Investigations on preparations and thermal properties of microencapsulated phase change materials

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Abstract. A series of microencapsulated phase change materials (micro-PCMs) were synthesized using suspension-like polymerization method. The micro-PCMs contained butyl stearate (BS) and octadecane (OC) as binary core materials. Trimethylolpropane triacrylate (TMPTA) and Trimethylolpropane trimethacrylate (TMPTMA) were introduced in polymerization system to respectively react with methyl methacrylate (MMA) or divinylbenzene (DVB) to form shell materials. SEM images showed that these micro-PCMs had compact surfaces and relatively spherical morphology, the diameter ranged from 5 to 40 μm. DSC results indicated that the microencapsulation ratio could be reached as high as 82 wt.%.

1. Introduction

Microencapsulated phase change materials (micro-PCMs) have good application prospects in the area of thermal energy storage (TES). Micro-PCMs consist of core and shell materials. The core materials are microencapsulated with different polymer shells, formed via polymerization process. The core materials show phase change properties and the shell materials act as the protection layer.

Compared with bulk PCMs, when protected by shell materials, micro-PCMs have the advantage of preventing leakage and being contaminated by other materials. Meanwhile, the size of the micro-PCMs can be tuned from nm to mm via different coating approaches, which resulted in the wide utilization in solar energy storage [1, 2], heat transfer [3, 4] and buildings [5, 6], etc. For instance, Li et al. introduced a kind of novel copper-powder-sintered frame/paraffin to form stable PCMs as heat sink in light-emitting diodes (LED), and the results showed that it can decrease the highest temperature of LED by about 16 °C, moreover, compare with traditional aluminum alloy heat sinks, it could also improve the LED brightness by about 4% [7].

In this paper, various cross-linking agents were introduced in polymerization system to form different shells. Chemical structure, morphologies and thermal properties were all studied, and the results suggested that these prepared micro-PCMs could be used as desirable thermal energy storage materials.
2. Experimental

2.1 Materials

The core materials were Octadecane (99 %) and butyl stearate (BS, ≥98 %, Sinopharm Chemical Reagent Co. Ltd, China). The initiator was 2, 2′-azobisisobutyronitrile (AIBN, 98 %). Monomers such as, methyl methacrylate (MMA, 99 %, 30 ppm MEHQ as stabilizer), divinylbenzene (DVB, 80 %, mixture of isomers, 1000 ppm TBC stabilizer, Alfa Aesar, Thermo Fisher Scientific, China), trimethylolpropane triacrylate (TMPTA, 85%, 600 ppm MEHQ as stabilizer), Trimethylolpropane and trimethacrylate (TMPTMA, 98%, 250 ppm MEHQ as stabilizer). The stabilizer was sodium salt of styrene-maleic anhydride copolymer (TA, Shanghai Leather Chemical Works, China).

Octadecane, AIBN, MMA, TMPTA and TMPTMA were supplied by Aladdin Chemical Reagent Co. Ltd, China.

The chemical structures of the related reagents were schematically displayed in figure 1.

![Chemical structures of used reagents.](image)

(a) BS; (b) MMA; (c) DVB; (d)TMPTA; (e) TMPTMA; (f) TA.

2.2 Preparation of the micro-PCMs

The preparation process comprise the following steps: first, octadecane, butyl stearate and AIBN were mixed at 40 °C to form dispersed phase. Second, de-ionized water and TA form continuous phase. Third, dispersed phase was added into continuous phase, and the mixture was homogenized at 1200 rpm for 20 min to form oil-in-water emulsion. Forth, kept the emulsion stirred at 85 °C for 6 h. Five, resultant microcapsules were filtered, and used the de-ionized water to wash the samples for 3 times. Finally, these samples were dried in an oven for two days.

The compositions and the dosages of the related reagents were listed in Table 1.

2.3 Characterizations of micro-PCMs

Fourier transformed infrared (FT-IR) spectra were tested by a spectrophotometer (Nicolet 6700, USA). The morphologies of micro-PCMs were investigated by Field emission scanning electron microscope (FE-SEM, ZEISS SUPRA® 55, Carl Zeiss, Germany). Differential scanning calorimeter
(DSC1, METTLER TOLEDO, Switzerland) measured the phase transition properties of the microcapsules.

The microencapsulation ratios were defined as following equation 1 [8]:

\[ R \% = \left( \frac{\Delta H_{m,\text{micro-PCMs}}}{\Delta H_{m,\text{OCBS}}} \right) \times 100 \text{ wt.\%} \] (1)

Where, \( \Delta H_{m,\text{OCBS}} \) is the melting enthalpy of the bulk PCMs, \( \Delta H_{m,\text{micro-PCMs}} \) is the melting enthalpy of the micro-PCMs.

Table 1. Basic compositions and thermal performances of the micro-PCMs.

| NO. | Octadecane (g) | BS (g) | MMA (g) | DVB (g) | TMPTA (g) | TMPTMA (g) | \( T_{\text{mp}} \) (°C) | \( \Delta H_m \) (J/g) | R (%) (Wt.%) |
|-----|----------------|--------|---------|---------|-----------|-----------|----------------|----------------|-------------|
| 1   | 3.00           | 3.00   | 3.00    | --      | 3.00      | --        | 29.2           | 72.6           | 65.8        |
| 2   | 3.00           | 3.00   | --      | 3.00    | 3.00      | --        | 28.3           | 90.5           | 82.0        |
| 3   | 3.00           | 3.00   | 3.00    | --      | --        | 3.00      | 27.3           | 68.5           | 62.0        |
| 4   | 3.00           | 3.00   | --      | 3.00    | --        | 3.00      | 28.2           | 56.3           | 51.0        |
| 5   | --             | 6.00   | --      | 3.00    | --        | 3.00      | 28.8           | 56.2           | 54.0        |
| 6   | 6.00           | --     | --      | 3.00    | --        | 3.00      | 32.1           | 113.7          | 52.6        |

* a. Melting peak temperatures of the micro-PCMs.  
* b. Melting enthalpies of the micro-PCMs.  
* c. Microencapsulation ratios of the micro-PCMs.

3. Results and discussion

3.1 Chemical structure of the PCMs and the micro-PCMs

FT-IR spectra of the micro-PCMs were represented in figure 2. The belongings of these absorption peaks were analyzed as follows [9, 10]: The peaks ascribed to C=C stretching and bending mode of benzene ring were located at at about 1620 cm\(^{-1}\) and 1115 cm\(^{-1}\), respectively. The peak assigned to C–H stretching vibration of –CH\(_2\) was at about 1460 cm\(^{-1}\). The peaks belonged to stretching vibration of carbonyl group and C–O bond in esters were at about 1730 and 1167 cm\(^{-1}\), respectively. The peak assigned to C–H symmetrical deformation vibration of –CH\(_3\) was at about 1370 cm\(^{-1}\), the peaks belonged to C–H asymmetrical and symmetrical stretching vibration of –CH\(_2\) were at about 2920 and 2850 cm\(^{-1}\), respectively.

Figure 2. FT-IR spectra of the micro-PCMs.
3.2 Thermal properties of the micro-PCMs

Phase change performances of these micro-PCMs were listed in table 1 and figure 3. The melting temperatures of these microcapsules were in the range of 27 °C to 32 °C. The melting enthalpy and the melting peak temperature of octadecane and butyl stearate were 216.0 J/g, 104.0 J/g and 30.7 °C, 28.2 °C, respectively. When used TMPTA as cross linking agent, these microcapsules with DVB as monomer had higher heat capacity, for example, sample 2 had higher microencapsulation ratio. However, when introduced TMPTMA, sample 3 had higher thermal capacity than sample 4. The reasons might be attributed that TMPTA had lower steric effects when it polymerized with MMA it could form better shell than that of DVB. Additionally, when the samples had the same shells, the micro-PCMs containing butyl stearate had better morphologies than that of octadecane, such as sample 5 and 6. Therefore, all the samples had good thermal properties.

![DSC curves of the micro-PCMs](image)

3.3 Morphology of the micro-PCMs

Figure 4 displayed SEM images of the micro-PCMs, these microcapsules were synthesized with regular diameters ranging from 5 to 40 μm and most of them had relatively compact surfaces and spherical profiles. These micro-PCMs contained three different kinds of core materials, namely octadecane, butyl stearate and OCBS. OCBS was octadecane and butyl stearate mixture, and the weight ratio of octadecane and butyl stearate was 1/1. The micro-PCMs had TMPTA and MMA had more flexible surface, for example sample 1 and 2 had more dimples on the surface. However, when the shell used more rigid shells, such as TMPTMA and DVB, they could form more spherical shells such as sample 4. Besides, when the micro-PCMs had the same shells, the micro-PCMs containing only butyl stearate as core materials had better shells, for example sample 5 had better morphologies than that of sample 6. Therefore, all the micro-PCMs had good morphologies and they had desirable application prospect in the field of thermal energy storage.
4. Conclusions

A series of micro-PCMs with different shells were obtained by suspension-like polymerization method, the cross-linking agents, TMPTA and TMPTMA was respectively introduced in polymerization process to form different shells. Chemical structures, morphologies and thermal properties of these prepared microcapsules were all investigated. The results indicated that, first, the microencapsulation ratio of the micro-PCMs was in a high range from 51 wt.% to 82 wt.%. Besides, most of the microcapsules had relatively spherical profiles and compact surfaces and the diameters
ranged from 5 to 40 $\mu$m. And finally, all the above results suggested that these prepared micro-PCMs had good application prospect in the field of thermal energy storage.

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