



Preparation and thermal reliabilities of microencapsulated phase change materials with binary cores and acrylate-based polymer shells



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ABSTRACT

Using suspension-like polymerization method, a series of microencapsulated phase change materials (micro-PCMs) with acrylate-based polymer shells and binary core materials were prepared. The phase change properties of the binary mixtures composed of paraffin and butyl stearate were investigated. SEM photographs showed that these micro-PCMs have relatively spherical profiles and compact surfaces with diameter ranging from 10 to 80 μm . DSC results indicated that the microencapsulation ratio of these micro-PCMs ranging from 46 wt% to 68 wt%. Moreover, after being subjected to thermal-cycling test for 500 times, these micro-PCMs kept good thermal reliabilities that the microencapsulation ratio decreased by less than 4 wt%. TGA analysis demonstrated that these micro-PCMs can ensure their thermal stability below 210 °C.

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1. Introduction

In recent years, driven by the urgent need of thermal management, microencapsulated phase change materials (micro-PCMs) have caused considerable interest in the fields of thermo-adaptable textiles [1,2], construction materials [3,4] and air-conditioning [5]. As decisive performances, thermal stability and reliability, microencapsulation ratio, phase change temperature, have been being studied with much attention. Generally, these performances are closely relative, thus many reports focus on the optimizing experiment conditions involving the selection of shell and core materials, polymerization method.

Saturated hydrocarbons, such as, *n*-tetradecane [6], *n*-heptadecane [7], *n*-eicosane [8], *n*-docosane [9], *n*-octacosane [10] and paraffin [11], have been successfully microencapsulated with polymethyl methacrylate (PMMA) shell. However, these above-mentioned micro-PCMs have the microencapsulation ratio ranging from 30 wt% to 40 wt%. Meanwhile, for the polystyrene (PSt) micro-PCMs containing *n*-tetradecane [12], *n*-hexadecane [13] or paraffin [14] the microencapsulation ratios were about 50 wt%. But styrene is inclined to form PSt polymer particles rather than PSt micro-PCMs in polymerization system [11,15]. Therefore,

more and more attention has been focused on improving the microencapsulation ratio of micro-PCMs. An effective ways is adding certain amount of cross-linking agent to *co*-polymerize with monomers and form network structure *co*-polymer shells for the microcapsules. Moreover, the results certified that not only can the *co*-polymer shells increase the microencapsulation ratio, but are capable of improving the thermal stability of the micro-PCMs. Sánchez-Silva et al. concluded that the encapsulation ratio of P(MMA-*co*-St) micro-PCMs containing paraffin was as twice as that of PSt micro-PCMs [16]. Additionally, Li et al. [17] and You et al. [1] respectively introduced divinylbenzene (DVB) as cross-linking agent in their polymerization system and successfully prepared P(St-*co*-DVB) micro-PCMs containing *n*-octacosane with the microencapsulation ratio both was more than 60 wt%. Besides, Fang et al. synthesized micro-PCMs containing *n*-octacosane with P(St-*co*-BA) shell (BA is short for butyl acrylate), and they pointed out that the microencapsulation ratio of these micro-PCMs was higher than 50 wt% [18]. Furthermore, when the *co*-polymer shell was polymerized with DVB and BA, the microencapsulation ratio of the micro-PCMs containing *n*-hexadecane was as high as 70 wt% [19]. All the above-mentioned researches indicated that appropriate *co*-polymerization systems are able to improve the microencapsulation ratio of micro-PCMs effectively.

In our previous work [20–23], the binary system of paraffin and butyl stearate with different weight ratio was introduced in the micro-PCMs as the core materials. The results indicated that the phase change temperature of these micro-PCMs could be adjusted from 28 °C to 35 °C by changing the weight ratio of

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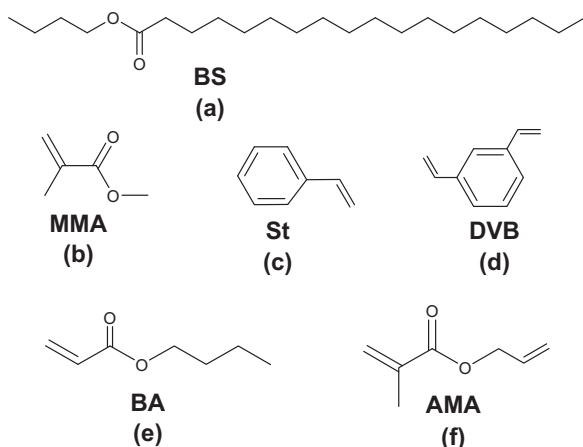


Fig. 1. Chemical structures of used reagents.

paraffin and butyl stearate. Besides, the influences of the binary core of the micro-PCMs on the microencapsulation process and thermal performances and stabilities were also systematically studied. Additionally, after 500 times thermal cycling test, the microencapsulation ratio loss of these as-prepared polyurea/polyurethane micro-PCMs was less than 13 wt%.

In this research work, in order to improve the thermal reliabilities of the micro-PCMs, we investigated the influence of different acrylate-based cross-linking agent on the thermal properties of micro-PCMs with paraffin and butyl stearate binary core materials. The results indicated that these as-prepared micro-PCMs kept excellent thermal reliabilities that the microencapsulation ratio decreased less than 4 wt% after 500 times thermal-cycling test.

2. Experimental

2.1. Materials

Paraffin (Nanyang Paraffin Fine Chemical Factory, China), butyl stearate (BS, Sinopharm Chemical Reagent Co. Ltd, China) were selected as core materials. 2,2'-azobisisobutyronitrile (AIBN, 98%, Aladdin Chemical Reagent Co. Ltd, China) was chosen as initiator. Monomers such as, methyl methacrylate (MMA, Sinopharm Chemical Reagent Co. Ltd, China), butyl acrylate (BA, Aladdin Chemical Reagent Co. Ltd, China), allyl methacrylate (AMA, 97%, Alfa Aesar a Johnson Matthey Company, China), styrene (St, Sinopharm Chemical Reagent Co. Ltd, China), divinylbenzene (DVB, 80%, Aladdin Chemical Reagent Co. Ltd, China). Sodium salt of styrene-maleic anhydride copolymer (TA, Shanghai Leather Chemical Works, China) was selected as stabilizer. The chemical structure of the above-mentioned reagents was schematically displayed in Fig. 1.

2.2. Preparation of micro-PCMs

The suspension-like polymerization system involves two phases: the dispersed phase containing organic reagents, such as, core materials, monomers and initiator; the continuous phase including TA and de-ionized water. The dosages and the compositions of the corresponding organic reagents were shown in Table 1.

The preparation was carried out as follows: (i) The dispersed phase was mixed under electromagnetic stirring at 40 °C for 15 min and homogeneous oil solution was obtained; (ii) the dispersed phase was then added into the continuous phase (including 3.0 g TA and 70 g de-ionized water) and kept for 10 min at 40 °C with water thermostat bath to form oil-in-water emulsion; (iii) the oil-in-water emulsion was further homogenized with an emulsifier at 8500 rpm for 5 min to form homogeneous stable emulsion; (iv)

the stable emulsion was placed into a 250 ml three-neck round-bottomed flask with a mechanical stirrer and water thermostat bath, and the suspension-like polymerization process proceeded at 85 °C for 6 h under the stirring speed of 550 rpm.; (v) The resultant micro-PCMs were filtered and washed with de-ionized water for three times, and finally dried in an oven at 45 °C for 48 h.

2.3. Thermal reliability test of micro-PCMs

These as-prepared micro-PCMs were subjected to repeated cycles of melting and freezing using heating-cooling cyclic oven (BPH-060A, Bluepard Experimental Equipment Co. Ltd, China). Each sample was tested through 500 cycles of alternative heating and cooling in the temperature range of 15–50 °C. The heating or cooling rate was 1 °C/min, and each sample was kept for 5 min at 15 °C or 50 °C. These samples were enclosed in filter paper in order to absorb the core materials that possibly leaked out of the microcapsules in thermal treatment [20–23].

2.4. Characterizations of micro-PCMs

Fourier transformed infrared (FT-IR) spectra were obtained using a spectrophotometer (VERTEX 70, BRUKER, Germany). The spectrum was collected by scanning number of 32 at a resolution of 4 cm⁻¹ in the wave number range of 400–4000 cm⁻¹.

The morphologies of these as-prepared micro-PCMs were investigated using a field emission scanning electron microscope (FE-SEM, S-4800, HITACHI, Japan). Samples were coated with gold, and observed under secondary electron mode with an accelerating voltage of 1.0 kV.

The melting and freezing behaviors of the micro-PCMs were measured using a differential scanning calorimeter (DSC, 823e, Mettler Toledo, Switzerland). Every time, 6–7 mg sample was placed in an alumina pan, and the sample chamber was purged with argon at a constant flow rate of 60 ml/min. Considering the low thermal conductivity of micro-PCMs, the phase transition properties of samples were determined by varying the temperature from 0 to 50 °C with the heating and cooling rate of 5 °C/min [24].

The thermal stabilities of all the samples were determined using a thermal gravimetric analyzer (TGA, TGA/DSC 1, Mettler Toledo, Switzerland) at a linear heating rate of 10 °C/min in argon (50 ml/min) with the temperature range from 25 °C to 600 °C. Every time, 8–9 mg sample was placed in an alumina pan for measurement.

The microencapsulation ratio of these as-prepared micro-PCMs was calculated using the following Eq. (1) [11,25]:

$$C\% = \left(\frac{\Delta H_{\text{micro-PCMs}}}{\Delta H_{\text{PB}}} \right) \times 100 \text{ wt\%} \quad (1)$$

where $\Delta H_{\text{micro-PCMs}}$ is the melting enthalpy of the micro-PCMs;

ΔH_{PB} is the melting enthalpy of the binary core materials, which was composed of paraffin and BS, as listed in Table 1, the binary system of paraffin and BS was introduced in the micro-PCMs as the core materials. PB is short for paraffin and BS mixture with the weight ratio of 1.00:1.00.

3. Results and discussion

3.1. Chemical structure of PCMs and micro-PCMs

Fig. 2 showed the FT-IR spectra of paraffin, BS, PB, and the micro-PCMs, respectively. Considering BS, MMA, BA and AMA are all esters, and DVB both have benzene group, the attribution of the absorption peaks were analyzed and summarized as follows [16,26,27]: the peaks at 2957, 2924 and 2854 cm⁻¹ were caused by C–H stretching vibration of –CH₃ and –CH₂, respectively.

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