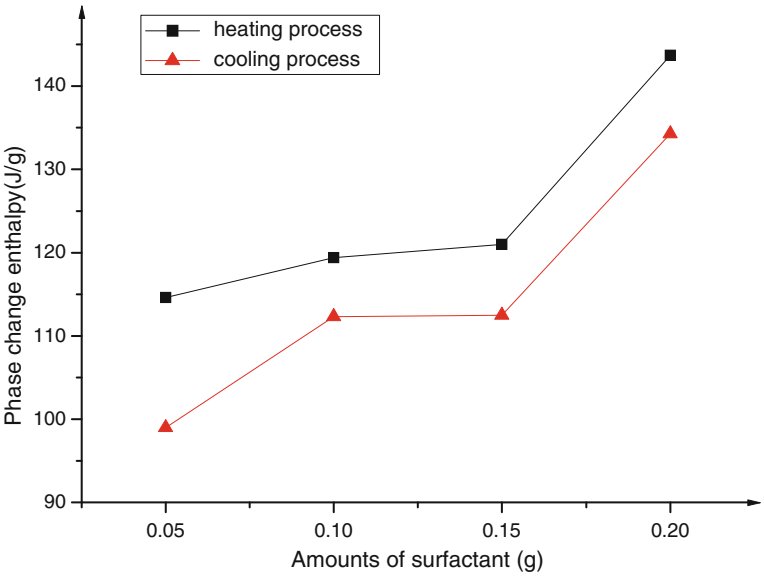


Fig. 7 Effect of the AS on phase-change enthalpy

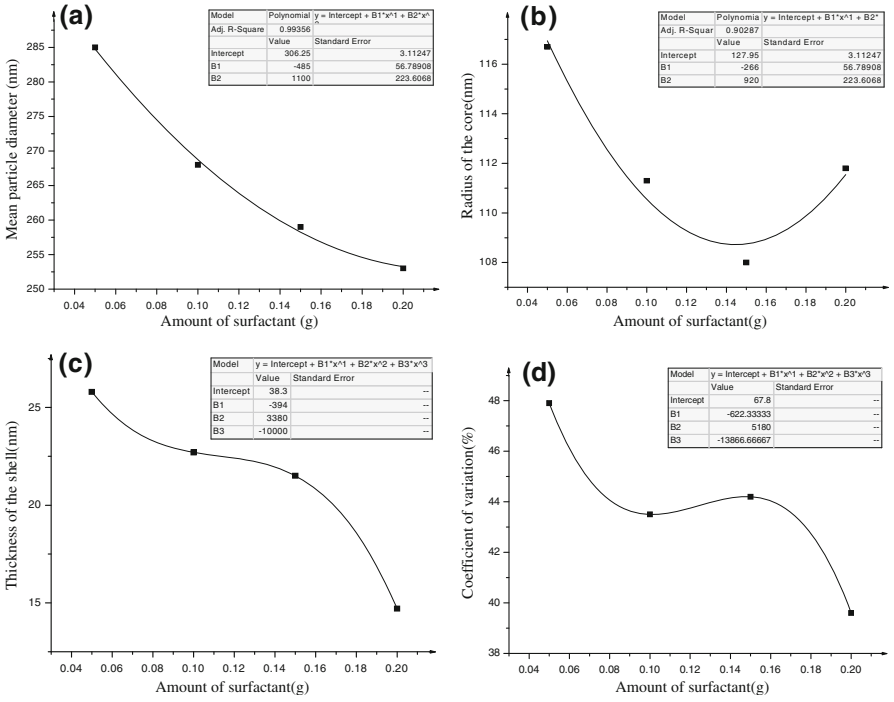


Fig. 8 Effect of the AS on the diameter characteristic: **a** mean particle diameter; **b** radius of the core; **c** thickness of the shell; and **d** coefficient of variation

on diameter characteristic; the curves are fitted by the Origin8.0. The mean particle diameter (D_0) of nanocapsules decreases from 285 to 253 nm with the AS increasing from 0.05 to 0.20 g (Fig. 8a), the radius of the core (r_1) decreases from 116.7 to 108.0 nm and then increases to 111.8 nm (Fig. 8b) and the thickness of the shell (t) of nanocapsules decreases from 25.8 to 14.7 nm (Fig. 8c). It is mainly because the droplet number of forming miniemulsion increased with the AS increasing so that the particle size of miniemulsion became smaller. Finally, the particle size and the radius of the core of nanocapsules were smaller. However, the r_1 appears increasing trends in AS20, the reason may be the droplet number has reached a limit in about AS15, excessive surfactant may have the opposite effect to increase the droplet number. The coefficient of variation (CV) also decreases with the AS increasing generally (Fig. 8d), which illustrates that the particle size of miniemulsion becomes more uniform with the increasing of the AS. But the CV in AS15 only has a small difference with AS10, it also may because the AS in the range of 0.10–0.15 g has identical effect in the preparation process of nanocapsules.

Degree of undercooling

Undercooling is a major drawback to organic PCMs. Degree of undercooling (ΔT) is the difference between the melting starting temperature (T_m) and crystallization starting temperature (T_c). The degree of undercooling of pure hexadecane and nanocapsules prepared with different AS is shown in Fig. 9. It can be seen that the ΔT of pure hexadecane decrease average 94% after being encapsulated when using different AS. The main reason is that the hexadecane was encapsulated in lots of circular shell which has high thermal conductivity so that the ΔT of nanocapsules

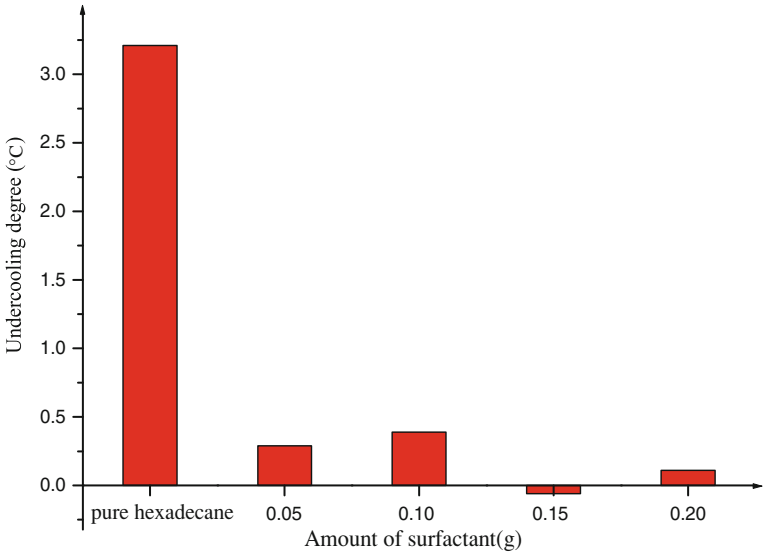


Fig. 9 Effect of the AS on degree of undercooling

decreased significantly. There is no undercooling when the AS is 0.15 g. It is mainly because the radius of the core is the smallest in AS15, which leads to prepared nanocapsules have very high thermal conductivity. The emergence of negative number is the cause of the test error of the MDSC-Q100. But the ΔT is only a little difference with the increasing of the AS. It indicates the increasing of AS has no clear effect to the ΔT of prepared nanocapsules.

Conclusion

The preparation and properties of nanoencapsulated PCMs are demonstrated. The appearance of the nanocapsules particles is spherical basically. The hexadecane was contained in the nanocapsules very well. Meanwhile, the particle size distributes is about 30–600 nm, and the mean particle diameter is about 270 nm. The nanocapsules have good thermal stability. No hexadecane leaked out from the nanocapsules after being heated at 100 °C for 12 h, and the morphology of the nanocapsules has not changed basically.

The AS is better in 0.20 g. In a certain range, the phase-change enthalpy increases with the increasing of the AS, but the mean particle diameter decreases. The surfactant has great influence to decrease the particle diameter, the coefficient of variation, the thickness of the shell, and the radius of the core. Encapsulation can decrease the degree of undercooling of hexadecane obviously.

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