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ORIGINAL CONTRIBUTION

Preparation, characterization, and thermal properties of microPCMs containing *n*-dodecanol by using different types of styrene-maleic anhydride as emulsifier

Fei Yu · Zhong-Hua Chen · Xing-Rong Zeng

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Abstract Microcapsules containing polar phase change material (PCM) *n*-dodecanol were synthesized by in situ polymerization using melamine-formaldehyde resin as shell and styrene-maleic anhydride copolymer (SMA) as emulsifier. The effects of polarity of PCM and types and amounts of SMA emulsifier on the properties of microencapsulated PCMs (microPCMs) were studied and characterized by using Fourier transform infrared spectroscopy, scanning electron microscopy, differential scanning calorimetry, thermogravimetric analysis, and laser particle diameter analyzer. The results show that thermal properties of microPCMs are affected greatly by the types and amounts of SMA. Anionic SMA emulsifier is suitable for the encapsulation of *n*-dodecanol. The polarity of PCM leads to the higher adding amount of SMA emulsifier. When mass ratio of emulsifier to *n*-dodecanol is 4.8%, the phase change latent heat and encapsulation efficiency reach to the maximum value of 187.5 J/g and 93.1%, respectively. Irregular spherical microPCMs with mean diameter of 30.6 μm and phase change temperature of 21.5 °C are obtained and can be used for energy storage.

Keywords Microcapsule · Phase change material · *n*-dodecanol · Styrene-maleic anhydride · Melamine-formaldehyde · In situ polymerization

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Introduction

Energy storage plays important roles in conserving available energy and improving its utilization, since many energy sources are intermittent in nature and energy crisis is up to us today [1]. Thermal energy storage and utilization has attracted more and more attention recently by using phase change materials (PCMs), which has been widely applied in many fields such as solar energy storage, temperature-adaptable greenhouses, energy-storage household refrigerator, energy efficient buildings, smart textiles, and so on [2–6]. This latent heat energy storage provides much higher energy storage density with a smaller temperature swing when compared with the sensible heat storage method.

Although the PCMs have very high latent heat, the bulk PCMs are not easy to be applied in conventional energy storage system with heat exchangers, particularly during the withdrawal of energy from the storage system. The PCMs freeze on the heat exchanger surface resulting in a poor heat-transfer rate due to their low thermal conductivity [7]. Microencapsulated PCMs (microPCMs) have many advantages for practical application, such as increasing heat transfer area, reducing PCM reactivity towards the outside environment and controlling the changes in the storage material volume as phase change occurs [8] and provides an effective way to solve the problems.

A lot of literatures have reported the fabrication and properties of microPCMs containing different types of PCM as core, such as *n*-alkanes (including *n*-octadecane [9–13], hexadecane [14–16], *n*-docosane [17], paraffin [18–20], fatty acid [21], and polyethylene glycol [20], which have been used in building materials [22–24], fabric [25, 26], paper [27], foam [28], and so on. Especially, microPCMs containing octadecane and paraffin with high thermal storage density and low phase change temperature got the most attention, which can be used for building energy saving. However, there are few reports about the microencapsulation of polar PCM unitary fatty alcohol and the influence of the polarity of PCM on the properties of microPCMs, which has the same high thermal storage capacity.

Melamine-formaldehyde (MF) resin, urea-formaldehyde (UF) resin, polystyrene (PS), polyurethane (PU), Phenolic Resin, and gelatin-gum Arabic were usually used as the shell materials [9–20] for the microencapsulation of PCMs. The mechanical strength and permeability of microcapsules by using MF resin as shell material are better than that of the others for its high cross-linking density.

Emulsifier plays important roles in the preparation of microcapsules. With the help of emulsifier, the core materials emulsion can be stable and then the prepolymer is adsorbed and deposited on the surface of core particles [29]. Different from traditional small molecular emulsifier such as sodium dodecyl sulfate, the macromolecular emulsifier styrene-maleic anhydride copolymer (SMA) possesses stronger adsorbability and dispersibility in oil-in-water emulsion system. In addition, the copolymer can be modified into different types of emulsifier such as anionic SMA emulsifier, cationic SMA emulsifier and nonionic SMA emulsifier. The anionic SMA emulsifier has been applied in the preparation of microcapsules [30], but the study on the effect of different types and amounts of SMA emulsifier on the properties and morphology of microPCMs by in situ polymerization is comparative little.

MicroPCMs containing unitary fatty alcohol *n*-dodecanol ($C_{12}H_{26}O$) were prepared with MF resin as the shell material by in situ polymerization. The influence of the polarity of PCM and the types and amounts of macromolecular emulsifier SMA on the thermal properties microPCMs were discussed and the morphologies of microPCMs were characterized in this study.

Experimental

Materials

Melamine (purity 99 wt.%, Sichuan Chemical Works Group Ltd) and formaldehyde (37 wt.% aqueous solution, A.R., Guangzhou Dongfanghong Chemical Factory) were used as shell-forming monomers. *N*-dodecanol (C.P., Shanghai Chemical Reagent Factory) and paraffin (C.P., Shanghai Huashen Recover Equipment Co., Ltd.) were used as core material. Sodium styrene-maleic anhydride copolymer (SMA1000HNa, 40 wt.% aqueous solution, Sartomer Company, USA) was used as anionic emulsifier. Styrene-maleic anhydride amic acid (SMA1000MA, 35 wt.% aqueous solution, Sartomer Company, USA) was used as nonionic emulsifier. Styrene-maleic anhydride imides (SMA1000I, light yellow solid, Sartomer Company, USA) was used as cationic emulsifier after being dissolved in acid aqueous solution. 2-Dimethylamine Ethanol (MA-95, purity 95 wt.%, Taiwan Deuchem Company) and citric acid (purity 99.5 wt.%, A.R., Tianjing Yaohua Chemical Reagent Company) were used as pH regulators.

Preparation of microPCMs

Synthesis of MF prepolymer Twenty grams of melamine, 43 g of 37 wt.% formaldehyde aqueous solution and 20 ml of distilled water were mixed together and adjusted to pH 9 with MA-95. Then the mixture was stirred at 70 °C for 3 h to prepare 42 wt.% of MF prepolymer aqueous solution.

Preparation of PCM emulsion Twenty-five grams of PCM (*n*-dodecanol) and 30 ml of distilled water were emulsified mechanically with different types of emulsifier (Table 1) and different amounts of emulsifier (Table 2) at a stirring rate of 4,500 rpm for 60 min. The PCM emulsion was adjusted to pH 4 by 36 wt.% citric acid solution. The preparation process of paraffin emulsion is the same to that of *n*-dodecanol.

Fabrication of MicroPCMs The MF prepolymer solution was slowly added into the PCM emulsion to start an in situ polymerization at 70 °C with a stirring rate of 400 rpm. After all of the MF prepolymer aqueous solution was added, it was continuously stirred for 180 min at 70 °C with a rate of 600 rpm. Then, resultant microcapsules in the slurry were filtered, washed with 50 wt.% ethanol–water solution of 50 °C

Table 1 Components of MicroPCMs prepared with different types of SMA emulsifier

	Sample			
	Control	A_1	A_2	A_3
Emulsifier	–	SMA1000I	SMA1000MA	SMA1000HNa
Emulsifier type	–	cationic	nonionic	Anionic
Emulsifier mass (g)	0	1.2	1.2	1.2
n-dodecanol (g)	25	25	25	25
MF prepolymer solution (g)	11	11	11	11

Table 2 Components of MicroPCMs prepared with different amounts of SMA1000HNa

	Sample							
	Control	B_1	B_2	B_3	B_4	B_5	B_6	B_7
SMA1000HNa (g)	0	0.2	0.4	0.8	1.2	1.6	2	2.4
n-dodecanol (g)	25	25	25	25	25	25	25	25
MF prepolymer solution (g)	11	11	11	11	11	11	11	11

for once and distilled water for twice, and then dried at 50 °C to obtain microcapsule power.

Characterization

Fourier transform infrared spectroscopy

The chemical structures of microcapsules, MF prepolymer, MF resin and *n*-dodecanol were analyzed by Bruker Vector 33 Fourier transform infrared spectroscopy (FTIR) spectrometer (Germany). The samples were ground and mixed with KBr to make pellets, and FTIR spectra in absorbance mode were recorded among the range of 450 to 4,000 cm^{-1}.

Differential scanning calorimetry

Thermal storage properties of microcapsules were measured by Netzsch differential scanning calorimetry (DSC) 204F differential scanning calorimeter (Germany) at a heating rate of 10 °C/min among the range of 0–60 °C under nitrogen atmosphere. The phase change latent heat and phase change temperature of microPCMs were obtained from the analyzing results of DSC curves using Netzsch TA4.

Calculation of encapsulation efficiency

The content of PCM in microcapsules can be estimated according to the measured phase change latent heat:

$$PCM\ content(\%) = H_w / H_p \times 100\%,$$

where H_w is the phase change latent heat of microcapsules (J/g) and H_p is the phase change latent heat of PCM (*n*-dodecanol of 248 J/g or paraffin of 204.5 J/g).

The encapsulation efficiency of microcapsules can be calculated as the ratio of the measured PCM content in microPCMs to the theoretical value depending on the amount of PCM and MF prepolymer added in the system of fabrication.

Thermogravimetric analysis

Dried microcapsules were analyzed by using Netzsch TG 209F thermogravimeter (Germany) at a heating rate of 20 °C/min among the range of 30–600 °C under nitrogen atmosphere.

Scanning electron microscopy

The dried microPCMs were adhered to the sample stage and the surface of samples was sprayed with gold. The surface morphology of microcapsules was observed by using JEOL JSM-6380 scanning electron microscopy (Japan) at an accelerated voltage of 15 kV.

Measurement of microPCMs diameter

The mean diameter and diameter distribution of microPCMs were measured by using Beckman Coulter LS13320 laser particle diameter analyzer (USA) in a diluted dispersion of the microPCMs in ethanol.

Results and discussion

Effects of types of SMA emulsifier on the properties and morphology of microPCMs

DSC curves of microPCMs prepared with different types of SMA emulsifier

Figure 1 shows the DSC curves of microPCMs containing *n*-dodecanol prepared with different types of SMA emulsifier and without any emulsifier.

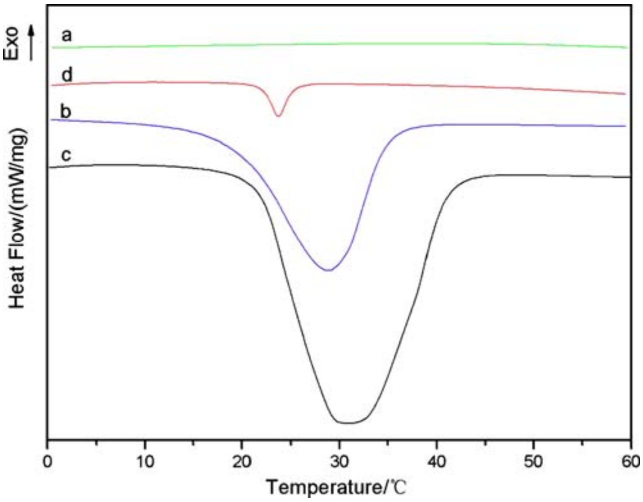


Fig. 1 DSC curves of microPCMs prepared with different types of SMA emulsifier: (**a**) SMA1000I; (**b**) SMA1000MA; (**c**) SMA1000HNa and (**d**) without any emulsifier

It can be seen from of Fig. 1a that there are not any endothermic peaks, which indicated that no *n*-dodecanol has been encapsulated in microcapsules prepared with cationic emulsifier SMA1000I. However, there is a little endothermic peak in curve (d) of Fig. 1, which indicated that little of PCM *n*-dodecanol has been encapsulated in microcapsules prepared without any emulsifier. There is one obvious endothermic peak existing in curve (b) and (c) of Fig. 1 between the temperature of 20 and 40 °C, respectively, and the latter is much bigger than the former. It indicates that *n*-dodecanol with the phase change temperature of about 21 °C has been encapsulated in the microcapsules prepared with nonionic emulsifier SMA1000MA and anionic emulsifier SMA1000HNa, respectively, and the encapsulation amount of microcapsules using SMA1000HNa is much higher than that of SMA1000MA.

Table 3 shows the thermal storage properties of microPCMs prepared with different types of SMA emulsifier and without emulsifier. The results of Fig. 1 and Table 3 indicate that the type of SMA emulsifier has great influence on the process of encapsulation and the encapsulation efficiency of *n*-dodecanol using MF resin as the shell material through in situ polymerization.

The SMA emulsifier can be hydrolyzed with the help of acid or alkali in the oil-in-water (O/W) system, which plays two important roles in the fabrication of microcapsules: one is dispersion effect and the other is charge effect. The molecular structures and hydrolyzed formulas of the three types of SMA emulsifier are showed in Fig. 2.

The three types of SMA emulsifier are polymeric surfactant of C–C bonding main chain with both hydrophobic side chain (including benzene groups) and hydrophilic side chain (including carboxylic groups, imide groups, and amide groups), and they are sufficiently amphiphilic to be adsorbed by surfaces and interfaces. The anionic SMA emulsifier with anionic carboxylic groups can form relatively strong negative electron field, while the cationic SMA emulsifier with hydrolyzed imide groups can form positive electron field. Because of the side chains of nonionic SMA emulsifier possessing both carboxylic groups and amide groups, the core particles are positive charged and negative charged partially.

The arrangement of the three types of SMA emulsifier on core particles and the fabrication processes of microcapsules with them are showed in Fig. 3.

Because of the higher chemical potential of the SMA emulsifiers in water solution than that on the surface of oil particles, the SMA emulsifiers should be adsorbed spontaneously by the oil particles with aromatic group spreading inside and hydrolyzed group outside. As soon as the SMA emulsifiers arrange directional, the difference of chemical potential become reduced and the system of core emulsion can be stable with different charge by using different types of emulsifier.

In acid environment, MF prepolymer exhibits positive charge due to the reaction between hydroxymethyl groups and hydrogen ions. The positive charged prepolymer is attracted strongly by core particles with negative electron field by using anionic SMA emulsifier, and the reaction of microencapsulation takes place on the surface of core particles under the effect of acid and heat to form the membrane of microcapsules. In the system with cationic SMA emulsifier, MF prepolymer is rejected by the core particles with the same positive charge and no core material is encapsulated. In the system with nonionic SMA emulsifier, MF prepolymer of positive charge is attracted on the surface of core particles partially, and the encapsulation is not completely enough. In the system without any emulsifier, a little of MF prepolymer is deposited on the surface of core particles with the hydroxy groups due to the weak hydrogen bonding interaction.

Morphology of microPCMs prepared with different types of SMA emulsifier

Figure 4 shows the scanning electron microscopy (SEM) micrographs of microPCMs prepared with different SMA emulsifier or without any emulsifier. It can be seen from Fig. 4a that all the microcapsules prepared with cationic SMA emulsifier are loose and irregular, which are

Table 3 Thermal storage properties of microPCMs prepared with different types of SMA emulsifier and without emulsifier

Sample	Emulsifier	Type of emulsifier	M_w of emulsifier[a]	Phase change temperature[b] (°C)	Phase change latent heat (J/g)
Control	–	–	–	22.0	3.7
A1	SMA1000I	Cationic	5,000	–	0
A2	SMA1000MA	Nonionic	5,500	20.0	87.4
A3	SMA1000HNa	Anionic	5,500	21.5	187.5

[a] The weight average molecule weights (M_w) of three types of SMA emulsifier are supplied by US Sartomer Company

[b] The phase change temperature is the extrapolated onset temperature of phase changing

Fig. 2 The molecular structures and hydrolyzed formulas of the three types of SMA emulsifier: (**a**) SMA1000I, (**b**) SMA1000MA and (**c**) SMA1000HNa

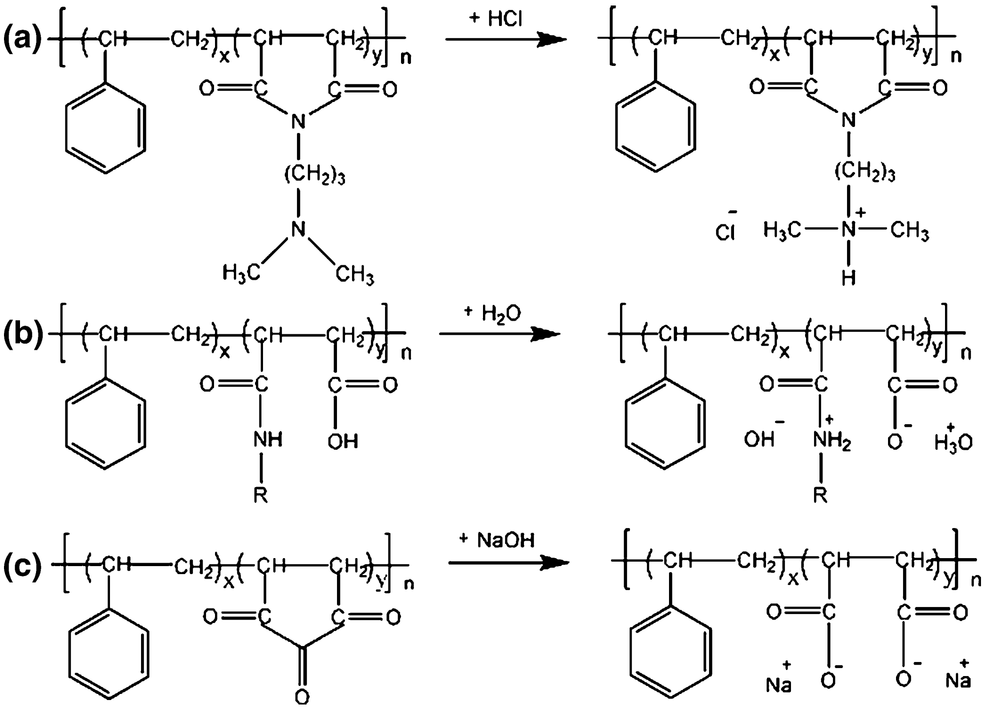
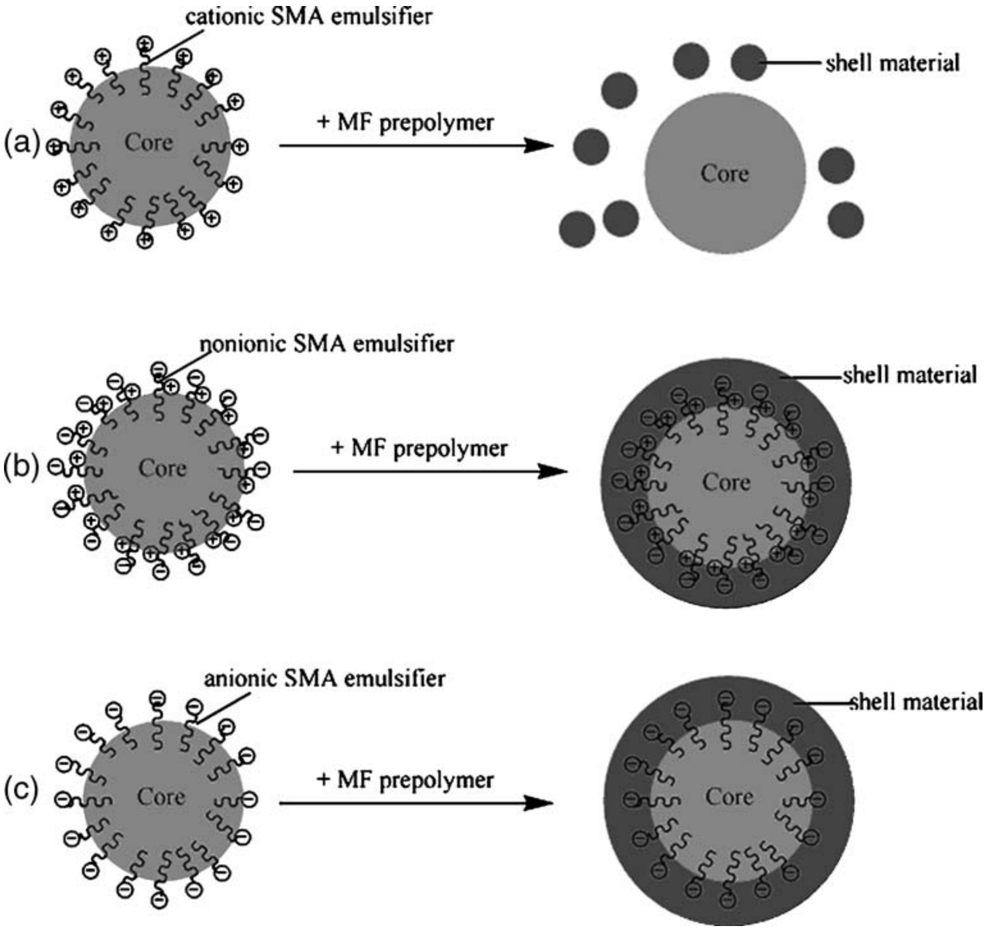
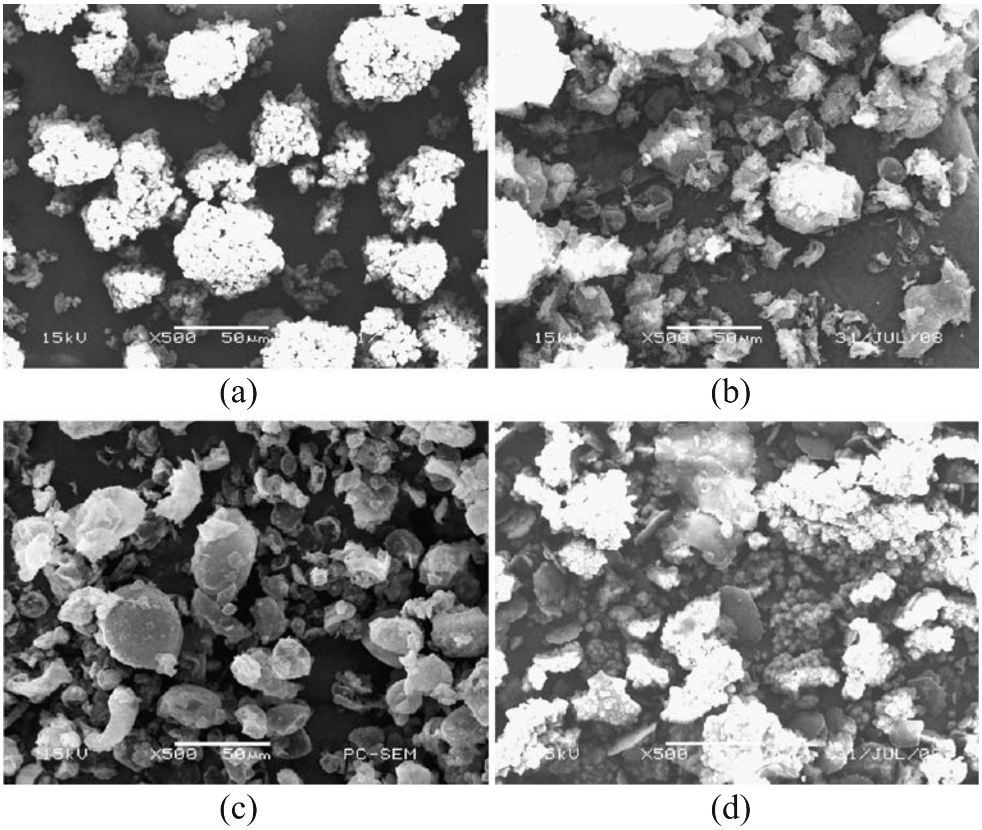


Fig. 3 The arrangement of three types of SMA emulsifier and the fabrication process of microcapsules by using (**a**) SMA1000I, (**b**) SMA1000MA or (**c**) SMA1000HNa





(a) (b)

(c) (d)

Fig. 4 SEM micrographs of microPCMs prepared with different types of SMA emulsifier: (**a**) SMA1000I, (**b**) SMA1000MA, (**c**) SMA1000HNa and (**d**) without any emulsifier

aggregates of smaller spherical MF particles. According to the analyzing of results of DSC, it can be concluded that most of MF prepolymer is synthesized in the water phase due to charge rejection. Figure 4b shows that some of microcapsules are irregular spherical with rough surface and some are irregular fragments, indicating that some of MF prepolymer is deposited on the surface of core material and some is synthesized in the water phase. As is seen from Fig. 4c, most of the microcapsules are irregular spherical with the mean diameter of about 30 μm, which can be attribute to the polarity of *n*-dodecanol. It can be deduced that the entire MF prepolymer were nearly deposited on the surface of core material with the help of charge effect of anionic SMA emulsifier. From Fig. 4d, it can be seen that most of the microcapsules prepared without any emulsifier are loose and flake, and the remained microcapsules are irregular aggregates of small spherical particles, which may contain a little core material.

In conclusion, anionic SMA emulsifier is helpful to the encapsulation of hydrophobic core material *n*-dodecanol by using MF resin as shell material through in-situ polymerization, but cationic SMA emulsifier is harmful for the microcapsule formation, and the effect of nonionic SMA emulsifier is intermediate.

Effect of the amount of SMA emulsifier on the properties, particle size, and morphology of microPCMs

According to the analysis of the effect of SMA emulsifier type on the properties microPCMs, anionic SMA emulsifier SMA1000HNa was chosen to prepare the microPCMs containing polar PCM *n*-dodecanol. Paraffin as the traditional non-polar PCM was chosen to be encapsulated in the same system and the influence of polarity of PCM on the properties of microPCMs are studied. The effects of the amounts of SMA1000HNa on the properties, particle size, and morphology of microPCMs are discussed in this section.

Effect of polarity of PCM and amount of SMA emulsifier on the thermal storage properties of microPCMs

Figure 5 shows that both of the phase change latent heats of the two microPCMs containing *n*-dodecanol or paraffin increased significantly firstly with the increasing of the amount of SMA1000HNa and reached the maximum values of 187.5 and 138.7 J/g when the mass ratio of emulsifier SMA1000HNa to PCM is 4.8% and 3.2%, respectively. Then both of them decreased gradually after the mass ratio of emulsifier to PCM exceeded 4.8% and 3.2%, respectively. It

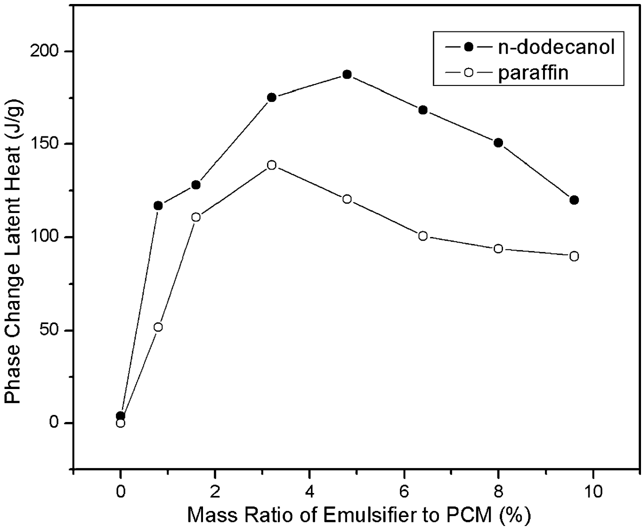


Fig. 5 Effect of the amounts of SMA emulsifier on the phase change latent heat of microPCMs containing *n*-dodecanol or paraffin

can be seen from Fig. 6 that the changing of the encapsulation efficiency of the two microPCMs is nearly the same to that of phase change latent heat with the increasing of the amount of SMA1000HNa. As for most of the microcapsules, the encapsulation efficiency of *n*-dodecanol is higher than that of paraffin with the same amount of SMA1000HNa. The phase change latent heat of microPCM containing *n*-dodecanol is higher than that of paraffin with the same amount of SMA1000HNa, which can be attributed to the higher encapsulation efficiency of *n*-dodecanol and the higher phase change latent heat of *n*-dodecanol with 248 J/g. The microPCMs containing *n*-dodecanol have greater storage ability of thermal energy than that of paraffin, which is sure to have a better application potential for energy saving.

When the amount of emulsifier is low, the core materials are not closely adsorbed by the emulsifier molecules and the particles cannot be encapsulated completely by the shell material. Then the encapsulation content and efficiency increase as the emulsifier content increases and reached the maximum value when the adsorption of emulsifier molecules in the surface of core particles is saturated. When the mass ratio of emulsifier to PCM exceeds the optimal value, the content of emulsifier are too high and the excessive emulsifier can absorb the MF prepolymer and interact with each other, leading to the adhesion of microcapsules and the decreasing of encapsulation efficiency.

However, when the encapsulation efficiency of microPCMs reached the maximum value, the amount of SMA1000HNa for *n*-dodecanol is higher than that of paraffin, which may be attributed to the electronic interaction of the polar groups in *n*-dodecanol and SMA emulsifier. More SMA emulsifier is needed to reach the saturation adsorption in the surface of *n*-dodecanol droplets. The polarity of PCM leads to the higher adding amount of SMA emulsifier. When the mass ratio of emulsifier to PCM is 4.8%, the encapsulation efficiency for *n*-dodecanol reached its maximum value of 93.1%. As for paraffin, its maximum value of encapsulation efficiency is 82.4%, when the mass ratio of emulsifier to PCM is only 3.2 %.

Effect of the amount of SMA emulsifier on the diameter distribution of microPCMs

Figure 7 shows the diameter distributions of microPCMs prepared with different amounts of anionic SMA emulsifier SMA1000HNa. The amount of SMA1000HNa has great influence on the mean diameter and diameter distribution of microPCMs containing *n*-dodecanol.

The mean diameter of microPCMs decreases from 54.7 to 21.8 μm as the amount of SMA emulsifier increases from 0% to 9.6%, generally. After the mass ratio of emulsifier to PCM exceeds 1.6%, the mean diameter decreases slightly continuously and changes little among the range of 20 to 30 μm. An exceptional increasing of mean diameter from 23.2 to 30.6 μm occurs, when the mass ratio of emulsifier to PCM increases from 3.2% to 4.8%. The results indicate that the core material can be dispersed into smaller particles with the increasing of the amount of SMA emulsifier, but the encapsulation content of *n*-dodecanol reaches its maximum when the mass ratio of emulsifier to PCM is 4.8%, leading to an exceptional slight increasing of the particle size.

When the mass ratio of emulsifier to PCM is lower than 1.6%, there are two peaks in the distribution curves, but as

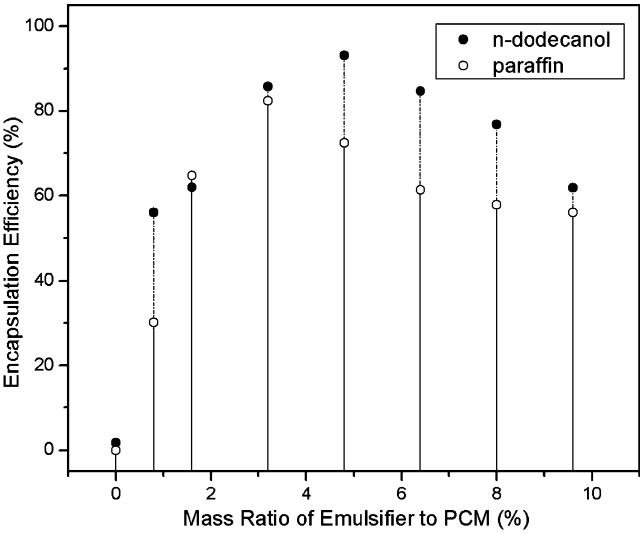
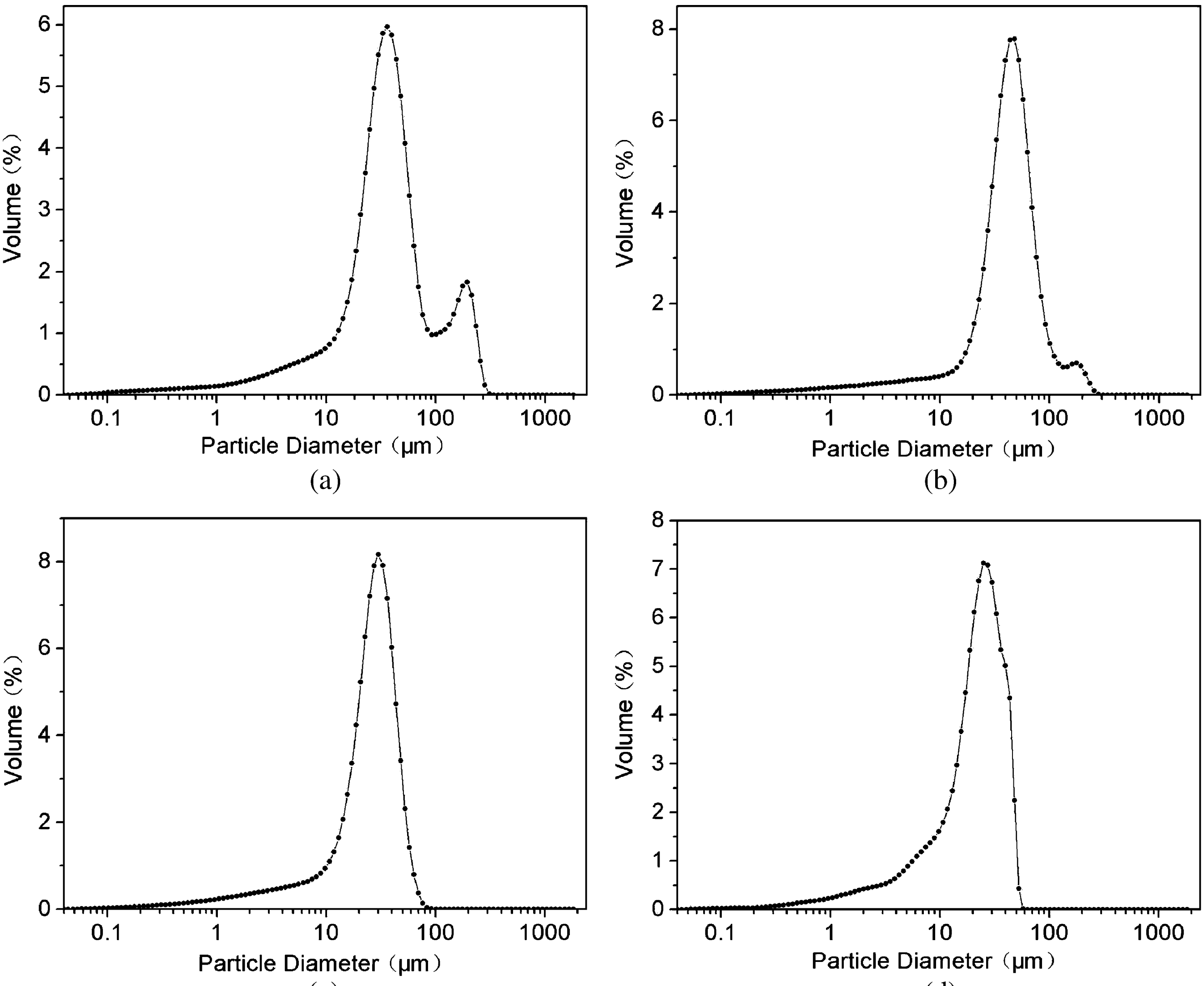


Fig. 6 Effect of the amounts of SMA emulsifier on the encapsulation efficiency of microPCMs containing *n*-dodecanol or paraffin



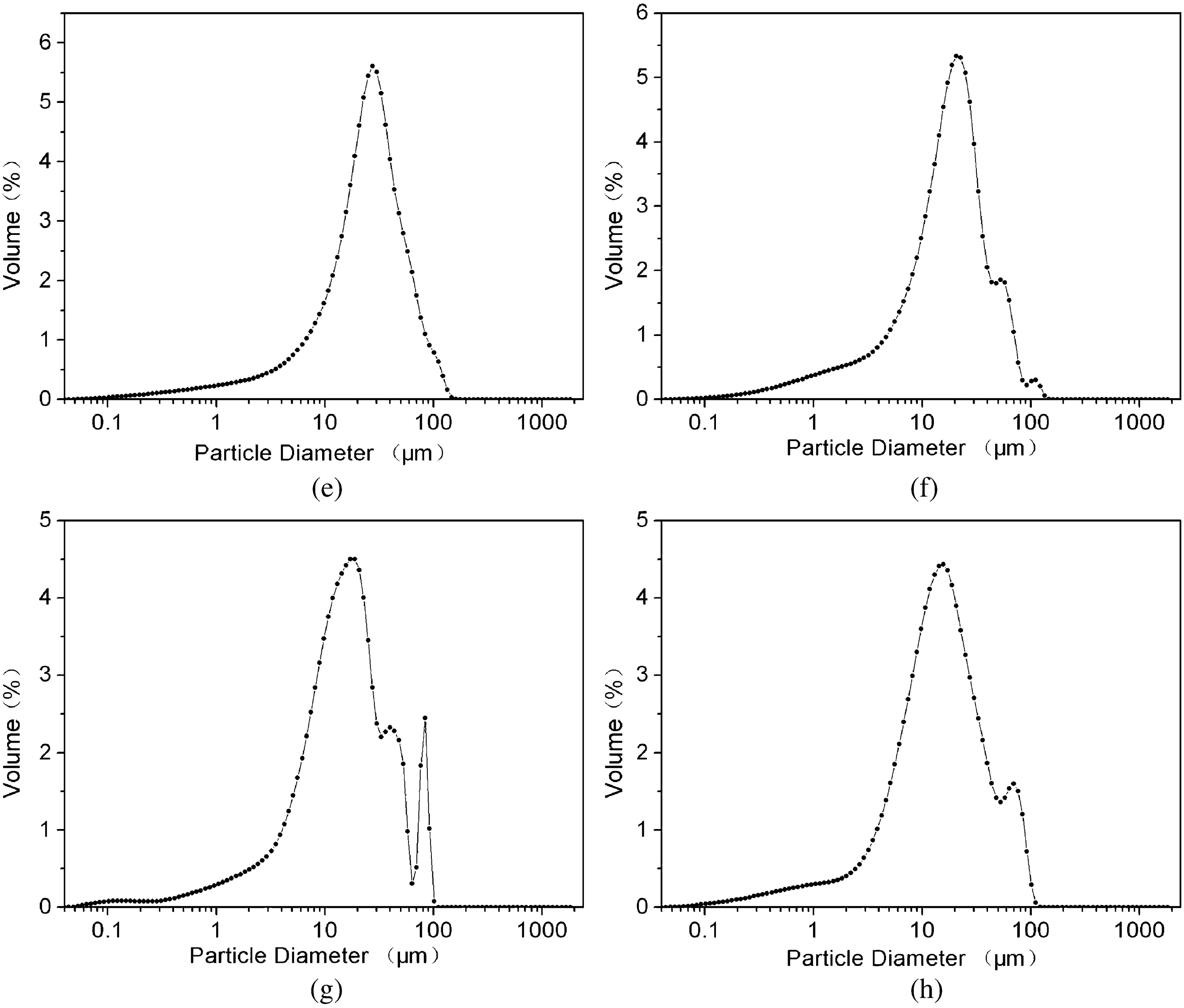
(a) (b) (c) (d)

Fig. 7 Diameter distribution of microPCMs prepared with different mass ratios of emulsifier to PCM: (**a**) 0, (**b**) 0.8%, (**c**) 1.6%, (**d**) 3.2%, (**e**) 4.8%, (**f**) 6.4%, (**g**) 8.0% and (**h**) 9.6%

the mass ratios change in the rang of 1.6% to 4.8%, the number of peaks in distribution curves decreases to 1. When the mass ratios of emulsifier to PCM is higher than 4.8% and lower than 9.6%, the number of peaks in distribution curves increases to 3, but when the mass ratio of emulsifier to PCM is 9.6%, the number decreases to 2. The polydispersity index of distribution curve decreases from 1.486 to 1.003 as the mass ratio of emulsifier to PCM is lower than 1.6% and then increases afterwards with the increasing of the amount of SMA emulsifier. The results indicate that the content of emulsifier is not high enough to disperse the core material evenly and steadily when the mass ratio of emulsifier to PCM is lower than 1.6%. Moreover, the diameter distribution is narrow with only one peak in the curve and the polydispersity index is close to 1 when the mass ratio of emulsifier to PCM ranges from 1.6% to 4.8%. However, when the mass ratio of emulsifier to PCM exceeds 4.8%, there is excessive emulsifier in the water phase, leading to the adhesion of microcapsules. The polydispersity index increased to 1.434 as the mass ratio of emulsifier to PCM reached to 9.6%.

Morphology of microPCMs prepared with different amounts of SMA emulsifier

Figure 8 shows the SEM micrographs of some microPCMs prepared with different amounts of anionic SMA emulsifier SMA1000HNa. It can be seen from Fig. 8a that the microcapsules of sample B_1 are irregular with some hemispheres and some fragments, due to the less amount of emulsifier for fabricating microcapsules when the mass ratio of emulsifier to PCM is only 0.8%.



(e) (f)

(g) (h)

Fig. 7 Continued.

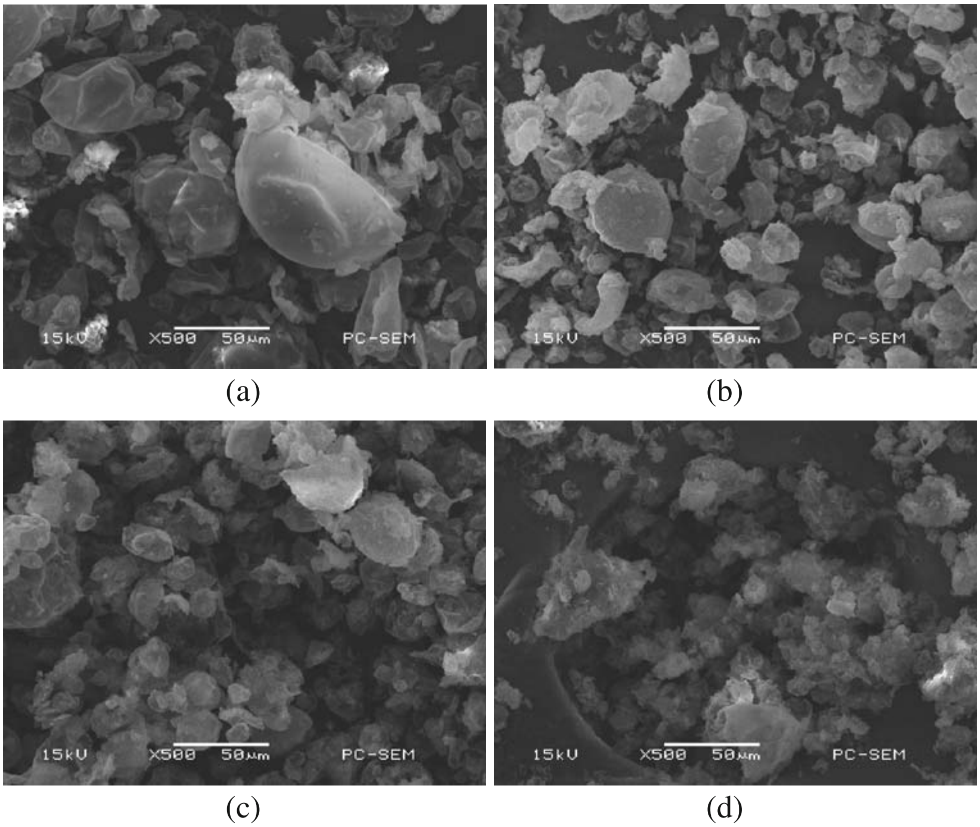
Figure 8b show clearly that the microcapsules in sample B_3 is irregular spherical and compact. It can be seen from Fig. 8c that the microcapsules in sample B_4 is irregular spherical and compact with a little rough surface, which can be attributed to unencapsulated MF resin. The particle diameter range of sample B_4 is wider than that of sample B_3, which is consistent with the results of diameter measurement. In Fig. 8d, the microcapsules of sample B_7 prepared with excessive emulsifier are floccules and some are big aggregates, which can be attributed to the adhesion of MF resin in the fabrication process of microcapsule. The amount of SMA1000HNa has great influence on the morphology and particle size of microcapsules, which is consistent with the results of thermal storage properties and diameter measurement of microPCMs.

FTIR of microPCMs

The FTIR spectra of MF prepolymer, shell material MF resin, microPCM samples, and core material pure *n*-dodecanol are presented in Fig. 9.

The strong and wide absorption peaks at approximately 3,364 and 3,400 cm^{-1} in Fig. 9a and b are attributed to the superposition of O–H and N–H stretching vibrations. In addition, the intensity of absorption peak of Fig. 9a is higher than that of Fig. 9b, indicating that there are a lot of active hydroxy groups and amine groups in MF prepolymers for the following polycondensation to fabricate microcapsules. According to the work of Salaün [31], the peaks at 1,565 and 814 cm^{-1} in Fig. 9a are assigned, respectively, to the in-plane and out-of-plane vibrations of

Fig. 8 SEM micrographs of microPCMs prepared with different mass ratios of emulsifier to PCM: (**a**) 0.8%, (**b**) 3.2%, (**c**) 4.8% and (**d**) 9.6%



triazine ring, and the corresponding peaks of shell material MF resin lie at 1,554 and 812 cm^{-1} in Fig. 9b, respectively. The weak peak at 1,168 cm^{-1} of Fig. 9a and the peak at 1,162 cm^{-1} of Fig. 9b are corresponding to the C–O–C stretching vibrations. The moderate strong peak at 1,008 cm^{-1} of Fig. 9a and the weak peak at 993 cm^{-1} of Fig. 9b are attributed to C–O stretching vibrations of alcohol compounds, indicating that the number of active hydroxy groups in MF resin is much less than that of MF prepolymers due to the cross-linking of hydroxymethyl precondensate.

The strong and wide absorption peaks at approximately 3,346 cm^{-1} in Fig. 9e of core material is assigned to O–H stretching vibrations of *n*-dodecanol. The multiple strong

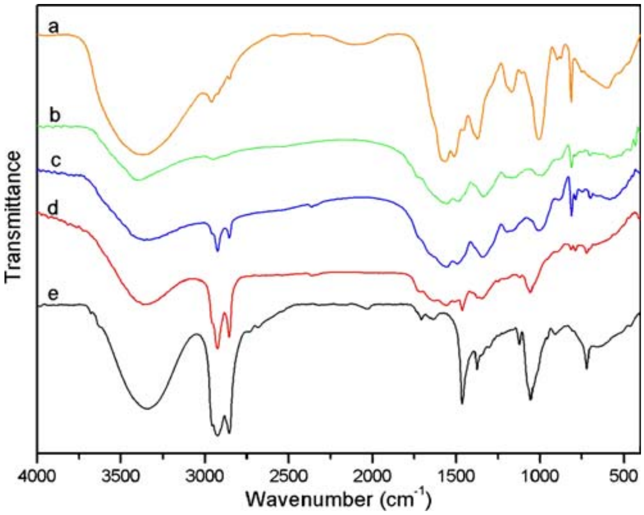


Fig. 9 FTIR spectra of (**a**) MF prepolymer, (**b**) MF resin, (**c**) microPCM sample control; (**d**) microPCM sample B$_4$ and (e) *n*-dodecanol

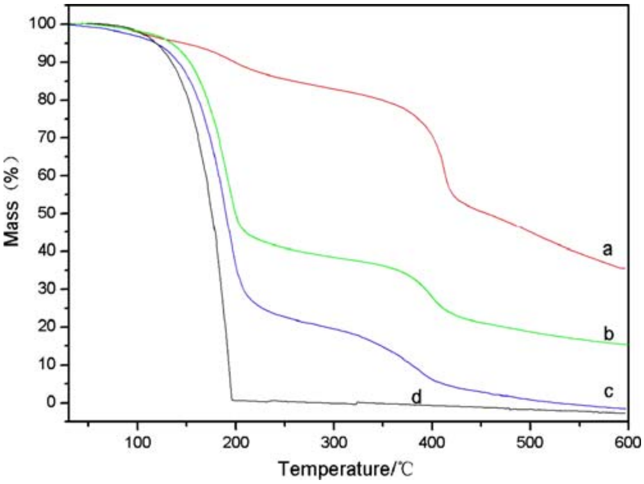


Fig. 10 TG curves of (**a**) MF resin, (**b**) microPCM sample B$_2$, (**c**) microPCM sample B$_4$ and (**d**) *n*-dodecanol

peaks at 2,923 cm^{-1} and 2,854 cm^{-1} are associated with aliphatic C–H stretching vibrations of methyl and methylene groups. In addition, the moderate strong peak at 1,057 cm^{-1} is related to C–OH stretching vibration of primary alcohol.

The characteristic peaks of aliphatic primary alcohol *n*-dodecanol at approximately 2,923, 2,854, and 1,057 cm^{-1} can be observed in Fig. 9c and d of microcapsules containing *n*-dodecanol, indicating that *n*-dodecanol has just been microcapsulated with no reaction between *n*-dodecanol and MF resin. However, the corresponding peaks in Fig. 9c are significantly weaker than that of Fig. 9d, which can be attributed to the much less content of *n*-dodecanol in microPCM control than that of microPCM B_4. In addition, the characteristic peaks of MF resin at approximately 1,550 and 814 cm^{-1} are all observed in Fig. 9c and d also, indicating that *n*-dodecanol has been encapsulated as core material successfully with MF resin as shell material.

Thermogravimetric analysis of microPCMs

Figure 10 shows the TG curves of MF resin, microPCMs containing different contents of *n*-dodecanol, and pure *n*-dodecanol.

In Fig. 10a, there are two steps of small mass loss starting from 76.3 and 176.3 °C, which may be contributed to the volatilization of the residual reagents and water, respectively. Moreover, the significant mass loss process occurring from 403.6 °C in Fig. 10a may be assigned to the decomposition of MF resin.

It can be seen from Fig. 10d that the mass loss process of *n*-dodecanol starts at approximately 151.1 °C and ends at 197 °C with only one step, which is corresponding to the volatilization of *n*-dodecanol. Moreover, the onset temperature of mass loss for *n*-dodecanol is much lower than that of MF resin, indicating that the thermal stability of MF resin is much better than that of pure *n*-dodecanol.

Figure 10b shows that there are two steps of significant mass loss of 61.7% and 23.1% starting from 177.3 to 371.2 °C, respectively. In addition, the mass loss of the first step is a little more than the measured core content of microPCM B_2 by DSC, which can be attributed to the evaporation of the core material *n*-dodecanol and some reagents, indicating that the shell of microPCMs is broken and the core material *n*-dodecanol starts to be evaporated in this step. The second step of mass loss in Fig. 10b is corresponding to the decomposition of MF resin and the extrapolated onset temperature of mass loss is lower than that of pure MF resin.

In Fig. 10c, the mass loss process of microPCM B_4 containing more content of *n*-dodecanol is similar to that of microPCM B_2 with two steps. The mass loss of the first step of microPCM B_4 is 79.3%, which is higher than that of microPCM B_2, attributing to the evaporation of *n*-dodecanol and some residual reagents. The mass loss of the first step of microPCM B_4 is 20.7%, which can be attributed to the decomposition of MF resin. The two extrapolated onset temperature of 166.9 and 353.9 °C for the two steps of mass loss are slightly lower than that of microPCM B_2, respectively.

Moreover, both of the onset temperatures of microPCMs B_2 and B_4 in the first step of mass loss are higher than that of pure *n*-dodecanol, indicating that the thermal stability of PCM increases after being microencapsulated. However, the thermal stability of microPCMs decreases slightly with the increasing of core content.

Conclusion

A novel microPCMs containing unitary fatty alcohol *n*-dodecanol with MF resin as the shell material were successfully prepared through in situ polymerization by using different types of SMA emulsifier. The type and amount of SMA emulsifier have great influence on the properties and morphology of microPCMs. The anion SMA emulsifier is suitable for fabricating of microcapsules in this polymerization system. The amount of SMA emulsifier has great effect on the thermal storage properties, thermal stabilities, mean diameter, and diameter distribution of microcapsules. With the increasing of the amount of SMA emulsifier, the phase change latent and encapsulation efficiency increase at first and decrease later, and the mean diameter decreases generally. The polarity of PCM leads to the higher adding amount of SMA emulsifier. The thermal stability of microcapsules decreases slightly with the increasing of core content and exhibits a certain protective ability for core materials. The SEM micrographs show that microcapsules are irregular spherical and compact with mean diameter of 30.6 μm when the mass ratio of emulsifier to PCM is 4.8%, which is consistent with the results of diameter measurement. The microcapsules containing *n*-dodecanol with phase change latent heat of 187.5 J/g at 21.5 °C are sure to have a better potential for energy storage than traditional microPCMs containing paraffin.

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