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Synthesis and properties of microencapsulated phase change materials for thermal energy storage materials

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This work presents and discusses the microencapsulation of pentadecane in polystyrene shell as thermal energy storage materials. The emulsion polymerisation method was used for the microencapsulation process. Styrene (S) was used as monomer to obtain polystyrene (PS) and ethylene glycol dimethacrylate was used as crosslinking agents. The influence of the core:shell mass ratio on the encapsulation process and the physical properties of the resulting microcapsules have been studied. The surface morphologies of the microencapsulated phase change materials (microPCMs) were studied by scanning electron microscopy (SEM) and the thermal properties of the MicroPCMs were investigated by differential scanning calorimetry (DSC). SEM photographs showed that these microPCMs have relatively spherical profiles with diameter ranging from 10 to 80 μm. It was determined that, the phase change enthalpies of melting and freezing were about 83.2 J/g and 81.8 J/g, respectively. The results show that pentadecane was microencapsulated successfully and its properties very suitable for thermal energy storage applications

Keywords*:* phase change material, thermal energy storage, latent heat, polystyrene

INTRODUCTION

Heating and cooling are the main energy-consuming sectors in many countries [1]. Therefore it can be said that developing new energy storage devices are as important as developing new sources of energy [2]. Phase change materials (PCMs) which can be used as thermal energy storage material provides a high heat storage density and has the capability of storing a large amount of heat during the phase change process with a small variation of PCM volume and temperature [3]. Microencapsulated phase change materials have a wide range in thermal energy storage applications [4]. PCMs such as paraffin and fatty acids are microencapsulated with the purpose of make PCMs easier and safer to handle, increase the heat transfer area and protect material from environment [5].

Many studies use paraffin wax hydrocarbon mixtures as thermal energy storage materials [6]. Most of the researchers working on the microencapsulation of PCM have based their work on alkanes, waxes or paraffins [7]. Pentadecane which was used as core material in this study is known as saturated aliphatic hydrocarbon with the chemical formula C15H32. It has a suitable melting temperature (8.720C) and large latent heat storage capacity (176.15 J/g) especially for cooling applications.

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Recently, styrene and styrene copolymers have been utilized in a wide range of experiments as shell materials for PCM microcapsules [8-13].

This work mainly focuses on microencapsulation of pentadecane in polystyrene shell as thermal energy storage materials. The properties of microPCMs have been characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectral analysis.

EXPERIMENTAL

Pentadecane purchased from Sigma was used as a PCM. Styrene (>99%; Sigma Aldrich Company, USA) was used as a shell material; ethylene glycol dimethacrylate was used as a crosslinking agent and it was distilled before use. The initiator of ammonium peroxodisulfate (Merck, Germany) and other analytical reagents (tert-butylhydroperoxide (70%; Merck, Germany), Triton X-100 (Merck, Germany), iron (II) sulfate 7-hydrate ($FeSO_47H_2O$) (Panreac, Spain), and sodium thiosulfate ($Na_2O_3S_2$) (Merck, Germany)) were used without further purification. All experiments were conducted with distilled water.

A typical emulsion polymerization process was used in this study [8]. The chemicals and amounts that were used during the microenoencapsulation process are summarized in Table 1.

First solution (I) was prepared and then stirred for 30 minutes at 40˚C. Then second solution (II) was added slowly to solution I and stirring was

continued at 1000 rpm. Then, third solution (III) was added to the emulsion and heated to 95˚C. The solution was stirred for 3-4 hours and then was cooled to room temperature and washed with water five times. Finally, it was separated by filtration and dried at a room temperature for 72 hours. In this study two different core material:shell ratios 1: 1, 1.5:1, respectively, were chosen to prepare the microPCM1, and microPCM2.

Table 1. Emulsion copolymerization recipe

	İngredients	Amount
I	Water	30 ml
	Pentadecane	10 g
	Triton X100	0,4 g
II	Styrene	10 g
	EGDMA	4 g
	$FeSO_4.7H_2O$ solution	0,5 ml
	Amonyum persulfat	0.25 g
III	$Na_2O_3S_2$	0.06 g
	tert-butylhydroperoxide	0,25 ml

The morphology of microPCMs was analyzed by SEM (JEOL JSM-600). The thermal properties of pentadecane and microPCMs were measured using a DSC and the (Perkin Elmer Diamond) with a heating/cooling rate of 5˚C/min in the range of -15–30˚C. During DSC analysis, about 5 mg of sample was used. DSC analyses were repeated three times for each sample. The thermal properties data were calculated from the average of three measurements. The determination of the phase change material content in the microPCMs followed from the formula:

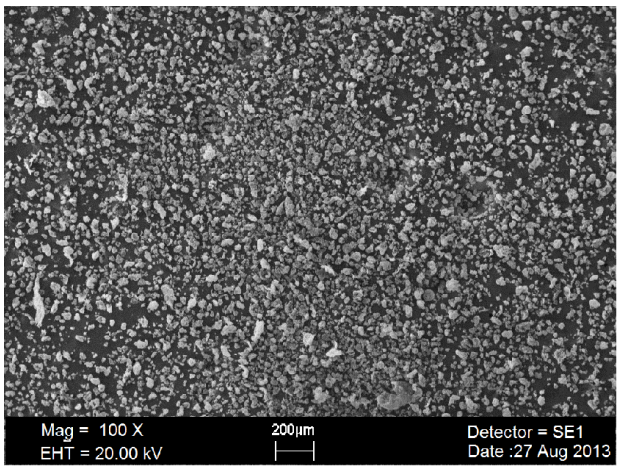
$$PCM\% = \frac{\Delta \text{HmicroPCMs}}{\Delta \text{HPCMs}} \times 100\% \qquad (1)$$

where ΔHmicroPCMs is the melting enthalpy of the micro-PCMs; ΔHPCMs is the melting enthalpy of the PCMs.

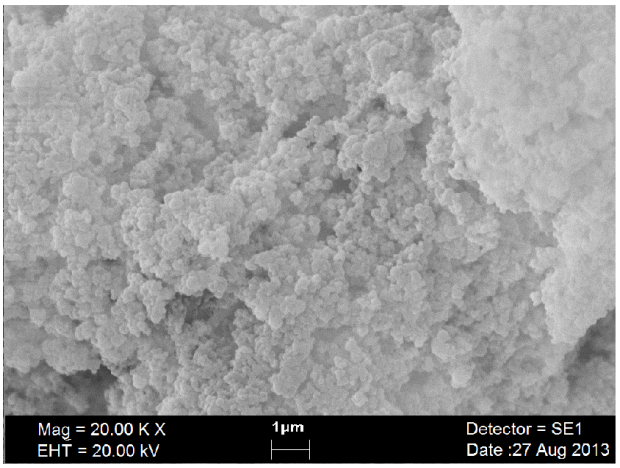
FTIR spectra of pentadecane and microPCMs were obtained in the spectral wavelength range of 400–4000 cm^{-1}, using a Perkin Elmer FTIR spectrometer with Attenuated Total Reflectance (ATR) at room temperature.

RESULTS AND DISCUSSION

In the microencapsulation of pentadecane emulsion polymerization method were used. The geometrical profile of the microcapsules was analyzed by SEM. As can be seen clearly, the microcapsules seen in Fig.1 were spherical without broken particles; the particle size distribution was approximately uniform with diameter ranging from 10 to 80 µm. SEM results confirm that pentadecane encapsulated successfully in this study.



(a)



(b)

Fig.1. SEM micrographs of MicroPCM

DSC curves of pentadecane and microPCMs were shown in Fig.2 to Fig.4 and the results are summarized in Table 2. From the DSC, temperatures of melting and freezing were determined as 8.7 and 8.0°C for pentadecane; 8.1 and 8.0 °C for microPCM1 and 8.2 and 8.3 °C for microPCM2. The latent heats of melting and freezing were found to be 176.1 and −187,2 J/g for pentadecane; 68.7 and −66.5 J/g for microPCM1 and 83.2 and −81.8 J/g for microPCM2, respectively. The microencapsulation ratio of pentadecane was calculated as 39 wt % and 47 % respectively for microPCM1 and microPCM2 by using Equation 1.

As expected, increasing the amount of core material led to an increase in the encapsulation ability and latent heat storage capacity.

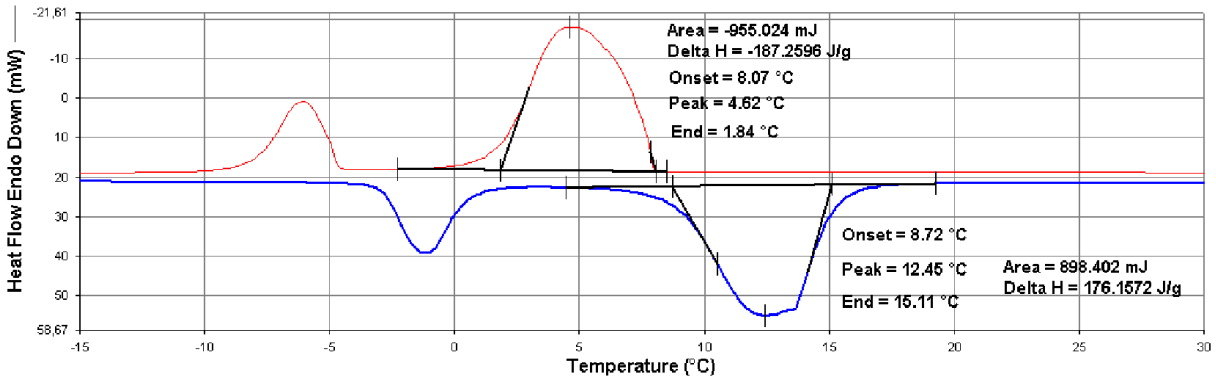


Fig.2. DSC Curves of Pentadecane

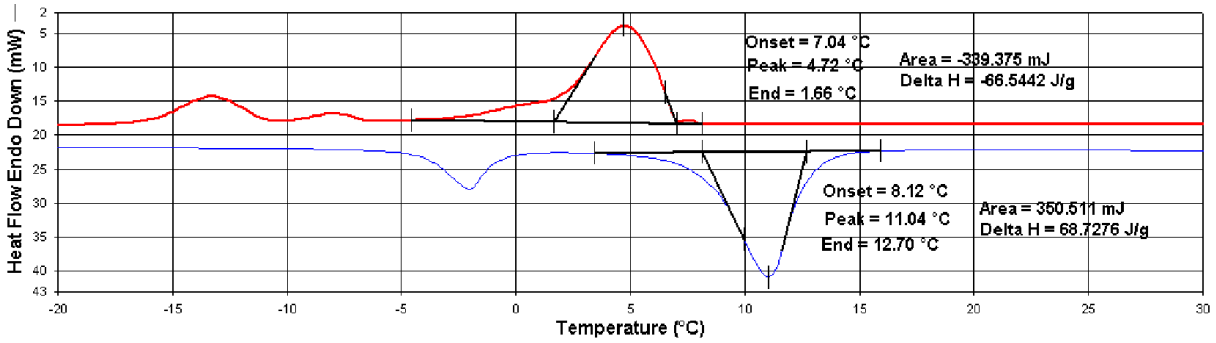


Fig.3. DSC Curves of MicroPCM1

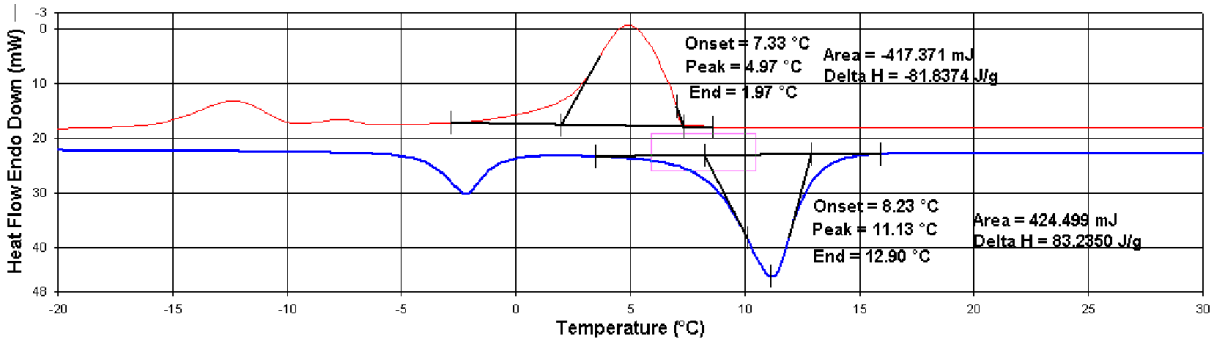


Fig.4. DSC Curves of MicroPCM2

Table 2. Thermal properties of pentadecane and MicroPCM

Sample	Core:Shell	Tom(°C)	Tpm(°C)	Tem(°C)	Hm ($J.g^{-1}$)	Toc(°C)	Tpc(°C)	Tec(°C)	Hc ($J.g^{-1}$)	pentadecane content (wt%)
Pentadecane	-	8.72	12.45	15.11	176.15	88.07	4.62	1.84	187.25	100
microPCM1	1:1	8.12	11.04	12.70	68.72	78.04	4.72	1.66	-66.54	39.01
microPCM2	1.5:1	8.23	11.13	12.90	83.23	78.33	4.97	1.97	-81.83	47.25

T_{om}: Onset melting temperature of DSC curve.
T_{oc}: Onset crystallizing temperature of DSC curve.
T_{pc}: Crystallizing peak temperature of DSC curve.
T_{pm}: Melting peak temperature of DSC curve.
T_{ec}: Endset crystallizing temperature of DSC curve.
T_{em}: Endset melting temperature of DSC curve.
H_c: Crystallization enthalpy of PCMs in DSC curve
H_m: Melting enthalpy of PCMs in DSC curve.

The chemical structure was investigated using Fourier transformed infrared spectrophotometer.

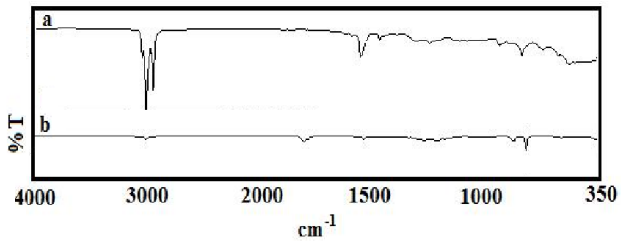


Fig.5. FTIR of (a) pentadecane and (b) microencapsulated pentadecane

The FTIR spectra of pentadecane and microencapsulated pentadecane are presented in Fig.5. Pentadecane which were used in this study are characterized with absorptions due to C–H stretching and bending. It is obvious that there is a double peak at a wave number of 3000–2850 cm^{-1} caused by the C–H stretching vibration. Additionally, the C–H scissoring (1470–1450 cm−1), methyl rock (1370–1350 cm−1), and long-chain methyl rock (725–720 cm−1) are noted in this spectrum like as reported before [8]. It can be concluded that although the peaks corresponding to C-H stretching vibration and C–H scissoring are overlapped with PS shell material, some of the characteristic peaks belonging to the core material slightly preserve itself after microencapsulation.

CONCLUSIONS

Alkanes, which were used as core materials in this study, are appropriate for many thermal energy storage applications due to their suitable melting temperatures (8.72^0C) and large latent heat storage capacity (176.15 J/g) and the fact that they do not have toxic properties. In this research, pentadecane was microencapsuled with a polystyrene shell via an emulsion polymerization technique. DSC results confirm that microencapsulated pentadecane could be considered to have good potential for energy storage. The DSC results revealed that the melting temperature and latent heat of microPCM1 and microPCM2 were 8.1 ^{0}C ; 68.7 J/g and 8.2^0C ; 83.2 J/g respectively. The microencapsulation ratio of pentadecane was calculated as 39 wt % and 47 % respectively for microPCM1 and microPCM2. As expected, increasing the amount of core material led to an increase in the encapsulation ability and latent heat storage capacity. SEM micrographs showed that the microencapsulated pentadecane had approximately spherical profiles. Based on all results; we recommend the prepared pentadecane/polystyrene microcapsules for thermal energy storage applications as novel microPCM with latent heat storage capacities and properties.

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