Nanoencapsulation of n-Octadecane Phase Change Material with Polyaniline Shell for Thermal Energy Storage

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Abstract. Nanoencapsulated n-octadecane with polyaniline shell as composite thermal energy storage material was synthesized using emulsion polymerization method. In this composite material, the n-octadecane was employed as the core material that is the latent heat storage phase change material (PCM), and the polyaniline acted as the shell material which can avoided the leakage of the melted n-octadecane. The scanning electronic microscope (SEM) and transmission electron microscope (TEM) were used to determine microstructure of nanoencapsulated n-octadecane with polyaniline shell. The fourier transformation infrared spectroscope (FT-IR) and X-ray diffraction (XRD) were employed to determine chemical structure of these composites. The thermal properties were shown by the differential scanning calorimeter (DSC).

Introduction

The phase change material (PCM) application in latent thermal storage energy plays a crucial role in thermal energy storage technology, since the phase change material can absorb, store or release large amounts of latent heat over phase changes[1, 2, 3]. The most important advantage of PCM is high energy storage densities at almost constant temperature. Thus, tremendous efforts of PCM have been developed and numerous improvement have been achieved. Specially, the n-octadecane was the well-known PCMs due to applied to textiles with a suitable melting temperature. In addition, the n-octadecane are nontoxic, non-corrosive, chemically inert, easily obtained and have no unpleasant odor [4, 5]. Obviously, this phase change temperature of n-octadecane is comfortable for the human body and it possess the advantages of high latent heat (227 J/g). Then, the nanoencapsulation technique can successfully avoid the leakage of n-octadecane from their location when the phase change occurs.

Polyaniline (PANI) not only possess good environment stability, but also can be made in a variety of morphology [6]. Thus, it is worthwhile to employ PANI as supporting material to prepare composite PCMs. In this study, we proposed a facile method to fabricate the n-octadecane/PANI nanocapsules with different ratios of n-octadecane to polyaniline. The PANI was selected as shell material in order to fabricate environmentally friendly the nanoencapsulation process in an aqueous system.

Experimental

Materials

All reagents were of analytical grade and were obtained commercially. A aniline was distilled under reduced pressure prior to use. All other reagents were used as received without further purification. Deionized water was used throughout the experimental process.

Preparation of nanoencapsulated PCMs

A series of nanoencapsulated PCMs were prepared as follows. 0.12 g of styrene maleic anhydride (SMA) and 0.1 g NaOH were mixed with 50 mL water. The mixture was stirred for 0.5 h at 80 ℃ to form the transparent solution. The transparent solution were mixed and followed by adding Aniline and n-octadecane with desired amounts, 1.5/1 g, 1.25/1.25 g, 1/1.5 g, that are named as S1, S2, S3, respectively. After being pre-emulsified by a homogenizer at a rate of 10000 rpm for 10 min, miniemulsification was continued by ultrasonicating the mixture for 10 min at 70 % amplitude at 45 ℃. Then, ammonium persulfate (APS) was dissolved in 10 mL of water and dropped into the mixture to initiate the polymerization. The molar ratio of aniline and APS should be kept to be 1:1. The mixture was stirred for 12 h at 0-5 ℃ and the polymerization was completed.

Characterization

The surface morphology and microstructures of the nanoencapsulated PCMs were revealed using a scanning electron microscope (SEM, ZEISS SUPRA55) (FE-SEM) and a transmission electron microscope (TEM, JEOL JEM-100CX II) operating at 200 kV, respectively. IR spectra were recorded with a Nicolet 6700 Fourier spectrometer using KBr pellet (400– 4000 cm^{-1}). And, the wide angle X-ray diffraction (XRD) experiments were carried out on a X-ray powder diffraction (XRD, M21X) with Cu Kα radiation (40 kV, 150 mA, λ =1.5406 Å). The thermal energy storage properties of n-octadecane and the composite PCMs were characterized by differential scanning calorimetry (DSC, Mettler DSC822e) from -5 to 60 ^{o}C with the heating rate of 5 ^{o}C/min in nitrogen atmosphere.

Results and discussion

Morphology characterization of the n-octadecane/PANI nanocapsules

Fig. 1 presents SEM and TEM photographs of S1, S2 and S3. The n-octadecane was encapsulated in the shells of the PANI. The PANI shells provided the mechanical strength for the pure n-octadecane and prevented the leakage of the melted n-octadecane. As shown Fig. 1a-c, that morphologies of S1, S2 and S3 are spherical with nano-sized of 500-700 nm. It is seen from Fig. 1d-f that microstructures of S1, S2 and S3 are core-shell structure.
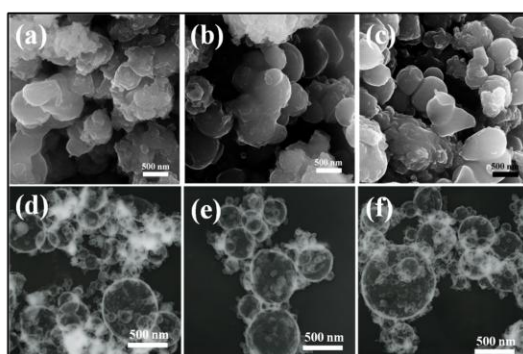
Fig.1. SEM and TEM photographs of S1 (a) and (d), S2 (b) and (e), S3 (c) and (f).

The FT-IR spectra of PANI, n-octadecane and n-octadecane/PANI nanocapsules are displayed in Fig. 2. The peak of n-octadecane can be ascribed as follows. The band appeared at 2853 cm^{-1} and 2953 cm^{-1}, which is ascribed to the absorption of the C-H stretching vibration of methylene and methyl groups, and the absorption peak at 1466 cm^{-1} and 721 cm^{-1} are associated with C-H bending vibration of methyl groups and C-H in-plane rocking vibration of methylene groups. In the PANI spectrum, the absorption peaks at 1568 cm^{-1} and 1486 cm^{-1} correspond to the C-C stretching vibration of quinonoid and benzene rings, respectively. The absorption peak at 1297 cm^{-1} is related to the C-N stretching vibration of the secondary aromatic amine.

The spectra of n-octadecane/PANI nanocapsules shows clearly spectra of both characteristic peaks of n-octadecane and PANI, which indicate that clearly n-octadecane exists nanocapsules. What is more, no new peak appeared, indicating no chemical interaction occurred among PANI and n-octadecane.
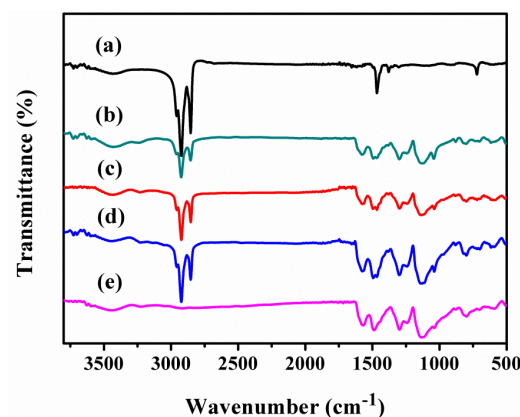

Fig. 2. FT-IR spectra of the (a) n-octadecane, (b) S1, (c) S2 , (d) S3 and (e) PANI.

Fig. 3. shows the XRD patterns of the n-octadecane, S3, S2 and S1. The XRD pattern of PANI in S1, S2 and S3 agrees with Ref [7]. The characteristic peaks of 20° and 25° are corresponding to (020) and (200) crystal planes of PANI. The microcapsule samples S3 mainly revealed the characteristic peaks of n-octadecane coordinate with the strong diffraction intensity of crystalline n-octadecane. The characteristic peaks at 19.24°, 19.81° and 23.31° are assigned to (0 1 0), (0 1 1), and (1 0 5) which are related to the crystal of n-octadecane. Therefore, the XRD pattern not only comfirm the existence of n-octadecane inside nanocapsules, but also demonstrate the good crystallinity of n-octadecane within the nanocapsules.
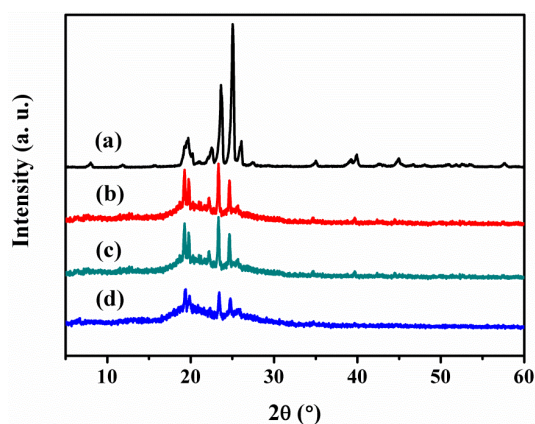
Fig. 3. XRD patterns of the (a) n-octadecane, (b) S3, (c) S2 and (d) S1.
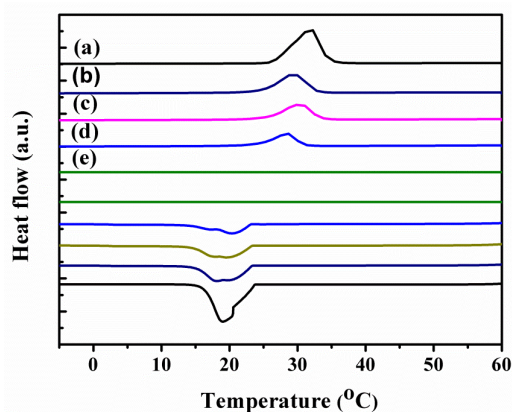
Fig. 4. The melting and solidifying DSC curves of (a) n-octadecane, (b) S3, (c) S2, (d) S1 and (e) PANI.

Fig.4 shows the DSC curves of pristine n-octadecane, PANI and S1, S2, S3 fabricated at different monomer/PCM ratios, respectively. The phase transition temperature and latent storage capacity were shown in Table 1. By considering these results, it can be clearly stated that S1, S2 and S3 exhibit very stable phase change behaviors in their heating and cooling periods. The pristine n-octadecane has also melting peak at 29.5 ^{o}C, and freezing peak at 21.1 ^{o}C. The different composite PCMs, namely S1, S2 and S3 showed melting peak at 27.5, 27.9 and 28.3 ^{o}C, and freezing peak at 20.9, 20.3 and 21.2 ^{o}C, respectively. The sub-cooling degree of S1, S2 and S3 were reduced which can provides an important advantage for composite PCMs. With the increase of the feed amount of n-octadecane, the ΔH_m of S1, S2 and S3 will increases. In particular, ΔH_m of S3 are 105.4 J/g indicating a relatively best energy storage capacity.

Table 1. DSC data of the n-octadecane, S1, S2 and S3.

Sample	T_{pm} (℃)	ΔH_m (Jg^{-1})	T_{pc} (℃)	ΔH_c (Jg^{-1})
PANI	-	-	-	-
S1	27.5	63.3	20.9	67.4
S2	27.9	92.4	20.3	94.5
S3	28.3	105.4	21.2	108.4
n-octadecane	29.5	227.4	21.1	233.7

Note: T_{pm}, Peak temperature on DSC heating curve; T_{pc}, Peak temperature on DSC cooling curve.

Conclusions

In summary, the spherical nanocapsules of PANI-shelled n-octadecane were prepared. These nanocapsules have relatively higher energy storage capacity of 63.3-105.4 J/g and a proper mean diameter of 500-700 nm within the scale desirable for textile coatings.

Acknowledgments

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