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MICROENCAPSULATION OF D-MANNITOL BY A SOL-GEL PROCESS

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ABSTRACT

D-mannitol (DM) is a phase change material (PCM) for medium temperature thermal energy storage. In this paper the preparation of microencapsulated d-mannitol by a sol-gel process is reported. The microencapsulation of d-mannitol was confirmed by characterization using a scanning electronic microscope (SEM) and Fourier transform infrared spectroscopy (FT-IR) analysis. The thermal properties of the microencapsules were measured by a differential scanning calorimeter (DSC) instrument. The thermal stability of the synthesized DM microencapsules was investigated by means of thermogravimetric analyzer (TGA). The results show that the microencapsulated d-mannitol have a high phase change latent heat of 220.3 J/g and improved thermal stability.

Keywords: phase change material, microencapsulation, mannitol, sol-gel, silica

NONMENCLATURE

Abbreviations	
AR	analytical regent
DM	d-mannitol
DSC	differential scanning calorimeter
FT-IR	Fourier transform infrared spectroscopy
MEDM	microencapsulated d-mannitol
PCM	phase change material
SEM	scanning electronic microscope
TEOS	ethyl orthosilicate
TGA	thermogravimetric analyzer
Symbols	
R	encapsulation ratio

1. INTRODUCTION

Phase change materials can absorb/release a large amount of latent heat during phase change process. The latent heat for the same mass/volume of PCM is much higher than that of sensible heat. Therefore, PCMs are usually used in thermal energy storage [1, 2].

Encapsulation is an effective way to isolated PCM from the environment to prevent leakage and corrosion and also to enhance the thermophysical properties of PCMs [3]. There are many technologies for encapsulation of solid–liquid phase change materials, including in-situ polymerization, complex coacervation, solvent extraction/evaporation method and sol–gel method [4]. The sol–gel method is mainly used for PCM encapsulation by inorganic materials which usually have higher thermal conductivity compared to organic materials [5].

Many researchers have focus on encapsulation of organic PCMs such as the widely studied paraffin and fatty acids [6-8] , whereas there are only a few study on encapsulation of such PCMs having higher phase change temperatures which is also important in applications such as utilization of solar energy [9]. Nomura encapsulated metal based PCM and proved the possibility of using microencapsulated PCM for high temperature thermal energy storage [10]. D-mannitol is a medium temperature PCM that has high latent heat of fusion and thus has a good potential in thermal energy storage applications [11]. It was demonstrated that DM encapsulation improved its thermal properties but the reaction conditions should be strictly controlled [12]. Therefore, in this paper a novel method for the encapsulation of DM was proposed and demonstrated.

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2. MATERIALS AND METHODS

2.1 Materials

The d-mannitol was used as core material. Its analytical regent (AR) was obtained from the Aladdin company. Ethyl orthosilicate (reagent grade from the Aladdin company) was used as the precursor. Cyclohexane (AR) was purchased from Tianjin Damao chemical reagent company, China. Span 80 was purchased from Guangzhou chemical reagent company, China. All chemicals were of reagent quality and used without further purification. Deionized water was used in the experiments.

2.2 Synthesis of microcapsules

The microencapsulated D-mannitol with silica shell were synthesized through a sol–gel progress. The whole reaction process was in a three-necked flask with continuously mechanical stirring. A typical synthetic procedure is described as follows: 5g D-mannitol was dispersed into 15 ml deionized water. The oil phase was 50ml cyclohexane containing 0.6g Span80 as surfactant. The prepared water phase was added to the oil phase and stirred in a three-mouth flask for half an hour, and continuously stirred at a rate of 800rpm. Then, the TEOS was added to the whole emulsion with stirring the system for 12h. The capsules prepared was washed by cyclohexane and dried for 24h.

2.3 Characterization of the microencapsules

The morphology and microstructure of the microencapsulated d-mannitol composites were observed using a scanning electronic microscope (SEM, SU8010, Hitachi Inc., Japan). The FT-IR spectra of the microencapsules were recorded on a Nicolet 6700 spectrometer from 400 to 4000cm^{-1} and compared with those of the DM and SiO_2. The thermal properties were measured with a DSC instrument (DSC3 STAR, METTLER TOLEDO, Switzerland) in nitrogen atmosphere from 40℃ to 200℃ at a heating rate of 10℃/min. The thermal stability of the microencapsulated d-mannitol composites with SiO_2 shell was determined by a thermogravimetric analyzer (Pyris1 TGA, Perkin-Elmer) from 50℃ to 500℃ with a linear heating rate of 10℃/min in nitrogen atmosphere.

3. RESULTS AND DISCUSSION

3.1 Morphology of the microencapsules

The morphologies of the microencapsules are shown in Fig 1. It was observed that the DM microencapsules are spheres. The MEDM had unsmooth surfaces. The reason is that the rapid diffusion of the surfactant accelerated the hydrolysis and condensation of TEOS onto the surfaces of the PCM droplets [13]. It is also shown in Fig 1 that the particle sizes of the microencapsules are evenly distributed and mainly in the range of 150-250nm.

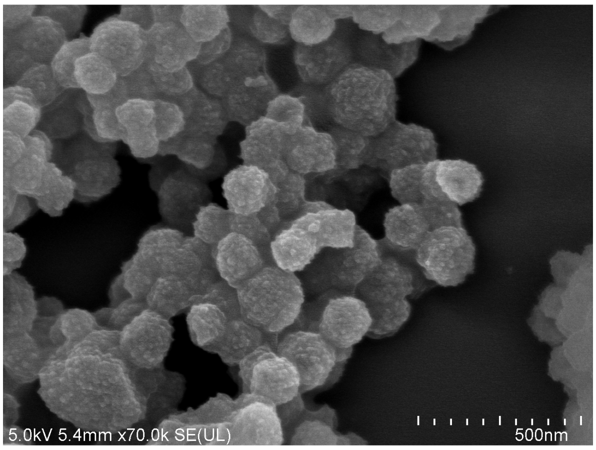

Fig 1 SEM image of the microencapsules

3.2 FT-IR analysis of the microencapsules

The FT-IR spectra of the DM, SiO_2 and MEDM are presented in Fig 2. The spectrum of the SiO_2 is shown in Fig 2a. The peaks at 1104, 800 and 474cm^{-1} signify the bending vibration of the Si–O functional group; the peak at 960cm^{-1} is assigned to the Si–OH functional group; and the vibrational spectra of 3000-3700 cm^{-1} and 1600-1700 cm^{-1} denote the stretching frequency of O-H. As shown in Fig 2b, in the fingerprint region (1500–500 cm^{-1}) peaks were observed at 1400 cm^{-1} and 881 cm^{-1} which denote the bending vibration of CH3, stretching vibration of C-O of alcohols and phenols functional class, while O-H bending, C-H bending and C-H vibrations were assigned to peaks at 1080 cm^{-1}, 881 cm^{-1}, and 720 cm^{-1}. As shown in Fig 2c, the FT-IR spectra of the MEDM is similar to that of DM except that the peak of 1080 is much wider, which is due to the combination of the 1104 peak of SiO_2, suggesting the successful encapsulation of DM with silica shell.

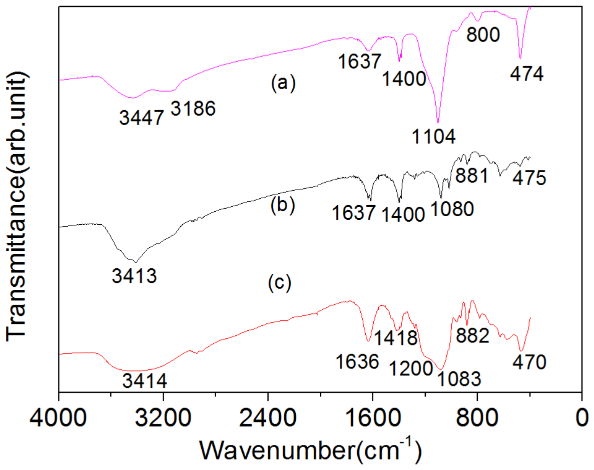

Fig 2 The FT-IR spectra of (a) SiO2, (b) DM, (c) MEDM

3.3 Thermal properties of the microencapsules

Fig 3 shows the DSC curves for the melting process of the DM and the MEDM. The melting temperatures are measured to be 170.0℃ and 170.5℃ for the DM and the MEDM, respectively. The melting temperature of the MEDM was very close to that of the DM. By comparing the encapsulates to the original DM substance, we can see that the slight change in the melting point might be because the DM was coated by the silica shells, so the melting point of MEDM was a little higher than that of the pure DM crystals. The melting peak between 40℃ and 100℃ might be the phase change latent heat of water because some water had been encapsulated into the MEDMs during the process.

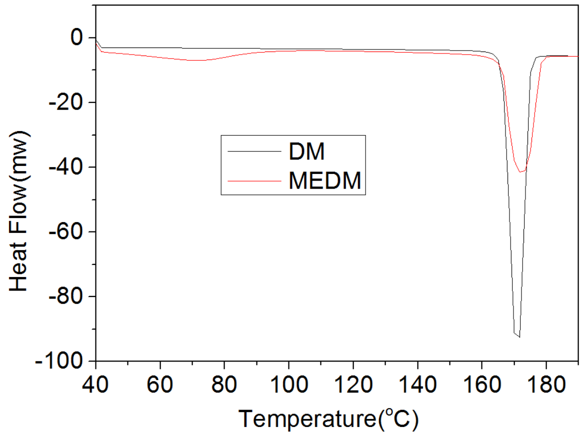

Fig 3 The DSC melting curves of the DM and microencapsulated DM

The phase change latent heat of the DM and MEDM were calculated from the DSC curves in Fig 3 and the results are given in Table 1. The latent heat value of the MEDM was lower than that of the DM because only DM absorbs thermal energy during the heating process. Higher content of the DM in the microcapsules results in a higher latent heat storage capacity. Therefore, encapsulation ratio can be used to characterize the performance of microencapsulated PCM which can be calculated from the DSC data by the following equation:

$$R = (\Delta H_{M,MEDM}/\Delta H_{M,DM})*100\% \qquad (1)$$

where R is the encapsulation ratio of the MEDM, $\Delta H_{M,MEDM}$ and $\Delta H_{M,DM}$ represents the melting latent heat of the MEDMs and DM, respectively. As shown in Table 1, the encapsulation ratio value of 71% was obtained as calculated by Eq. (1). Though it is lower than that in the literature [12], the latent heat of the present MEDM is higher maybe due to different DM used in the experiment. Moreover, the conditions of the present study are easier to be fulfilled which make the proposed method competitive.

Table 1 DSC data of the DM and MEDM

Sample	Melting point (℃)	Latent heat （kJ/kg)	Encapsulation ratio (%)
DM	170.0	303.6	-
MEDM	170.5	220.3	71%

3.4 Thermal stability of the microencapsules

The TGA curves of the DM and the MEDM are presented in Fig 4. Their thermal decompositions were performed in the programmed temperature range of 40-500℃. Fig 4 shows that the weight loss of the DM starts at 270°C and ends at 370°C. The TGA curve of the DM is sharp and only one step was observed due to the thermal degradation of DM molecules. The mass loss was attributed to complete decomposition and evaporation of DM. As for the MEDM, there are two-step thermal decomposition processes. The first step of decomposition occurs between 270 ℃ and 350℃, which corresponds to the thermal decomposition of the DM. The second step of weight loss takes place after 350 °C, which this is mainly due to decomposition of some of the silica shells and the DM therein. It should be noted that the mass percentage of the MEDM is still higher than 40% even at temperature up to 480℃, which means that there should be some DM in the remained sample at 480℃ since the encapsulation ratio was 71% resulting in a silica fraction of 29%. The MEDMs are composites of DM and silica, so the mass fraction of the MEDMs are higher than that of DM at the same temperature above 350℃. From the results one can see that the SiO_2 shells can retard the decomposition of DM, indicating that the thermal stability of the DM can be improved through microencapsulation by SiO_2 shell.

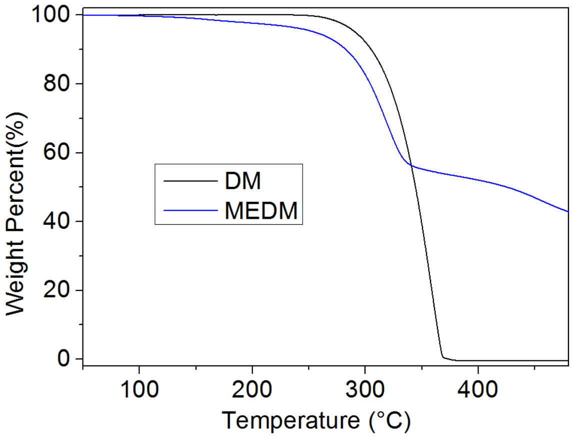

Fig 4 The TGA curves of the DM and microencapsulated DM

4. CONCLUSIONS

A method for the preparation of microencapsulated DM was proposed. The microencapsulation was confirmed by SEM and FTIR observation. The results show that the phase change temperature, latent heat of phase change and encapsulation ratio of the microencapsulates is 170.5℃, 220.3 J/g and 71%, respectively. The thermal stability of the MEDMs as observed by TGA was improved due to the protection of DM by the silica shell. The results demonstrate the effectiveness of the proposed method and the potential of the MEDMs in high temperature thermal energy applications.

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