Preparation and characterization of acrylic resin encapsulated n-dodecanol microcapsule phase change material

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Abstract
Nontoxic, low-cost microcapsule phase change materials (MicroPCMs) were successfully manufactured via suspension polymerization, in which n-dodecanol was employed as the core material and crosslinked polymethyl methacrylate as the wall material. Alkylphenol polyoxyethylene ether (OP-10), polysorbate-20 (Tween-20), sodium salt of styrene-maleic anhydride polymer (SMA), sodium dodecyl sulfonate (SDS), and hexadecyltrimethylammonium chloride (1631) were employed as emulsifiers to investigate the effects of the type and amount of emulsifier on MicroPCMs. In addition, the effects of different types of crosslinking agents on the fabrication of MicroPCMs were investigated. Scanning electron microscopy was used to observe the micro-morphology of MicroPCMs. The chemical structure of the MicroPCMs was detected via Fourier transform infrared spectroscopy. The thermal properties and thermal stability of the MicroPCMs were analyzed using a differential scanning calorimeter and a thermal gravimetric analyzer, respectively. Particle size distributions of the MicroPCMs were measured using a particle size analyzer. The results demonstrate that MicroPCMs with regular morphology were prepared when the mass ratio of the SMA to the oil phase was 3%, and the latent heat and yield of the MicroPCMs were 80.29 J g⁻¹ and 84%, respectively. Furthermore, the MicroPCMs were successfully synthesized using pentaerythritol triacrylate containing the hydroxyl group as the crosslinking agent with an average particle size of 14.18 μm and excellent thermal stability.

1. Introduction

Energy storage technology is crucial in the field of energy research. It influences the effective use of thermal energy [1]. Phase change materials (PCMs), which are used as energy storage materials, have received an increasing amount of attention in recent years. A central principle guiding the use and development of phase change materials is that materials will be in phase transition when the ambient temperatures rise or fall; PCMs absorb or release thermal energy to achieve heat storage or heat release. The characteristics of PCMs are that the temperature remains constant during the phase change process and that the energy storage density is large [2–5]. These molecules are generally microencapsulated and can be applied to various surfaces, such as fibers, floors, and walls [6–8].

Microcapsule phase change materials (MicroPCMs) comprise a core material and wall material. Several studies on MicroPCMs have demonstrated that alkanol was used as the core material, the advantages of which are high phase change enthalpy and low cost. Yin et al [9] prepared MicroPCMs of melamine-formaldehyde resin encapsulated n-hexadecanol, with SiO₂ to modify the wall material; this in turn improved the impermeability of the wall material, and its thermal stability and strength. The phase transition temperature and phase transition enthalpy of the MicroPCMs were 52.56 °C and 163.67 J g⁻¹, respectively. Zhang et al [10] synthesized MicroPCMs with n-dodecanol as the core material and melamine formaldehyde resin as the wall material, and they modified the microcapsule with polyvinyl alcohol (PVA). The report indicated that PVA...
could not only decrease the microcapsule particle size but also improve the compactness of the microcapsule wall material. In addition, microcapsules with n-dodecanol as the core material were investigated by several researchers [11–13]; however, the formaldehyde in the literature listed above was contained in wall materials, a design attribute that is neither environmentally friendly nor beneficial to humans. In recent years, acrylic resin wall material has attracted the attention of several researchers [14–17]. This class of materials has the advantages of being harmless and possessing good film formation properties. Methyl methacrylate (MMA) [18], ethyl methacrylate [19], and allyl methacrylate [20] can be used as wall materials for microcapsules. Furthermore, several modification studies on acrylic resins have been performed, such as for increasing the strength of the wall material by adding divinylbenzene [21], and adding γ-methacryloxypropyl-trimethoxysilane to attain a novel MicroPCM with thermochromic properties [22]. The thermal stability of the wall material was improved when the content of SiO2 and TiC was increased [23]. However, most of the abovementioned studies are based on alkanes as the core material, and alkanes tend to be expensive; thus, they are not conducive for widespread application. The latent heat of n-dodecanol is 80% that of n-octadecane, although the price is 15% that of n-octadecane; thus, n-dodecanol is more commonly used.

For the abovementioned reasons, we used n-dodecanol as the core material, and the MMA and the crosslinking agent as the wall materials; furthermore, the MicroPCMs were prepared via suspension polymerization. These MicroPCMs have the advantages of being low-cost and nontoxic compared to other MicroPCMs. In addition, the effects of the emulsifier type and crosslinking agent type on MicroPCMs are discussed in this paper.

2. Experimental

2.1. Materials

MMA (C.P., Shanghai Lingfeng Chemical Reagent Co., Ltd) and n-dodecanol (DA, C.P., Shanghai Lingfeng Chemical Reagent Co., Ltd) were used as the monomer and the core material, respectively. The inhibitor of MMA was removed using 5% sodium hydroxide solution; MMA was then dried in CaCl2 overnight. Pentaerythritol triacrylate (PETA, 80 wt.%, Shanghai Aladdin Bio-Chem Technology Co., Ltd), divinylbenzene (DVB, 80 wt.%, Shanghai Aladdin Bio-Chem Technology Co., Ltd), and ethylene glycol dimethacrylate (EGDMA, 98 wt.%, Shanghai Aladdin Bio-Chem Technology Co., Ltd) were employed as the crosslinking agents. OP-10 (C.P., Shanghai Lingfeng Chemical Reagent Co., Ltd), Tween-20 (C.P., Sinopharm Chemical Reagent Co., Ltd), SMA (19 wt.%, Shanghai Leather Chemical Works), SDS (C.P., Shanghai Lingfeng Chemical Reagent Co., Ltd) and 1631 (97 wt.%, shanghai Aladdin Bio-Chem Technology Co., Ltd) were used as emulsifiers. Benzoyl peroxide (BPO, 75 wt.%, Shanghai Lingfeng Chemical Reagent Co., Ltd) was used as an initiator. Figure 1 shows the structural formulas of the crosslinking agents considered in this study.

2.2. Preparation of MicroPCMs

MicroPCMs containing n-dodecanol with polymethyl methacrylate (PMMA) and the crosslinking agent as a shell were prepared via suspension polymerization. A typical microencapsulation process was conducted as follows: (i) The water phase was prepared by mixing 100 g deionized water and an appropriate emulsifier. The addition of the emulsifier was in the ratio of the total weight of the core material and wall material; (ii) The 6 g MMA, 4 g crosslinking agent, 10 g n-dodecanol, and 0.3 g BPO were ultrasonically dispersed for 10 min to obtain an oil phase; (iii) The water and oil phases were poured into a 250 ml three-necked flask and stirred at 2000 rpm for 15 min to obtain an emulsion; (iv) The oxygen was removed with nitrogen at a flow rate of 80 ml min−1 for 5 min; (v) The emulsion was heated to 85 °C to start polymerization, while being continuously stirred at a rate of 300 rpm for 3 h; (vi) The resulting MicroPCMs were demulsified with 10 wt.% Al2(SO4)3 and washed three times with 30% ethanol solution to remove the unencapsulated n-dodecanol and then dried at 45 °C for 12 h.

2.3. Characterizations of MicroPCMs

A JSM-5900 scanning electron microscope (SEM) was used to observe the micro-morphology of MicroPCMs. Then, the samples were sprayed for 1 min with gold for the ease of observing the morphology of the MicroPCMs. The chemical properties of the MicroPCMs were analyzed using a Nexus 670 Fourier transform infrared (FTIR) spectroscopy in a frequency ranging from 400 cm−1 to 4000 cm−1. A Hydro 2000MU(A) laser particle size analyzer was used to measure the particle size distribution of the MicroPCMs. During the experiment, distilled water was used as a dispersion medium during ultrasonic dispersion. A 404 F1 Pegasus differential scanning calorimeter (DSC) was used to test the thermal properties of the MicroPCMs, such as the melting temperature (Tm), freezing temperature (Tf), melting enthalpy (ΔHm) and the freezing enthalpy (ΔHf). The thermal properties were measured at a heating or cooling rate of 10 °C min−1 in the range of −20 °C–60 °C.
The content of PCM in MicroPCMs ($W_1$) was calculated as follows:

$$W_1 = \frac{\Delta H_{m\text{-MicroPCM}}}{\Delta H_{m\text{-PCM}}} \times 100\%$$  \hspace{1cm} (1)

where $\Delta H_{m\text{-MicroPCM}}$ is the melting enthalpy (J g$^{-1}$) of the MicroPCMs, and $\Delta H_{m\text{-PCM}}$ is the melting enthalpy of n-dodecanol (192.80 J g$^{-1}$).

The theoretical value of the content of PCM within the MicroPCMs can be defined as follows:

$$W_2 = \frac{m_{\text{core}}}{m_{\text{core}} + m_{\text{shell}}} \times 100\%$$  \hspace{1cm} (2)

where $m_{\text{core}}$ is the mass of n-dodecanol (g) and $m_{\text{shell}}$ is the weight of MMA and the crosslinking agent (g).

The encapsulation efficiency ($E_{en}$) of the core material is not only associated with the phase change latent heat but also related to the mass ratio of the core material in the MicroPCMs, which is calculated as follows [26]:

$$E_{en} = \frac{W_1}{W_2} \times 100\%$$  \hspace{1cm} (3)

A thermal gravimetric analyzer (TGA) 550 was used to test the thermal stability of MicroPCMs in the range of 30 °C–600 °C with a heating rate of 20 °C min$^{-1}$.

3. Results and discussion

3.1. Influence of emulsifier

3.1.1. Morphology of MicroPCMs

SEM images of MicroPCMs that were fabricated using PETA as a crosslinking agent, and with different types of emulsifier, are presented in figure 2. Figures 2(a) and (b) show that the MicroPCMs prepared using OP-10 and Tween-20 adhered to each other, and the surface of the MicroPCMs appears as hemispherical particles, with no regular core–shell structure. This is attributed to the emulsifying effectiveness of OP-10 and Tween-20 that decreased until 65 °C and 79 °C [27, 28], respectively, thereby resulting in demulsification. MicroPCMs with core–shell structures were obtained using anionic SMA as an emulsifier (figure 2(c)). This is attributed to the molecular chain of SMA that contains the hydrophobic aryl group and a negatively-charged hydrophilic carboxyl group. The SMA molecules were absorbed on the surface of the suspended droplets during high-speed stirring. The hydrophobic aryl group was indicated to be the oil phase and the hydrophilic carboxyl group was indicated to be the water phase. Negatively-charged fields were formed between droplets, which hindered collision between droplets and rendered the emulsion more stable. This is conducive for the preparation of the MicroPCMs [29]. However, as depicted in figures 2(d) and (e), the MicroPCMs that were prepared using ionic emulsifiers (SDS and 1631) are irregular, which can be attributed to the large amount of foam generated during
emulsification. Therefore, because MicroPCMs with core–shell structure were obtained using anionic SMA as an emulsifier, SMA was selected as the emulsifier for preparing MicroPCMs in this study.

Figure 3 shows micrographs of the MicroPCMs fabricated using different accession amounts of the SMA emulsifier. Figure 3(a) shows that there is a small amount of spherical MicroPCMs in the sample that was prepared using 1% SMA of size 10–20 μm. Additionally, several polymer particles of size 2–4 μm were formed, and this may be attributed to the small amounts of SMA emulsifier present in the system. Furthermore, fewer molecules were adsorbed on the surface of the suspended droplets; this is because there was a weak negative electric field between the droplets, which resulted in the poor stability of the emulsion, and MMA and PETA reacted to form polymer particles.

Increasingly spherical MicroPCMs appeared and the surface of MicroPCMs smoothened when the SMA emulsifier was increased to 3%. However, when the amount of the emulsifier was increased, the surface of the MicroPCMs became rough and the shells were broken, as shown in figures 3(c)–(f). The reason is that the amounts of added SMA in system is in excess compared to the steric effect of the prominent benzene ring of the SMA molecular chain, making it difficult for n-dodecanol to be encapsulated by the wall material. The surfaces
of the MicroPCMs exhibit holes and breakage, which indicates that the accession amount of emulsifier is excessive. In summary, the optimal amount of SMA is 3%.

3.1.2. Chemical characterization

Figure 4 presents the FTIR spectra of the polymer shell, n-dodecanol, and the MicroPCMs (prepared with the SMA emulsifier). The peaks that appear at 1731 cm$^{-1}$ and 1147 cm$^{-1}$ in figure 4(a) are attributed to the C=O$^{[30]}$ and C–O–C stretching vibrations$^{[31]}$, respectively; the former peaks are characteristic of the polymer shell. Figure 4(b) shows that the methyl and methylene groups stretching vibration of n-dodecanol are detected at 2923 cm$^{-1}$ and 2854 cm$^{-1}$, respectively. The O–H bending vibrations of primary alcohol appear at approximately 1466 cm$^{-1}$ and 1378 cm$^{-1}$, and the peak of C–OH stretching vibrations of primary alcohol is observed at 1048 cm$^{-1}$[13]. In addition, the characteristic peaks of the wall material and core material can be observed on the spectra of the MicroPCMs. This indicates that the core material was encapsulated by the wall material, without chemical reactions between the core material and wall material.
3.1.3. Thermal properties of MicroPCMs

Figure 5 shows the heat storage properties of microcapsules manufactured with various amounts of SMA. The onset of phase change temperature was defined as the intersection of the extension line before the phase change and the tangent line of the maximum point of curvature after the phase change on the DSC curve. The peak area of the DSC curve was calculated as the phase change enthalpy. The values of the phase change enthalpies and phase change temperatures are listed in Table 1.

The largest latent heat of the phase change ($\Delta H_m = 80.29 \text{ J g}^{-1}$, $\Delta H_c = 77.01 \text{ J g}^{-1}$) of the MicroPCMs was obtained when the added SMA emulsifier was 3%. This indicates that the microcapsule can encapsulate greater amount of n-dodecanol. Some researchers have fabricated microcapsules containing n-dodecanol, including Su et al. [26], who prepared a n-dodecanol/methanol-melamine-formaldehyde microcapsule ($\Delta H_m = 61.60 \text{ J g}^{-1}$). Ma et al. [32] synthesized MicroPCMs of acrylic polymer containing n-dodecanol ($\Delta H_m = 38.90 \text{ J g}^{-1}$), and Wu et al. [11] manufactured a 1-dodecanol/melamine-formaldehyde microcapsule, $\Delta H_m = 66.52 \text{ J g}^{-1}$. The melting enthalpy of the MicroPCMs in this work was larger than those found in the current literature. This indicates that n-dodecanol/acrylic resin microcapsule could offer higher capacity of heat storage. Note that $T_m$ (19.38 °C) is lower than $T_c$ (19.73 °C) (shown in Table 1). This is attributable to the phase change temperature not being a certain value but rather a temperature range. The peak temperature or the onset temperature was defined as the phase change temperature for convenience; errors cannot be avoided when using 404 F1 Pegasus DSC to test thermal properties of MicroPCMs (which are acceptable).

Figure 6 shows that the encapsulation efficiency first increases and then decreases to reach the maximum ($E_{cn} = 82.25\%$) when 3% of the SMA emulsifier is added. This result has a vital effect on the encapsulation
Moreover, the yield of MicroPCMs was the largest (84%) when 3% of the SMA was added, as presented in Table 1. It is possible that a more stable emulsion can be obtained with such additions, and that n-dodecanol could be more easily encapsulated. The microcapsule shell showed no indication of breakage.

### Emulsifier content

| Emulsifier content (%) | $\Delta H_{\text{m}}$ (J g$^{-1}$) | $T_{\text{m}}$ ($^\circ$C) | $\Delta H_{\text{c}}$ (J g$^{-1}$) | $T_{\text{c}}$ ($^\circ$C) | Yield (%) |
|------------------------|------------|----------------|----------------|----------------|------------|
| 3                      | 80.29      | 19.38           | 77.01          | 19.73          | 84         |
| 5                      | 38.40      | 21.98           | 37.57          | 18.72          | 54         |
| 7                      | 46.30      | 20.01           | 46.58          | 19.50          | 61         |
| 9                      | 13.90      | 20.68           | 14.47          | 19.25          | 60         |
| 11                     | 13.50      | 20.52           | 14.02          | 19.31          | 53         |

Note: $\Delta H_{\text{m}}$, melting enthalpy; $T_{\text{m}}$, melting temperature; $\Delta H_{\text{c}}$, freezing enthalpy; $T_{\text{c}}$, freezing temperature; Yield, the ratio of MicroPCMs mass to raw material mass.

### 3.2. Influence of crosslinking agent

#### 3.2.1. Morphology and diameter distribution of MicroPCMs

Figure 7 shows the SEM photographs of MicroPCMs fabricated using various crosslinking agents. The masses of the raw materials used in the MicroPCMs are listed in Table 2 (S1–S3). The mass of n-dodecanol and MMA are 10 g and 6 g in all the samples, respectively. Figure 7(a) shows the surface morphology of microcapsules prepared with PETA as the crosslinking agent. The surface is smooth and the particle size is 10–20 μm. In addition, dimples appear on the shell of spherical MicroPCMs. This is attributed to the density of PMMA being greater than that of MMA and to the volume of n-dodecanol shrinking when a change from the melting state to crystalline occurred [11, 33, 34]. The surface morphology of the MicroPCMs that were fabricated using DVB as the crosslinking agent was extremely rough, whereas those with EGDMA as the crosslinking agent were spherical, as depicted in Figure 7(c); however, they have a rough surface. This is ascribed to the understanding that the n-dodecanol contains both long hydrophobic carbon chains and hydrophilic hydroxyl groups; thus, the n-dodecanol migrated from the oil phase to the water phase. This increased the hydroxyl groups at the interface, and resulted in the loose deposition of the polymer and a decrease in the compactness of the shell of the MicroPCMs [20]. In addition, Figure 7(c) shows a larger size microcapsule. This is attributed to the fact that the viscosity of EGDMA is larger than that of DVB, and that the particle size of the emulsion that contains the crosslinking agent, EGDMA, is bigger than that of DVB when stirred, thereby resulting in larger particles [35].

However, the DSC results show that except for the MicroPCMs prepared with PETA as the crosslinking agent, MicroPCMs prepared with DVB and EGDMA as crosslinking agents have no latent heat of phase change.
This indicates that the n-dodecanol was not encapsulated by the wall material. The broken particles show a microcapsule without a core–shell structure (figure 7(c)). This can be explained by the ability of the hydroxyl groups of the PETA to form hydrogen bonds with the hydroxyl group of the n-dodecanol. This ability is beneficial for the stability of the emulsion and helpful for the preparation of MicroPCMs with a core–shell structure.

To confirm the influence of the hydroxyl group of PETA on the preparation of MicroPCMs, the crosslinking agents, DVB and EGDMA were again incorporated into the MicroPCMs prepared with PETA. Table 2 (S4-S9) lists the weight of the raw materials of the MicroPCMs.

The surface features of the MicroPCMs with different doping contents of DVB and EGDMA were investigated using SEM (figure 8). There were no effects on the preparation of MicroPCMs when the doping amount of DVB and EGDMA was 0.1 g. Additionally, the broken shells of the MicroPCMs indicate that they have a core–shell structure (figures 8(a) and (b)). The doping amount of the second crosslinking agent was increased to 0.3 g, and the holes and the breakage appeared on the shell of the MicroPCMs. This indicates that the preparation of the MicroPCMs was influenced by the addition of DVB and EGDMA. Figures 8(e) and (f)

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**Table 2.** Weight of raw material of MicroPCMs.

| Sample | PETA (g) | DVB (g) | EGDMA (g) |
|--------|----------|---------|-----------|
| 1      | 4        | —       | —         |
| 2      | —        | 4       | —         |
| 3      | —        | 4       | —         |
| 4      | 3.9      | 0.1     | —         |
| 5      | 3.9      | —       | 0.1       |
| 6      | 3.7      | 0.3     | —         |
| 7      | 3.7      | —       | 0.3       |
| 8      | 3.5      | 0.5     | —         |
| 9      | 3.5      | —       | 0.5       |

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show that there are many spherical particles when the content of the second crosslinking agent is 0.5 g; however, the particles do not have a core–shell structure. The hydroxyl group of the crosslinking agent was considered to impact the preparation of the MicroPCMs with n-dodecanol as the core material.

Figure 9 shows the diameter distribution curve of the MicroPCMs fabricated using PETA as a crosslinking agent. There is only one peak in the diameter distribution curve and the distribution curve is narrow. This indicates that the distribution of the MicroPCMs is uniform. The particle size $D(0.5)$ means that the cumulative particle size distribution volume fraction is 50%, and $D(0.5)$ was defined as the average particle size of MicroPCMs. The result shows that $D(0.5) = 14.18 \mu m$, which is consistent with the result presented in figure 7(a).

3.2.2. Thermostability of MicroPCMs

Figure 10 depicts the thermal stability of n-dodecanol, PMMA, and MicroPCMs with PETA as the crosslinking agent. The weight loss process of the n-dodecanol starts at approximately 100 °C and ends at approximately 230 °C [30]. Figure 10(b) shows that there are two stages of weight loss. The first weight loss of

![Figure 8. SEM images of (a) S4, (b) S5, (c) S6, (d) S7, (e) S8, (f) S9.](image-url)
PMMA starts at approximately 125 °C, which could be because the MMA monomers were volatilized and the oligomers were decomposed. Furthermore, the weight loss of the second step begins at approximately 260 °C, which is attributed to the decomposition of PMMA. Figure 10(c) shows that there are two stages of weight loss of MicroPCMs with the PETA crosslinking agent. The first weight loss starts at approximately 140 °C, with a mass loss of 50%, and the decomposition temperature of MicroPCMs is higher than that of n-dodecanol. This indicates that the wall material plays an important role in protecting the core material from leakage; the onset decomposition temperature for the second stage is approximately 375 °C. This may be attributed to the decomposition of crosslinked PMMA [14]. To summarize, the thermal stability of MicroPCMs is improved by adding a crosslinking agent.

4. Conclusions

MicroPCMs of crosslinked PMMA encapsulated n-dodecanol were successfully synthesized via suspension polymerization. A number of emulsifiers were employed (OP-10, Tween-20, SMA, SDS, and 1631). The morphology of the MicroPCMs prepared with SMA emulsifier was regular and possessed a core–shell structure. The results of the FTIR spectra indicated that the n-dodecanol was encapsulated by the wall material. The shell of the MicroPCMs that were prepared with 3% SMA emulsifier was not broken. The highest latent heat of melting (80.29 J g⁻¹) and latent heat of freezing (77.01 J g⁻¹) for a microcapsule was obtained when the amount of SMA was 3%. The yield and the encapsulation efficiency of the MicroPCMs were 84% and 82.25%, respectively. MicroPCMs with a core–shell structure were prepared with PETA as a crosslinking agent, which resulted in an
average particle size of 14.18 μm. However, DVB and EGDMA were not advantageous in the preparation of the MicroPCMs owing to the lack of hydroxy groups on their molecular chains. The TGA results showed that the addition of PETA could improve the thermal stability of MicroPCMs. Hence, MicroPCMs composed of n-dodecanol show prospect for development in the area of energy storage. For instance, MicroPCMs could be applied to concrete floors to store solar energy. Future studies may aim to provide a working model of such energy storages.

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