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Preparation and characterization of nano-encapsulated *n*-tetradecane as phase change material for thermal energy storage

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ABSTRACT

Nanocapsules used as phase change material (PCM) were prepared by using *in situ* polymerization methods. *N*-Tetradecane was used as the core material. Urea and formaldehyde were used for the shell polymerization. Sodium dodecyl sulfate was used as the emulsifier and resorcin was used as the system modifier. The morphology of the nanocapsules was observed by a scanning electronic microscope (SEM). The thermal properties were investigated by a differential scanning calorimeter (DSC) and a thermogravimetry analysis (TGA). The SEM analysis indicated that the nanocapsules had general size of about 100 nm and the core material was well encapsulated. DSC analysis indicated that the mass content of *n*-tetradecane was up to 60%, which resulted in a high latent heat of fusion of 134.16 kJ/kg. TGA showed the thermal stability of the nanocapsules could be improved by the additives (NaCl) used in the polymerization. The nanocapsules could be applied for thermal energy storage and heat transfer enhancement.

1. Introduction

Latent heat storage is one of the most efficient ways to conserve thermal energy. Phase change materials (PCMs) which can absorb/release high latent heat during the melting/solidifying process, have been receiving attention for different applications in recent years. Unlike the sensible heat storage method, the latent heat storage method provides much higher energy storage density, with a smaller temperature difference between storing and releasing heat [1]. PCMs are developed for various applications due to their different phase change intervals: materials that melt below 15 °C are used for keeping coolness in air-conditioning applications, while materials that melt above 90 °C are used to drop the temperature if there is a sudden increase in heat to avoid ignition. All other materials that melt between these two temperatures can be applied in solar heating and for heat load leveling applications [2]. Materials that have been studied during the last 40 years are hydrated salts, paraffin waxes, fatty acids and eutectics of organic and non-organic compounds [3]. However, PCMs are not easy to be used directly in practical applications because of weak thermal stability, high supercooling effect and low thermal conductivity, etc. So micro/nano-PCM capsules have been developed to overcome these difficulties. Nano or micro-encapsulated phase change materials (NEPCMs or MEPCMs) can greatly increase the heat transfer efficient, enlarge the heat transfer area, reduce PCM reactivity towards the outside environment and control the changes in the volume as phase change occurs [4]. Unlike the functional microcapsules used in medicine and biology which are designed to release the core materials to the outer phase in a long period of time, the NEPCMs must preserve the core material in the polymer shells as long as possible through the heating/cooling cycles.

Various methods have been developed for the encapsulation of PCMs, such as complex coacervation [5], interfacial polycondensation [6] and *in situ* polymerization [7]. The *in situ* polymerization method is one of the most feasible techniques to encapsulate liquid PCMs from the oil/water (o/w) emulsions, many experiments have been carried out utilizing this technique [8–10]. In this paper, it is reported that the synthesis of NEPCM using *n*-tetradecane oil as the PCM and urea–formaldehyde resin as the shell material. *N*-Tetradecane ($C_{14}H_{30}$), which melts at 5.77 °C with a latent heat storage capacity of 217.55 kJ/kg (experimental data of sample no. 0 in Table 1), is a favorable organic PCM for thermal energy storage. Its phase change interval is between 0 and 10 °C, which matches the evaporating temperature regions of the conventional air-conditioning systems. So the latent heat of this PCM can be utilized during the thermal energy charging and discharging cycles in the air-conditioning systems.

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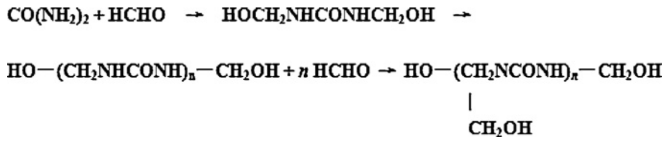
Table 1
DSC data of *n*-tetradecane and nanocapsules prepared with different amount of resorcin used as system modifier.

Sample no.	Melting			Solidifying			PCM content ratio (%)
	Onset temperature (°C)	Peak temperature (°C)	Latent heat of fusion (J/g)	Onset temperature (°C)	Peak temperature (°C)	Latent heat of fusion (J/g)	
0	5.77	7.99	217.55	2.48	2.36	−217.51	100.0
1	2.45	5.57	66.01	2.63	2.40	−66.39	30.4
2	4.41	7.19	103.57	2.01	1.78	−103.48	47.7
3	5.66	8.49	131.09	2.38	2.19	−129.83	60.3
4	5.67	9.01	134.16	2.97	2.81	−134.50	61.8

Note: Sample no. 0 represents pure *n*-tetradecane. Sample nos. 1, 2, 3 and 4 represent respectively nanocapsules prepared from o/w emulsion with 0.25% resorcin concentration, 1% resorcin concentration, 2% resorcin concentration and 5% resorcin concentration.



$$CO(NH_2)_2 + HCHO \rightarrow HOCH_2NHCONHCH_2OH \rightarrow$$

$$HO-(CH_2NHCONH)_n-CH_2OH + n\,HCHO \rightarrow HO-(CH_2\underset{\underset{CH_2OH}{|}}{N}CONH)_n-CH_2OH$$

Scheme 1. Reaction mechanism of urea–formaldehyde prepolymer.

2. Experimental

2.1. Materials

N-tetradecane ($C_{14}H_{30}$) (purity >99%, Switzerland Fluka Chemical Company) was used as the core materials. Urea (CH_4N_2O) (Reagent grade, Shanghai Laize Chemical Company) and formaldehyde (CH_2O) (37 wt.% aqueous solution, Shanghai Chemical Regent Company) were used as shell polymerization materials, sodium dodecyl sulfate ($C_{12}H_{25}OSO_3Na$) was used as oil–water emulsifier. Sodium chloride (NaCl), resorcin ($C_6H_6O_2$), sodium dodecyl sulfate ($C_{12}H_{25}OSO_3Na$), triethanolamine ($C_6H_{15}NO_3$) and formic acid (CH_2O_2) are all reagent grade and obtained from Shanghai Chemical Reagent Company.

2.2. Preparation of urea–formaldehyde prepolymer

3 g urea, 10 ml distilled water and 14 g formaldehyde solution were added into a 100 ml flask, the pH of the mixture was adjusted to 8–9 with triethanolamine, then the mixture was stirred at the rate of 200 rpm for 1 h, the temperature of the mixture was controlled at 70 °C by a thermostat water bath.

The suggested reaction mechanism of urea–formaldehyde prepolymer is shown in Scheme 1. The C–N bond, N–H and O–H group appear in the urea–formaldehyde prepolymer.

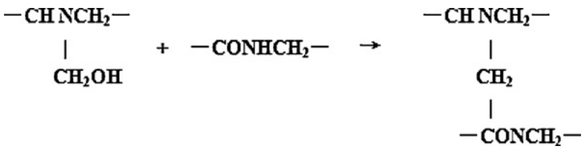
2.3. Preparation of o/w emulsion

SDS (0.5 g) was added into 300 g distilled water dissolved with resorcin and sodium chloride, the content ration of resorcin and chloride is different during several experiments. Then the solution was stirred and heated to 60 °C, 15 g *n*-tetradecane was added into the flask. The mixture was mechanically emulsified with a stirring rate of 1500 rpm at 60 °C for 30 min to obtain the o/w emulsion by the electromotion stirrer.

During the shell fabrication process of the nanocapsules, the condensation between the CH_2OH group and the NH group begins when the pH of the emulsion is adjusted to 3–4, which is shown in Scheme 2.

2.4. Preparation of nanocapsules

The prepolymer solution was added drop by drop into the o/w emulsion to start *in situ* polymerization and the stirring rate was adjusted to 200 rpm, then the pH of the mixture was adjusted to 3–4 with 40% formic acid solution, the temperature of the mixture was controlled at 60 °C during the whole process. After the pH adjustment, the reaction was continued with a stirring rate of 500 rpm for 4 h. After 4 h, the urea–formaldehyde polymer network is formed at



$$-\underset{\underset{CH_2OH}{|}}{CH}NCH_2- \; + \; -CONHCH_2- \rightarrow -CH\underset{\underset{\underset{\underset{-CONCH_2-}{|}}{CH_2}}{|}}{N}CH_2-$$

Scheme 2. Condensation between the CH_2OH group and the NH group.

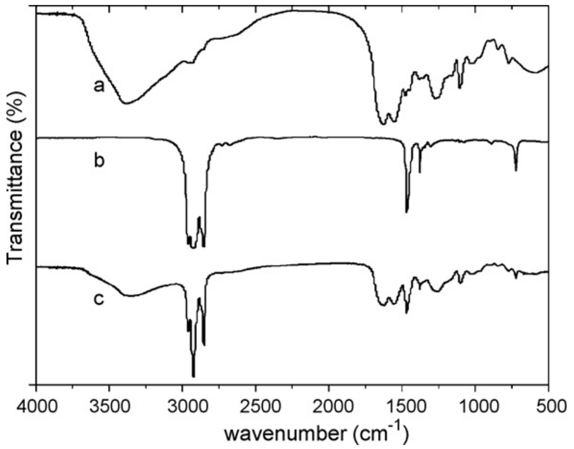


Fig. 1. FT-IR spectra of nano-encapsulated phase change materials. (a) Urea–formaldehyde resin shells. (b) Pure *n*-tetradecane. (c) Nano-encapsulated *n*-tetradecane of sample no. 4 with urea–formaldehyde resin shells.

the oil/water interface and eventually the *n*-tetradecane is encapsulated. The resultant nanocapsules were filtered and washed with distilled water at 70 °C for three times and dried in a vacuum oven for 20 h.

2.5. Characterization techniques

For SEM analysis, tiny amount of dried nanocapsule powders was adhered on a copper SEM stub by conductive adhesive and gold-coated in a high vacuum evaporation coating machine. The morphology and microstructure of the nanocapsules were observed through a scanning electronic microscopy (SEM, JSM-7000F, JEOL Inc., Japan). The structural analysis of *n*-tetradecane and nanocapsules were conducted by using a FT-IR (FTIR Spectra was recorded on a Nicolet Nexus870 from 500 to 4000 cm^{-1} with a resolution of 2 cm^{-1} at room temperature on a KRS-5 pellet.) spectrophotometer. The thermal properties of the microcapsules were obtained using a differential scanning calorimeter (Pyris 1 DSC, PerkinElmer) at 5 °C/min under a constant stream of argon at flow rate of 20 ml/min, the accuracy of enthalpy was ±5% and the accuracy of temperature was ±0.2 °C. The thermal stability of the nanocapsules was determined by thermogravimetric analysis (TGA) under a constant stream of nitrogen at flow rate of 20 ml/min, heated from 25 to 40 °C in 3 min and kept at 40 °C for 30 min. The working temperatures of this thermal energy PCMs are usually much lower than the room temperature and the highest environment temperatures in applications are below 30 °C, so in the TGA experiments, the samples are heated from 25 to 40 °C in 3 min and kept at 40 °C for 30 min to test their thermal stability.

3. Results and discussion

3.1. FT-IR analysis

According to the FT-IR spectra in Fig. 1, the stretching vibration of N–H and O–H is shown in the region of 3500–3000 cm^{-1}, C–H stretching or bending vibration is observed at 1477 cm^{-1}, a N–H stretching vibration at 1565 cm^{-1}, a C=O stretching vibration at 1625 cm^{-1}, a C–N stretching vibration at 1250 cm^{-1} and ether bridges at 1130 cm^{-1} are observed both in the polymer shells and the nanocapsules, so the formation of the urea–formaldehyde shell of the nanocapsules is confirmed. The absorption peaks of *n*-tetradecane at 2957, 2924, 2854 cm^{-1} also appear in the nanocapsule spectra, which confirm the encapsulation of the core materials.

3.2. Microstructure of nano-encapsulated n-tetradecane

Fig. 2(a) shows a scanning electron microscope (SEM) photograph of the nanocapsules, the nanocapsules have a regular sphere shape and the insert figure shows the spheres have general diameter of about 100 nm. The surface of the nanocapsules is rough, adhered with small urea–formaldehyde resin particles. Combined with the FT-IR and SEM analysis, the formation of NEPCM is confirmed.

Resorcin with hydroxy can react with formaldehyde to form bakelite, so resorcin is used as the cross-link agent to connect the urea–formaldehyde polymer networks, which can improve the encapsulation of the urea–formaldehyde polymer shell and increase the mass content of the core materials. But high resorcin concentration will increase the stickiness of the capsules and make them hard to form regular nano-spheres, which is clearly shown in Fig. 2(b).

3.3. Thermal properties of nano-encapsulated n-tetradecane

PCMs requires high latent heat storage capacity in thermal energy storage applications, for nano-encapsulated materials, only

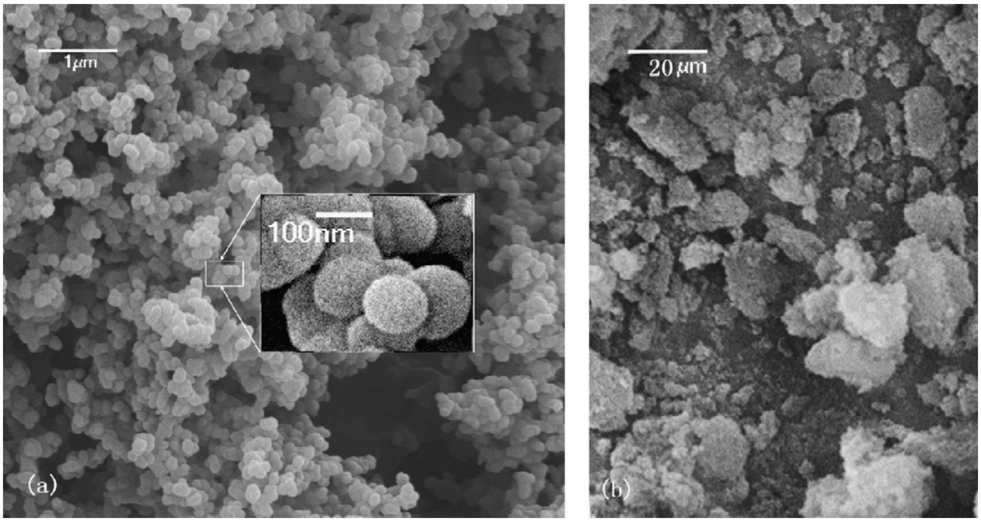


Fig. 2. SEM photos of nanocapsules. (a) Nanocapsules prepared with a resorcin concentration of 5%. (b) Nanocapsules prepared with a resorcin concentration of 10%.

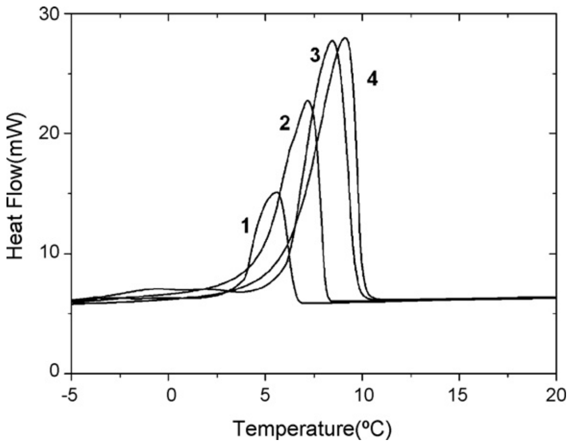


Fig. 3. The heating DSC curves of nanocapsules with (1) 0.25%, (2) 1%, (3) 2% and (4) 5% resorcin concentration used as system modifier in the preparation.

the core materials absorb/release thermal energy during the heating/cooling process, so high core material content will result in a high latent heat storage capacity. Using differential scanning calorimeter (DSC), the phase change temperature and the latent heat capacity could be determined. The DSC results of the nanocapsule samples are shown in Figs. 3 and 4 and Table 1. Comparing the latent heat data of nanocapsules and of pure *n*-tetradecane, the core material mass ratio could be determined by Eq. (1). The η is the mass ration of the PCM, $\Delta H_{\mathrm{NEPCM}}$ represents the latent heat of fusion of nano-encapsulated *n*-tetradecane, and ΔH_{PCM} represents the latent heat of fusion of *n*-tetradecane measured by the DSC.

$$\eta = \frac{\Delta H_{\mathrm{NEPCM}}}{\Delta H_{\mathrm{PCM}}} \times 100\% \tag{1}$$

As shown in Table 1, resorcin is used as the cross-link agent to connect the urea–formaldehyde polymer networks. Resorcin with hydroxy can react with formaldehyde to form bakelite. Sample nos. 1, 2, 3 and 4 in Table 1 represent respectively nanocapsules prepared from o/w emulsion with 0.25% resorcin concentration, 1% resorcin concentration, 2% resorcin concentration and 5% resorcin concentration. When increasing the resorcin concentration from 0.25% to 5%, the mass ratio of *n*-tetradecane increases from 30.4% to 61.8%. Resorcin can efficiently accelerate the polymerization, and make the prepolymer efficiently react at the o/w interface. It is found that urea–formaldehyde polymer capsules could be observed by SEM if resorcin is used in the o/w mixture. But the resorcin concentration cannot be increased over 10%, for it will greatly increase the stickiness of the solution and make it hard to obtain dried nano-spheres.

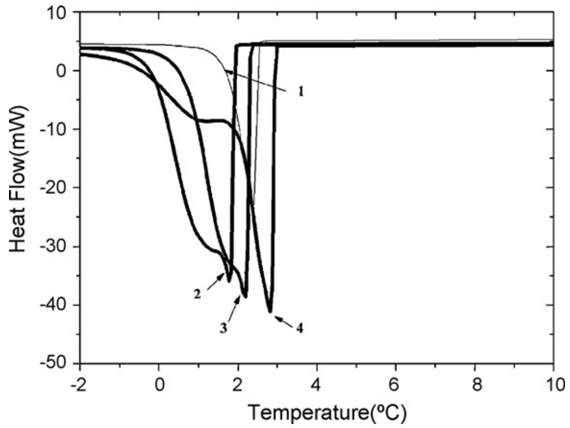


Fig. 4. The cooling DSC curves of nanocapsules with (1) 0.25%, (2) 1%, (3) 2% and (4) 5% resorcin concentration used as system modifier in the preparation.

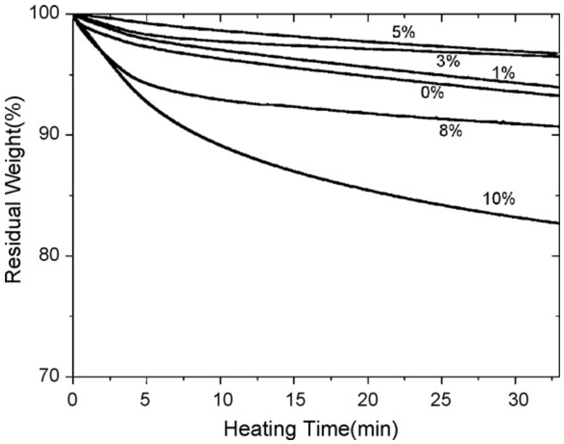


Fig. 5. TG curves of nano-encapsulated *n*-tetradecane with 0%, 1%, 3%, 5%, 8% and 10% NaCl concentration in the o/w emulsion.

As shown in Fig. 4, the latent heat released quickly during the cooling process. Comparing the onset melting temperatures with the onset solidifying temperatures, it is found that the pure *n*-tetradecane has a supercooling degree of 3.29 °C, the supercooling degrees of the nanocapsule samples are all below 3 °C. Sample 1 shows a supercooling degree of only 0.18 °C, but its PCM content is very low (only 30.4%). It can be concluded that the encapsulation of *n*-tetradecane could slightly decrease the supercooling degree of the PCM due to shell of nanocapsule could be used as crystal nucleus of the PCM, and the possible reasons can be explained in literature [11].

The origin of the thermal stability test is to determine leak loss of encapsulated *n*-tetradecane in nanocapsules during the heating process. The use of NaCl is to improve the encapsulation of the nanocapsules and increase the thermal stability of the nano-encapsulated *n*-tetradecane, which can be proved by the thermogravimetry analysis (TGA), shown in Fig. 5. Nanocapsules produced from the o/w emulsion containing 1–3% NaCl show less weight loss during the heating process due to NaCl can stabilize urea–formaldehyde prepolymer in the o/w emulsion and improve the encapsulation of the nanocapsules. As the concentration of NaCl is 8% and 10%, the greater weight loss can be observed in Fig. 5 due to the higher concentration of NaCl may result in the lower reaction rate of urea–formaldehyde prepolymer. In our experiments, 2–5% NaCl concentration will be suitable for the *n*-tetradecane encapsulation.

4. Conclusion

The preparation and characterization of nano-encapsulated *n*-tetradecane as phase change material are demonstrated, the obtained NEPCMs absorb heat at 5–9 °C with a latent heat storage capacity of 100–130 kJ/kg. The size of the nanocapsules is mainly controlled by the stirring rate during the emulsion process. A stirring rate 1500 rpm is suitable for the nano-encapsulation. As the resorcin concentration increases from 0.25% to 5%, the mass ratio of *n*-tetradecane increases from 30.4% to 61.8%. 2–5% NaCl concentration is suitable for the *n*-tetradecane encapsulation, and *n*-tetradecane can be encapsulated efficiently with good thermal stability, which made the nanocapsules attractive for thermal energy storage and heat transfer enhancement applications. This method can also be utilized to encapsulate many oil phase organic compounds for different applications to expand their functions and improve their performances.

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