Microencapsulation of *n*-Hexadecane as a Phase Change Material in Polyurea *

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Abstract　　For thermal energy storage application, polyurea microcapsules about 2. 5 μm in diameter containing phase change material were prepared using interfacial polycondensation method. In the system droplets in microns are first formed by emulsifying an organic phase consisting of a core material (*n*-hexadecane) and an oil-soluble reactive monomer, toluene-2, 4-diisocyanate (TDI), in an aqueous phase. By adding water-soluble reactive monomer, diamine, monomers TDI and diamine react with each other at the interface of micelles to become a shell. Ethylenediamine (EDA), 1, 6-hexane diamine (HDA) and their mixture were employed as water-soluble reactive monomers. The effects of diamine type on chemical structure and thermal properties of the microcapsules were investigated by FT-IR and thermal analysis respectively. The infrared spectra indicate that polyurea microcapsules have been successfully synthesized; all the TG thermographs show microcapsules containing *n*-hexadecane can sustain high temperature about 300 ℃ without broken and the DSC measurements display that all samples possess a moderate heat of phase transition; thermal cyclic tests show that the encapsulated paraffin kept its energy storage capacity even after 50 cycles of operation. The results obtained from experiments show that the encapsulated *n*-hexadecane possesses a good potential as a thermal energy storage material.

Keywords:　　Phase change material,　　Microcapsule,　　Interfacial polycondensation,　　*n*-hexadecane,
　　　　　　　　Thermal energy storage,　　Thermal analysis

Latent heat storage in phase change materials (PCMs) is preferable to storage of sensible heat in many applications where the temperature swing is small, because of the comparably high storage density and low cost [1]. A large number of PCMs have been investigated, including salt hydrate, paraffin wax and non-paraffin organic compounds, which melt and solidify at a wide range of temperatures, making them attractive in a number of applications. Paraffin waxes are cheap and have moderate thermal storage density, but low thermal conductivity and hence requiring large surface area to release and absorb heat. Heat storage by latent heat has been investigated as a promising technology for more than 50 years. Nevertheless, mainly due to problems with long term stability of the storage materials and containers, widespread use of latent heat storage has not been realized till today. A conventional PCM storage system with heat exchangers also presents some problems, particularly during the withdraw of energy from the storage system. The PCM freezes on the heat ex-

changer surface resulting in a poor heat-transfer rate due to the low thermal conductivity of paraffin wax. In order to overcome these difficulties, a new technique of utilizing microencapsulated PCM in energy storage has been developed recently. Microencapsulation of PCMs has been studied 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 (1) reduction of the reactivity of the paraffin with the outside environment, (2) it increases the heat transfer area, and (3) permits the core material, due to coating, to withstand frequent changes in volume of the storage material, as the phase change occurs [3]. Microencapsulation is a technique by which liquid droplets, solid particles or gas bubbles are coated with a continuous film of synthetic or natural polymers. Many methods have been developed for microencapsulation. Among them, the interfacial polycondensation technique is one of the most feasible methods [4]. During the encapsulation

with interfacial polymerization, monomers in their respective phases diffuse onto the oil-water interface where they react with each other to form a polymer surrounding the droplets. In this work, microencapsulation of *n*-hexadecane was carried out by interfacial polycondensation from different aliphatic diamine to investigate the effects of diamines in polyurea on various properties and to clarify the functions of the reactivity of diamines and the thermal properties of the core material.

1　Experimental

1. 1　Materials and equipment

Toluene-2, 4-diisocyanate（TDI）, ethylenediamine（EDA）and 1, 6-hexane diamine（HDA）of reagent grade used as shell-forming monomers were obtained from Shanghai Chemical Reagent Co. Hexadecane（Koch Light, 99%）was employed as core material. Nonionic surfactant, OP［（polyoxyethyleneoctylphenyl ether, with an average number of polyoxyethylene units of 10）from Shanghai Chemical Reagent Co.］was used as an emulsifier. Cyclohexane as solvent was reagent grade without further purification. Digital display electric agitator（DW-3-90W）and vacuum oven（DZF-6020）were purchased from Yuhua Instrument Co.（Gongyi city, Henan province）.

1. 2　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 40 mL distilled water, an organic solution of hexadecane（5 mL）, cyclohexane（5 mL）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 rpm to form an oil-in-water emulsion[5]. After stirring for 3 min, the different diamine compositions consist of EDA alone, HDA alone, and EDA and HDA in a molar ratio of 1: 1 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 interface, and the oil droplets were encapsulated to form the microcapsules. 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 oven at 30 ℃ for 48 h. During the drying process, cyclohexane, which is just a solvent media to dissolve TDI and hexadecane was evaporated completely.

1. 3　Analysis of the microcapsules

In order to determine the structure of the shell polymer, the Fourier transform（FT）IR spectra were obtained on the microcapsules with a computerized Nicolet Impact 400D spectrophotometer（ThermoNicolet USA）. The thermal properties of the microcapsules containing phase change material were measured by differential scanning calorimetry（DSC）（DSC141 Setaram, France）and thermogravimetry（TG）（setsys 16／18 Setaram, France）. The samples were heated at a rate of 10 ℃ ·min^{-1} up to 500 ℃ under high purity N_2 with a flow rate of 30 mL · min^{-1}. Mean particle size and distribution of microcapsules were determined with a laser particle analyzer（LS100Q Beckman Coulter Corp., USA）.

2　Results and Discussion

FT-IR spectra of the microcapsules prepared with different diamine were presented in Fig. 1. As seen in the figure, all the spectra show absorption bands at 1 660 cm^{-1} for the C = O stretching of urea formation. The N – H stretching was observed at 3 300 ~ 3 250 cm^{-1}. The IR spectra also show the completion of the reaction between diisocyanates and diamines by the disappearance of NCO absorption bands at 2 276 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 2 900 cm^{-1}. It was confirmed that the C – H
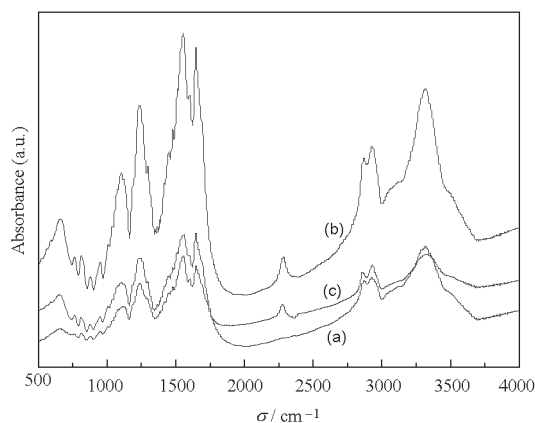
Fig. 1　FT-IR spectra of polyurea microcapsules
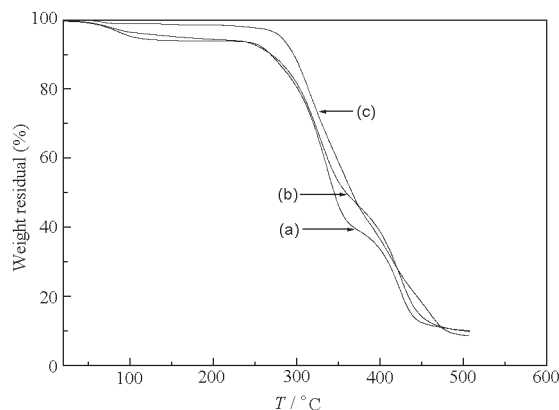（a）EDA,（b）1: 1 EDA／HDA,（c）HDA

Fig. 2　TG thermograms of polyurea microcapsules without containing *n*-hexadecane
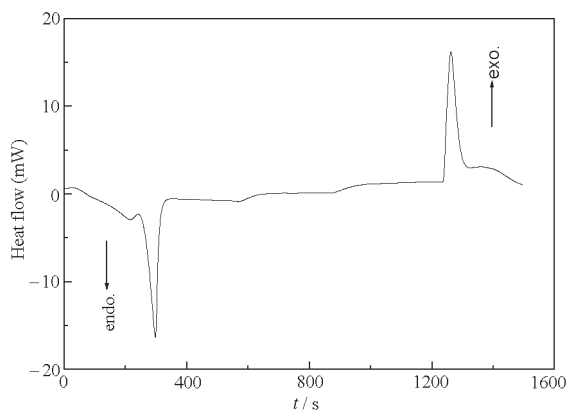a）EDA,（b）1: 1 EDA／HDA,（c）HDA

Table 1   Microencapsulated paraffin energy storage capacity(J · g⁻¹) at different thermal cycles

Thermal cycles	$\Delta H_{\mathrm{fus(EDA)}}$	$\Delta H_{\mathrm{fus(HDA)}}$	$\Delta H_{\mathrm{fus(EDA/HDA)}}$
5	65. 23	47. 85	52. 06
20	64. 69	47. 12	51. 73
50	64. 17	46. 79	51. 46

Table 2   Thermal characterization of microcapsules containing *n*-hexadecane

TDI (g)	EDA (g)	HDA (g)	Cyclohexane (mL)	Hexadecane (mL)	T_{onset} ℃	ΔH_{fus} J · g⁻¹	Efficiency (%)
1. 53	1. 21	0	5	5	15. 52	66. 09	50. 1
1. 52	0	1. 29	5	5	17. 55	48. 06	36. 4
1. 50	0. 60	0. 85	5	5	17. 41	52. 33	38. 9

peak of the HDA-based microcapsules was stronger than that of the EDA-based microcapsules, due to the former′s longer methylene chain, whereas the C = O peak of the latter was stronger than that of the former, due to the latter′s rapid reaction rate, resulting in a strong and multiple urea linkage.

　　TG thermograms of the polyurea microcapsules from different diamine were presented in Fig. 2. All the samples show an initial weight loss of about 50% from 282 to 350 ℃, and a subsequent weight loss of up to 90% until 450 ℃. Weight loss of the microcapsules by addition of EDA alone and 1: 1 EDA／HDA showed another stage during thermal decomposition, whereas weight loss of the microcapsules by addition of HDA alone decreased steeply. It is attributed to different shell thickness, which result from the different reactivity among them. This indicates that microcapsules with core material can withstand high temperature up to 282 ℃. So it can be handled conveniently during fiber spinning along with microcapsules containing PCM and used as heat transfer media.
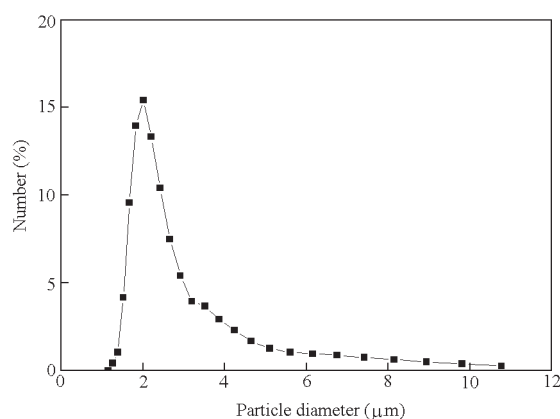
　　The thermal properties of the microcapsules containing phase change materials were evaluated using DSC, the instrument was firstly calibrated by indium and tin to ensure its accuracy. *n*-hexadecane is a desired phase change material due to its availability in a reasonable transition temperature range and its high latent heat. The encapsulated paraffin was subjected to repeated cycle of melting and solidification during the course of this experiment. Each sample was tested through 5, 20, 50 cycles

of alternative heating and cooling in the temperature range of 0 ~ 30 ℃. The microcapsules were sealed in a glass tube, then repeated heating in water bath and cooling in air. After many cycles, no liquid paraffin was observed during heating, this indicates that the shell can withstand frequent changes in volume. The energy storage or release capacity of encapsulated paraffin was measured by DSC after different thermal cycles, and the results are shown in Table 1. From Table 1, it was shown that the energy storage capacity of encapsulated paraffin was kept almost at the same value after many thermal cycles. A typical DSC diagram of energy storage and release capacities of the microcapsules produced by EDA was shown in Fig. 3. The efficiency of *n*-hexadecane encapsulation was about 45% in the experiments. All the results were summarized in Table 2. The melting point and heat of fusion of pure *n*-hexadecane measured by our instrument are 16. 7 ℃ and 236 J·g⁻¹, respectively. Encapsulated *n*-hexadecane showed a phase change over the same temperature range as that of the bulk, however, the melting point of samples exhibit slightly difference with pure *n*-hexadecane′s, the possible reason was put forward by Brown *et al.* [6]. If the microcapsule is rigid, it is reported that heat transfer occurs at constant volume and no change in phase change temperature occurs, the effective specific heat of encapsulated materials undergoing a phase change is related to the physical properties of the microcapsule enclosing them.

　　Fig. 4 shows the particle size distribution of polyurea micro-

Fig. 3   The output curve of the DSC for heating and cooling the microcapsules containing *n*-hexadecane prepared from EDA

Fig. 4   Particle size distribution of polyurea microcapsules from EDA containing *n*-hexadecane

capsules from EDA. The size of all the resulted particles was below 10 μm by stirring at a rate of 300 rpm, and their size distribution was narrow. The sample has an average diameter of 2.5 μm and the particles with a diameter between 2 and 4 μm dominate their volume fraction.

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正十六烷聚脲微胶囊化相变材料*

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摘要　用界面聚合法, 合成了直径大约 2.5 μm 可用于热能储存含相变材料的聚脲包覆微胶囊. 在含乳化剂的水溶液中, 将溶有芯材正十六烷的有机相乳化成微米级油性液滴, 随后加入的水溶性单体二胺与甲苯 2,4- 二异氰酸酯在胶束界面相互反应形成囊壁. 分别用乙烯二胺, 1,6- 己二胺和它们的混合物作为水溶性单体进行了研究. 并用红外光谱和热分析分别考察了不同胺类对微胶囊化学结构和热性质的影响. 红外谱图显示合成了聚脲微胶囊, 热重曲线表明含正十六烷的聚脲微胶囊能够耐受大约 300 ℃高温, 差示扫描量热测试表明所有样品均具有合适的相转变热, 冷热循环实验揭示微胶囊能够维持储热容量不衰减. 研究表明微胶囊化的正十六烷作为相变储热材料具有良好的应用前景.

关键词:　相变材料,　微胶囊,　界面缩聚,　正十六烷,　热能储存,　热分析
中图分类号:　O642.3