Chinese Chemical Letters Vol. 15, No. 6, pp 729-732, 2004
http://www.imm.ac.cn/journal/ccl.html

Preparation and Characterization of Microencapsulated Hexadecane Used for Thermal Energy Storage

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Abstract: Polyurea microcapsules about 2.5 μm in diameter containing phase change material for thermal energy storage application were synthesized and characterized by interfacial polycondensation method with toluene-2,4-diisocyanate and ethylenediamine as monomers in an emulsion system. Hexadecane was used as a phase change material and OP, which is nonionic surfactant, and used as an emulsifier. The chemical structure and thermal behavior of the microcapsules were investigated by FTIR and thermal analysis respectively. The results show encapsulated hexadecane has a good potential as a solar energy storage material.

Keywords: Phase change material, microcapsule, interfacial polycondensation, energy storage.

The application of phase change materials (PCM) for thermal energy storage capacities has received considerable attention recently, due to its intrinsic properties. However, there are some inherent drawbacks[1], such as: (1) during the freezing (heat release) process in typical latent heat storage devices, the PCM freezes on to the heat transfer surface, thereby, the thermal resistance was increased. In addition, the supercooling and poor thermal conductivity properties also affect the effective application of PCM in a system; (2) some PCMs are highly corrosive to certain container materials, hence, the material of the container should be selected for compatibility with the corrosive nature of PCM; (3) the PCMs, generally, exhibit a large change volume during phase transition and limit the use of simple containment and heat exchange geometry; (4) some PCMs are highly toxic, and require completely sealed storage system. In order to overcome these inherent difficulties, one of the promising ways to solve problems is to choose the encapsulated PCM as a storage material and heat transfer media. Encapsulation of PCMs has been studies for application to thermal energy fields such as heating and air conditioning of buildings, thermal insulation, thermal adaptable fibers, *etc*[2]. The advantages of microencapsulated paraffin wax are reduction of the reactivity of the paraffin with the outside environment, increase of the heat transfer area, and permission of the core material to withstand frequent changes in volume of the storage material, as the phase change occurs[3]. Microencapsulation is a physical or chemical process to engulf small solid or liquid particles of 1 to 1000 μm with a solid shell. Encapsulation was carried out by interfacial polycondensation forming polyurea microcapsules. In the system droplets are first

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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 interfacial of a micelle to become a shell.

Experimental

TDI and EDA used as shell-forming monomers were obtained from Shanghai Chemical Reagent Co. Hexadecane (Koch Light, 99%) was employed as core material. Nonionic surfactant, OP [poly(ethylene glycol) octylphenyl ether, from Shanghai Chemical Reagent Co.] was used as an emulsifier. The cyclohexane used was in reagent grade without further purification.

Preparation of Microcapsules

The microencapsulation was carried 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 40mL distilled water,an organic solution of hexadecane (5 mL), cyclohexane (5 mL), and toluene-2,4-diisocyanate (1.5 g) was prepared. The organic solution was added to the aqueous surfactant solution and the mixture was emulsified mechanically at rate of 300 rpm to form an oil-in-water emulsion[4]. After stirring for 3 min, EDA(1.2 g) diluted in 10 mL distilled water was slowly added into the emulsion system to start the interfacial polycondensation reaction between TDI and diamine at the oil-water interfacial. After addition, the reaction mixture was heated to 60℃ for 2 h. The obtained microcapsule slurry was decanted and washed with distilled water to remove remaining diamine and dried in a vacuum at 30℃ for 48 h.

Analysis of the Microcapsules

The structure of the shell polymer was determined by a computerized Nicolet Impact 400D spectrophotometer. The thermal properties of the microcapsules containing phase change material were evaluated by differential scanning calorimetry (DSC) (Setaram DSC141) and thermogravimetry (TG) (Setaram setsys 16/18). Mean particle size and distribution of microcapsules were determined with laser particle analyzer (LS100Q Beckman Coulter Corp. USA).

Results and Discussion

Figure 1 shows FT-IR spectra of the microcapsules prepared with EDA. The absorption bands at 1660 cm^{-1} indicated the C=O stretching of urea formation. The N-H stretching was observed at 3300-3250 cm^{-1}. The IR spectrum 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 2900 cm^{-1}.

Figure 1 FTIR spectra of polyurea microcapsules from EDA.

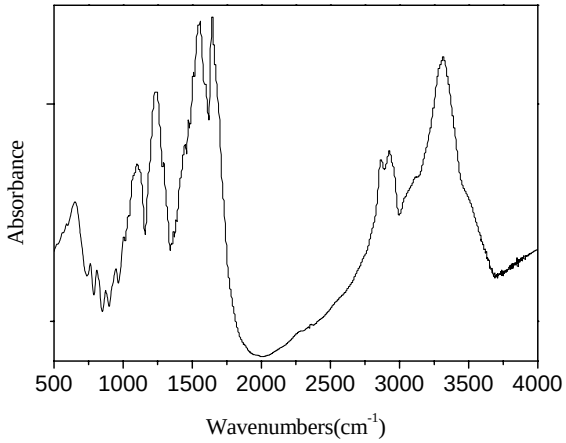
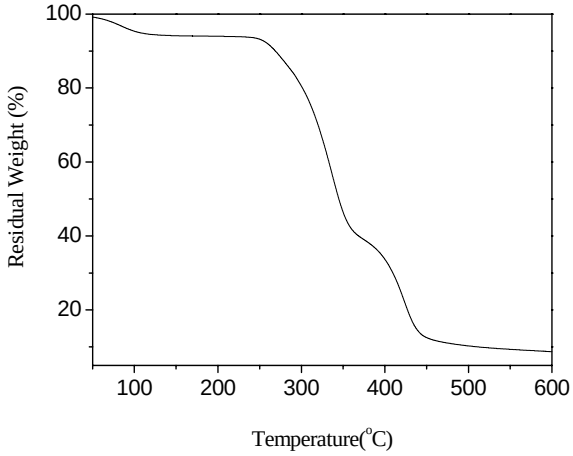


Figure 2 shows TG thermogram of the polyurea microcapsules from EDA. The sample shows an initial weight loss of about 50% from 282℃ to about 350℃, and a subsequent weight loss of up to 90% until 450℃. This indicates that microcapsules with core material can be suffered high temperature up to 282℃. It is very suitable for fiber spinning along with microcapsules containing PCM and heat transfer media.

Figure 2 TG thermograms of polyurea microcapsules from EDA without hexadecane.



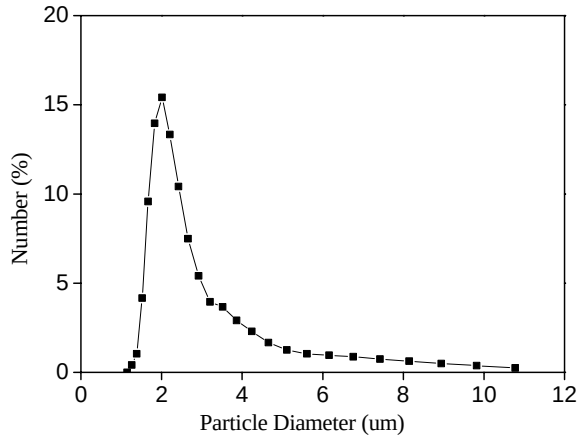
The thermal properties of the microcapsules containing hexadecane were evaluated using DSC, the instrument was calibrated by indium to ensure its accuracy. Hexadecane is a desired phase change material for its availability in a reasonable transition temperature range and high latent heat. The melting point (T_m) and the latent heat of fusion ($\triangle H_{fus}$) of hexadecane encapsulated in microcapsules measured by DSC were listed in **Table 1**. The melting point and fusion heat of pure hexadecane is 16.7℃ and 236 Jg^{-1}, respectively.

Table 1 Thermal characterization of microcapsules containing hexadecane.

TDI (g)	EDA (g)	Cyclohexane (ml)	Hexadecane (ml)	T_{onset} (℃)	T_{peak} (℃)	$\triangle H_{fus}$ (Jg^{-1})
1.53	1.21	5	5	15.52	18.57	66.09

Figure 3 shows the particle size distribution of polyurea microcapsules from EDA. It shows the microcapsules have comparatively narrow distribution in diameter range from 1.26 μm to 10 μm. The sample has an average diameter of 2.5 μm and the particles of diameter between 2 and 4 μm dominate their volume fraction.

Figure 3 Particle size distribution of polyurea microcapsules containing hexadecane.



References

1. A. Abhat, *Solar Energy*, **1983,** *30* (4), 313.
2. Y. G. Bryant, D. P. Colvin, **1988,** *US Patent* 4,756,958.
3. M. N. A. Hawlader, M. S. Uddin, M. M. Khin, *Applied energy*, **2003,** *74*, 195.
4. J.S. Cho, A. Kwon, C.G. Cho, *Colloid Polym. Sci.*, **2002,** *280*, 260.

Received 19 May, 2003