

Microencapsulation of *n*-Eicosane as Energy Storage Material

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For heat energy storage application, polyurea microcapsules containing phase change material, *n*-eicosane, were synthesized by using interfacial polymerization method with toluene-2,4-diisocyanate (TDI) and diethylenetriamine (DETA) as monomers in an emulsion system. Poly(ethylene glycol)octyl-phenyl ether (OP), a nonionic surfactant, was the emulsifier for the system. The experimental result indicates that TDI was reacted with DETA in a mass ratio of 3 to 1. FT-IR spectra confirm the formation of wall material, polyurea, from the two monomers, TDI and DETA. Encapsulation efficiency of *n*-eicosane is about 75%. Microcapsule of *n*-eicosane melts at a temperature close to that of *n*-eicosane, while its stored heat energy varies with core material *n*-eicosane when wall material fixed. Thermo-gravimetric analysis shows that core material *n*-eicosane, micro-*n*-eicosane and wall material polyurea can withstand temperatures up to 130, 170 and 250 °C, respectively.

Keywords phase change material, *n*-eicosane, microcapsule, interfacial polymerization, heat energy storage, thermal analysis

Introduction

In recent years, the use of phase change materials (PCMs) for heat energy storage has received extensive attention because of their increasing consumption of fossil fuel and worsened environment. Phase change materials can absorb, store and release large amounts of latent heat over a defined temperature range while the material changes phase or state. They have been employed for storage of heat energy due to their high latent heat of transition, high energy densities and low cost.¹ A wide range of PCM has been investigated, including salt hydrates, paraffin wax and non-paraffin organic compounds. Recently, a new technique has been developed utilizing microencapsulated PCM in energy storage, such as heating and air conditioning of buildings, thermal insulation, thermal adaptable fibers, etc.²

Microencapsulation is a physical or chemical process to engulf small solid or liquid particles of 1 to 1000 μm in diameter with a solid shell. The wall/shell material of the capsules can be formulated by a variety of materials including natural and synthetic polymers. *n*-Eicosane was chosen as core material in this work because it has a desirable melting point of about 36.5 °C and may be used in thermal adaptable fibers or buildings materials. The advantages of microencapsulated paraffin wax are reduction of the reactivity of the paraffin with the outside environment, increasing the total heat transfer area, and permitting the core material, due to coating, to withstand frequent changes in volume

of the heat storage material, when the phase change occurs.³ In our experiments, microencapsulation of *n*-eicosane was performed by interfacial polymerization forming polyurea microcapsules. In the system droplets are first formed by emulsifying an organic phase consisting of the core materials and an oil-soluble reactive monomer, **A**, in an aqueous phase. By adding water-soluble reactive monomer, **B**, monomers **A** and **B** react with each other at the interface of a micelle to become a shell. *n*-Eicosane is a phase change material desirable for application in heat energy storage due to its availability in a reasonable transition temperature range.

Experimental

Materials and equipment

Toluene-2,4-diisocyanate (TDI) and diethylenetriamine (DETA) used as shell-forming monomers were obtained from Shanghai Chemical Reagent Co. *n*-Eicosane (Beijing Chemical Co., C.P.) was employed as core material. Nonionic surfactant, poly(ethylene glycol)octyl-phenyl ether (OP), from Shanghai Chemical Reagent Co., was used as an emulsifier. Cyclohexane (Beijing Chemical Co.) used as a solvent was of reagent grade without further purification. Digital display electric agitator (DW-3-90W) and vacuum oven (DZF-6020) were purchased from Yuhua Instrument Co.

Preparation of microcapsules

The microencapsulation of *n*-eicosane was carried

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out in a 250 mL three-neck round-bottomed flask equipped with a mechanical stirrer. Prior to encapsulation, OP (1.25 g) was dissolved in 40 mL distilled water. An organic solution of *n*-eicosane (4 g), cyclohexane (5 mL) as solvent and TDI (1.5 g) was prepared. The organic solution was added to the aqueous surfactant solution and the mixture was emulsified mechanically at a stirring rate of 300 r/min to form an oil-in-water emulsion.⁴ After stirring for 3 min, diethylenetriamine (DETA) diluted in 10 mL distilled water was slowly added into the emulsion system to start the interfacial polymerization reaction between TDI and DETA at the oil-water interface. After addition of DETA, the reaction mixture was heated at 60 °C for 2 h. The obtained microcapsule slurry was decanted, washed with distilled water to remove unreacted DETA and dried in a vacuum oven at 30 °C for 48 h.

Analysis of the microcapsules

In order to define the structure of the shell polymer, the FT-IR spectra of two kinds of empty microcapsules were obtained with a computerized Nicolet Impact 400D spectrophotometer (ThermoNicolet, USA). The thermal properties of the microcapsules were evaluated using differential scanning calorimeter (DSC 141, Setaram, France, calibrated with pure indium, aluminum, tin and zinc) and thermogravimetry (TG) (setsys 16/18, Setaram, France).

Results and discussion

Mechanism of shell formation

The reaction scheme of shell formation is shown in Scheme 1. The polyurea shell is formed by reaction of the amine groups of DETA with isocyanate groups of TDI at the interface (Scheme 1-a). Interfacial polymerization of TDI and DETA occurs rapidly at ambient temperature. On the other hand, TDI monomers can be hydrolyzed slowly at the interface to produce amines, which react with TDI to form the shell of the polyurea microcapsules (Scheme 1-b). The latter interfacial reaction occurs on the oil side of the interface.⁵

Reactive ratio of TDI to DETA

In order to investigate the influence of the feed ratio of TDI to DETA on the polymerization, microcapsules were synthesized by using a fixed amount of TDI and different amounts of DETA. Under this condition, *n*-eicosane was not added and cyclohexane compensated for it. Since both *n*-eicosane and cyclohexane are non-polar hydrocarbons, a similar wall-shaped reaction is expected regardless of single composition or their mixture. Cyclohexane could be evaporated completely during drying process and empty capsules comprised of pure polyurea were obtained. The dry weights of microcapsules synthesized at different amount of DETA are shown in Figure 1. As seen in the graph, the dry weight of the microcapsules increased linearly as DETA feed increased from 0 to 0.5 g, but only a little incre-

Scheme 1 Wall-forming reaction of polyurea microcapsule

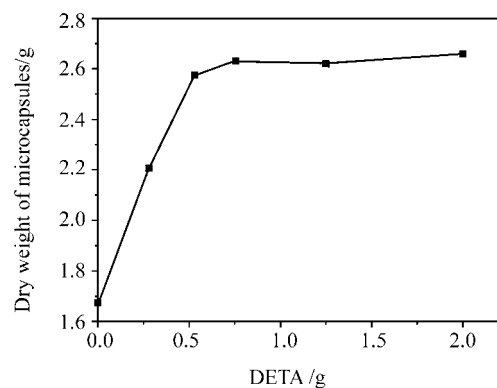
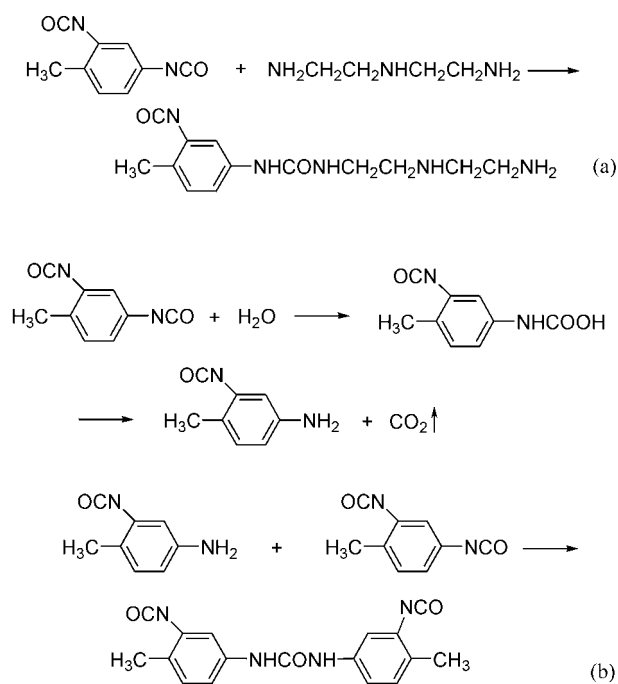


Figure 1 Dry weight of microcapsules synthesized using TDI/DETA/cyclohexane=1.5 g : (0—2) g : 7.6 g.

ment was observed as DETA weight increased from 0.5 g up to 2 g. This means that excess DETA can not react once TDI is depleted at the interface. From the curve, it can be concluded that the mass ratio of TDI to DETA is about 3 to 1.

Analysis of FT-IR spectra

FT-IR spectra of empty microcapsules prepared with and without DETA are presented in Figure 2. As seen in the figure, spectrum (b) contains an absorption band at 2276 cm^{-1} , which is assigned to an isocyanate group. It is the spectrum of a microcapsule synthesized only with TDI. The wall-formation reaction of TDI is limited at the interface of the oil droplet because water can not diffuse into the core of the oil droplet owing to the hydrophobic nature of the oil droplet, thus unreacted isocyanate groups remained in the core of the microcapsule. However, the spectrum (a) shows absorption bands at

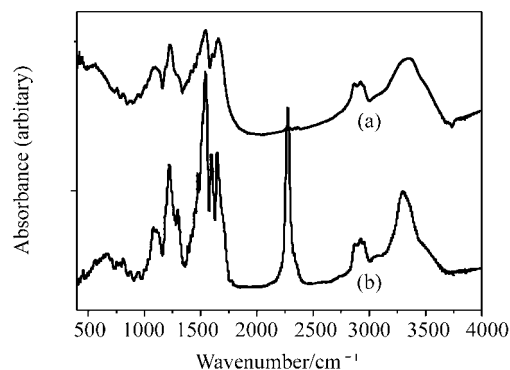


Figure 2 FT-IR spectra of empty polyurea microcapsules prepared with EDTA (a) and without EDTA (b).

1660 cm^{-1} for the C=O stretching of urea formation. The N—H stretching was observed at 3300—3250 cm^{-1} . The IR spectra also show the completion of the reaction between diisocyanates and diamines by the disappearance of NCO absorption bands at 2270 cm^{-1} and the appearance of the N—H and C=O absorption bands. Moreover, C—H stretching in the aliphatic methylene group of diamines was observed at 2910 cm^{-1} . This may be contributed to addition of DETA, which could react fast with TDI and hence no unreacted isocyanate group was observed in the microcapsule core. Because DETA is also compatible with the hydrophobic oil phase, it is believed to improve the diffusion into the interface.

Thermal characteristics of microcapsules

The thermal properties of microcapsules containing *n*-eicosane were evaluated using DSC. Measured melting point (T_m) and latent heat (ΔH_{fus}) for the microencapsulated *n*-eicosane are tabulated in Table 1. DSC curves of *n*-eicosane and micro-*n*-eicosane is presented in Figure 3. The core material, *n*-eicosane, used in our experiments melts at 36.5 °C and absorbs 123.2 joules of heat per gram.

From Table 1 and Figure 3, we know that capsulated *n*-eicosane shows a phase change over the same temperature range as that of the bulk, and that the latent heat of fusion varies with the feed amount of core material, *n*-eicosane. The encapsulation efficiency of *n*-eicosane was about 75% in the experiments, calculated with the following formula⁴:

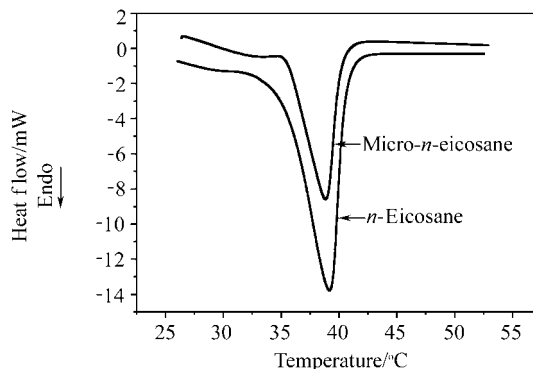


Figure 3 DSC curves of *n*-eicosane and microencapsulated *n*-eicosane synthesized using TDI/DETA/*n*-eicosane=1.5 g : 1.8 g:3.82 g, OP 1.25 g.

$$\text{Efficiency}/\% = \frac{\Delta H_{\text{fus}}(\text{micro})}{\Delta H_{\text{fus}}(\text{C20})} \times \frac{W_{\text{C20}}}{W_{\text{C20}} + W(\text{empty-micro})} \times 100$$

where $\Delta H_{\text{fus}}(\text{micro})$, $\Delta H_{\text{fus}}(\text{C20})$ are measured enthalpies of microcapsules containing *n*-eicosane and *n*-eicosane itself, respectively; W_{C20} and $W(\text{empty-micro})$ are the weights of fed *n*-eicosane and dried empty microcapsules, respectively.

TG thermograms of *n*-eicosane, micro-*n*-eicosane and the wall material, polyurea, were presented in Figure 4. The above three materials show initial loss at about 130, 170 and 250 °C, respectively. This indicates that the polymer shell can protect the encapsulated *n*-eicosane from escaping in the temperature range from 130 to 170 °C.

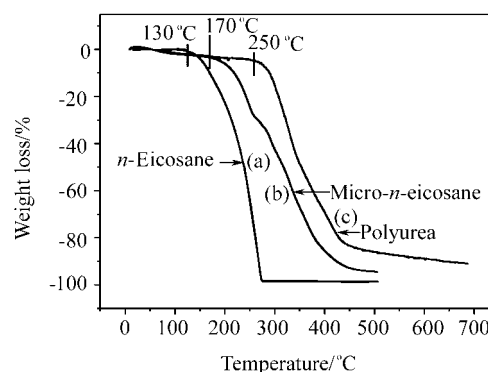


Figure 4 TG thermograms of (a) *n*-eicosane, (b) microcapsules containing *n*-eicosane and (c) wall material polyurea, respectively.

Table 1 Thermal characteristics of microcapsules containing *n*-eicosane

| TDI/g | DETA/g | Cyclohexane/g | <i>n</i> -Eicosane/g | $T_m/^\circ\text{C}$ | $\Delta H_{\text{fus}}/(\text{J}\cdot\text{g}^{-1})$ | Efficiency/% |
|-------|--------|---------------|----------------------|----------------------|--|--------------|
| 1.5 | 1.75 | 1.14 | 1.14 | 36.5 | 29.34 | 77.6 |
| 1.5 | 1.75 | 1.9 | 1.9 | 36.3 | 40.66 | 77.6 |
| 1.5 | 1.75 | 3.8 | 3.8 | 35.7 | 55.48 | 75.2 |
| 1.5 | 1.75 | 5.7 | 5.7 | 36.1 | 63.55 | 74.6 |

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