Preparation and characterization of Phase change material microcapsules by a core-shell-like emulsion polymerization method

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Abstract. Phase change material microcapsules (MicroPCMs) were synthesized by a core-shell-like emulsion polymerization method. Styrene and methylacrylic acid copolymer (PS-MAA) was used as a wall material, and paraffin was used as a core material in order to prepare spherical, high resistance and high enthalpy MicroPCMs. Scanning Electron Microscope (SEM), laser particle size analyzer, Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetry (TG) and Differential Scanning Calorimeter (DSC) were employed to characterize the MicroPCMs. The results indicated that the average particle size of MicroPCMs was 42.29 μm, and the content of paraffin within microcapsules was 57.6%. The melting temperature and crystallization temperature were 30.7 ℃ and 25.2 ℃. The melting enthalpy and crystallization enthalpy were -84.1 J/g and 91.3 J/g, respectively.

1. Introduction

Phase change materials (PCMs) are thermal energy storage materials that store and release heat energy at a constant temperature by undergoing a phase change [1]. PCM is a kind of interesting material for latent heat storage due to its high energy storage density and small temperature variation from storage to recovery [2]. Therefore, PCMs have attracted considerable interest in the fields of energy storage during the past decades. However, the direct application of PCMs is not easily due to their low thermal conductivity, flammability, instability and leakage problems [3]. A solution for those problems is microencapsulation of PCMs. Microencapsulation means that individual particles or droplets of solid or liquid material (the core) are surrounded or coated by a continuous film of polymeric material (the shell) to produce capsules from the micrometer to millimeter range [4]. Microencapsulation has many advantages, such as preventing the reaction of PCMs with the outside environment and the leakage of liquid PCMs, increasing heat-transfer area, providing constant volume [5-7].

Phase change material microcapsules (MicroPCMs) not only have the advantages of PCMs but also have the advantages of microcapsules. Therefore, MicroPCMs have drawn greater attention than traditional PCMs. Many methods have been used to prepare the MicroPCMs. Fang et al. [8] prepared nano-encapsulated n-tetradecane as phase change material for thermal energy storage by in situ polymerization. Alay et al. [9] prepared poly (methyl methacrylate)/n-hexadecane microcapsules using

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emulsion polymerization and studied the applicability to the textiles. Qiu et al. [10] fabricated microcapsules of n-octadecane with different n-butyl methacrylate as copolymer shells by a suspension-like polymerization method. Malekipirbazari et al. [11] microencapsulated paraffin with gelatin/gum Arabic as the wall by the complex coacervation method.

The aim of this paper is to synthesize MicroPCMs by a core-shell-like emulsion polymerization method. The paraffin is used as a core material and methylacrylic acid copolymer (PS-MAA) is chosen as the wall material.

2. Experimental

2.1. Materials
Styrene (St, A.R., Tianjin Fuchen Chemical Reagent Co., Ltd.), Methyl acrylic acid (MAA, A.R., Sinopharm Chemical Reagent Co., Ltd), Azodiisobutyronitrile (AIBN, C.R., Sinopharm Chemical Reagent Co., Ltd) and Sodium dodecyl sulfate (SDS,C.R., Sinopharm Chemical Reagent Co., Ltd) are used directly without further treatment. Paraffin is distilled from crude wax, and Water is purified by distillation before using.

2.2. Preparation of MicroPCMs
A core-shell-like emulsion polymerization method was used to fabricate the MicroPCMs. First, the paraffin was added to an aqueous solution of SDS and the mixture was heated to melt the paraffin. The mixture was emulsified under the stirring speed of 10000 rpm for 1min after the paraffin was melted and the paraffin emulsion was obtained. Then the paraffin emulsion was transferred to a four-necked flask equipped with a stirrer and a condenser and maintained for 10min at room temperature and at a stirring speed of 1000 rpm. Next, added the mixture of St, MAA and AIBN to the paraffin emulsion and dispatched the stirring speed to 400 rpm. The polymerization process was carried at the temperature of 75°C under the protection of N₂ for 6h rs. The reaction products were separated by vacuum filtering and were washed with boiling water for three times. The purified MicroPCMs were obtained after being dried in an oven at 50°C for 24 hrs. The experiment repeated three times, weighing the quality of the dried MicroPCMs and calculating the productive rate.

2.3. Characterization of MicroPCMs
Laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd.,UK) was used to determine the size and size distribution of MicroPCMs. The MicroPCMs were dispersed in distilled water and the pump speed set as 2000rpm. Scanning Electron Microscopes (SEM, JSM-IT300 and JEOL JSM-7500, Japanese electronics Co., Ltd.,Japan) were used to observe the morphologies and structures of MicroPCMs. All samples were coated with a layer of gold prior to the observation. Fourier Transform Infrared Spectroscopy (FTIR, Bruker Tensor27, Bruker Co., Ltd., Germany) was used to determine the FTIR spectra of paraffin, PS-MAA and MicroPCMs. The samples were mixed with KBr and pressed into a pellet. The FTIR spectra in absorbance mode were recorded within the range of 500-4000cm⁻¹. Thermogravimetry (TG, Netzsch TG209F1, Netzsch Instruments Ltd., Germany) was used to characterize the thermal stabilities of paraffin, PS-MAA and MicroPCMs. The heating was in the range of 30-600°C at the rate of 5°C/min in a nitrogen atmosphere. Differential Scanning Calorimeter (DSC, EXSTAR DSC6200, NSK LTD., Japan) was used to measure the thermal storage properties of paraffin, PS-MAA and MicroPCMs. The tests were in the range of 0-80°C at a heating or cooling rate of ±5°C/min in a nitrogen atmosphere.

3. Results and discussion

3.1. Preparation of MicroPCMs
This article is to explore whether MicroPCMs can be successfully synthesized by a core-shell-like emulsion polymerization method. On the one hand, the composition of the product should be
characterized; on the other hand, the productive rate also should be considered. The productive rate of MicroPCMs can be calculated by the following formula:

$$\text{productive rate} = \frac{m_{\text{MicroPCMs}}}{m_{\text{core}} + m_{\text{shell monomer}}} \times 100 \tag{1}$$

Where $m_{\text{MicroPCMs}}$, $m_{\text{core}}$, and $m_{\text{shell monomer}}$ are the weight of dried MicroPCMs, core and shell monomer, respectively. The mean productive rate is 81.8%, which is lower than the productive rate of PS-MAA [12].

### 3.2. Size and size distribution of MicroPCMs

The size and size distribution of the MicroPCMs are shown in figure 1. The average particle size of MicroPCMs is 42.29 μm and the distribution index is 2.19. As the figure 1 indicates that the particle size mainly distributed at 10 μm. Combining with the photographs of SEM in figure 2, we can deduce that the particles with larger size are uncoated paraffin. As seen from the figure 1, the distribution of the MicroPCMs is wide. Maybe this is caused by the inadequate emulsion of paraffin.

![Figure 1. Diameter distribution of the MicroPCMs.](image1.png)

**Figure 1.** Diameter distribution of the MicroPCMs.

![Figure 2. Morphology of the MicroPCMs.](image2.png)

**Figure 2.** Morphology of the MicroPCMs.

### 3.3. Morphology of MicroPCMs

It can be seen from SEM image A, the sizes of the particles are mainly between 5 μm and 25 μm. This is well in accordance with that shown in figure 1. SEM image B shows that the MicroPCMs have a spherical profile. However, there are many dimples on the surface of MicroPCMs. This could be attributed to the generation of reserved expansion space in the MicroPCMs fabrication process [13]. On one hand, the density of the polymer is higher than that of the monomers, on the other hand, the
volume of paraffin reduces as its phase changes from melting state to crystal state. Both factors lead to a generation of reserved expansion space during the progress of the MicroPCMs preparation, thus to the shrinkage of the shell [14-15].

3.4. Chemical characterization

Figure 3 shows the FTIR spectra of paraffin, PS-MMA and MicroPCMs. FTIR spectrum of paraffin has a typical multiple strong absorption peaks between 2850 cm\(^{-1}\) and 2950 cm\(^{-1}\). The peaks are the symmetric and asymmetric stretching vibration of CH\(_2\) and CH\(_3\). The absorption peak appears at 1467 cm\(^{-1}\) represents the unsymmetrical bending vibration of CH\(_3\) and scissors bending vibration of CH\(_2\) in aliphatic chain. The absorption peak appears at 1378cm\(^{-1}\) corresponding to the symmetric stretching vibration of and CH\(_3\) in aliphatic chain.

Figure 3. FTIR spectra of paraffin, PS-MMA and MicroPCMs.

The strong absorption peak appears at about 720 cm\(^{-1}\) corresponds to the in-plane bending vibration and characterizes that the alkane chains has more than methylene. FTIR spectra of PS-MAA have a typical multiple weak absorption peaks between 3100 cm\(^{-1}\) and 2900 cm\(^{-1}\). The peak indicates unsaturated C-H stretching vibration on the benzene ring. The strong absorption peaks appear at 699cm\(^{-1}\) and 758 cm\(^{-1}\) are out-plane deformation vibration of H on benzene ring, which is the characteristic peak of mono-substitution benzene ring. The strong absorption peak appears at 1698 cm\(^{-1}\) corresponding to the blue shift stretching vibration of C=O, and the weak absorption peak appears at 1400 cm\(^{-1}\) corresponding to stretching vibration of OH. These peaks indicate the existence of carboxyl group. From the above analysis we could surely come to the conclusion that the shell is the copolymer between St and MAA.

The FTIR spectrum of MicroPCMs not only includes the characteristic peak of paraffin but it also has characteristic peak of PS-MAA. So the MicroPCMs consists of core materials and wall materials. There are no addition peaks appear on the FTIR spectrum of MicroPCMs, which indicates that there are no chemical reaction between core materials and shell materials.

3.5. Thermal stability of MicroPCMs

Figure 4 shows TG curves of paraffin, PS-MMA and MicroPCMs. As is shown in the figure 4, paraffin started to lose its weight at approximately 147\(^\circ\)C, and it fast lost its weight from 147\(^\circ\)C to 212 \(^\circ\)C. The TG curve of paraffin is sharp because it is composed of linear alkane molecules. The shell material PS-MAA began to lose weight at approximately 366\(^\circ\)C and it completely lost its weight at about 437\(^\circ\)C. However, TG curve of MicroPCM mainly shows two steps of mass lose. The first mass lost occurred between 165\(^\circ\)C and 225\(^\circ\)C resulted from the weight loss of paraffin. The second mass
lost happened from 366℃ to 420℃ caused from the degradation of PS-MAA. The results indicate encapsulation of paraffin can delay the volatilizing.

3.6. Thermal properties of MicroPCMs

The content of PCM in microcapsules is an important factor for MicroPCMs, and it directly determines the phase change enthalpy and energy storage efficiency of MicroPCMs. The DSC curves of paraffin, PS-MMA and MicroPCMs are shown in figure 5 and the specific data are listed in table 1.

As figure 5 shows, the PS-MAA has no phase change behavior in the test range. Therefore, the content of paraffin in MicroPCMs can be calculated by the following formula [16]:

\[
\text{paraffin content} = \frac{\Delta H_{\text{MicroPCMs}}}{\Delta H_{\text{PCMs}}} \times 100
\]  

(2)

Where \( \Delta H_{\text{MicroPCMs}} \) and \( \Delta H_{\text{PCMs}} \) are the enthalpies of MicroPCMs or pure PCMs, respectively.

![DSC curves of paraffin, PS-MMA and MicroPCMs](image)

Figure 5. DSC curves of paraffin, PS-MMA and MicroPCMs.

| Sample       | Tpm/℃ | ΔHm (J/g) | Tpc/℃ | ΔHe (J/g) | PCM content/% |
|--------------|--------|-----------|--------|-----------|---------------|
| paraffin     | 30.9   | -146      | 23.3   | 167       | 100           |
| MicroPCMs    | 30.7   | -84.1     | 25.2   | 91.3      | 57.6          |

\(^a\) Tpm is melting temperature,

\(^b\) ΔHm is melting enthalpy;

\(^c\) Tpc is crystallization temperature;

\(^d\) ΔHe is crystallization enthalpy.

It can be seen from figure 5 and table 1 that the melting temperature and crystallization temperature of paraffin have no obvious change before and after the microencapsulation. So the microencapsulation doesn’t affect the thermal properties of paraffin. The paraffin content in MicroPCMs is about 57.6%. The melting temperature and crystallization temperature are 30.7℃ and 25.2℃. The melting enthalpy and crystallization enthalpy are -84.1 J/g and 91.3, respectively.

4. Results and discussion

MicroPCMs using paraffin as core materials are successfully prepared by core-shell-like emulsion polymerization. The average particle size of the MicroPCMs is 42.290 μm, and the content of paraffin
is 57.6%. The melting temperature and crystallization temperature are 30.7°C and 25.2°C. The melting enthalpy and crystallization enthalpy are -84.1 J/g and 91.3 J/g, respectively. The MicroPCMs prepared in this paper have potential application in the field of energy storage.

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