Synthesis, thermal properties and thermal reliabilities of microspheres with ester mixtures as phase change materials

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Abstract. Using suspension-like polymerization method, a series of microspheres with ester mixtures as phase change materials were prepared. Thermal properties of the binary mixtures like, paraffin/butyl stearate, paraffin/octadecyl methacrylate, and paraffin/dodecyl 2-methylacrylate, and ternary mixtures, like paraffin/butyl stearate/octadecyl methacrylate and paraffin/butyl stearate/ dodecyl 2-methylacrylate, were investigated. The phase change temperature of these binary and ternary systems could be adjusted by regulating the composition of them. SEM photographs showed that these microspheres have spherical profiles and compact surfaces with diameter ranging from 10 to 80 μm. DSC results indicated that the melting enthalpy of these microspheres ranging from 30 to 65 J/g. Moreover, after being subjected to thermal-cycling test for 500 times, these microspheres kept good thermal performances and reliabilities.

1. Introduction
Due to the aggravation of energy crisis, thermal energy storage (TES) has attracted ever-increasing attention. TES includes sensible heat storage, latent heat storage and thermo-chemical or combination of these. Compared with sensible heat storage and thermo-chemical system, latent heat storage is one of the most attractive type because large amount of thermal energy could be stored or released when the storage materials undergoes a phase change process within a narrow temperature interval. Therefore, more and more attention has been paid to latent heat storage system. 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 solar energy storage, heat transfer, construction materials and air-conditioning.

Compared with inorganic PCMs, organic PCMs like paraffin and saturated hydrocarbons are frequently used as core materials, due to their advantages in polymerization process and application [1, 2]. Nevertheless, esters [3, 4] like butyl stearate, are also excellent PCMs, and they can be microencapsulated and utilized as microencapsulated phase change materials (micro-PCMs) for thermal energy storage [5]. Due to the high cost and the polarity chemical structure of them, little information is available on the researches of these PCMs. Recently, Aydin et al [6] proposed that the high-chain fatty acid esters are new PCMs and have an excellent potential to be used as PCMs. The high-chain fatty acid esters of myristyl alcohol were synthesized by the reaction of the acids and alcohols with different carbon atoms, and the resultants displayed good thermal properties as PCMs. It
should be considered for the utilization of PCMs is that the selected PCMs must have appropriate phase change temperature with relatively high enthalpy. A sufficient strategy for adjusting phase change temperature is achieved by selecting or combining homologues PCMs. Up to now, saturated hydrocarbons [7-9] or fatty acids [10] with different carbon atoms are mixed respectively with other own family to form the binary or ternary systems, and these as-prepared mixtures with their own special phase change performances are utilized in the areas of thermal energy storage and thermal protections.

In our previous work [11-14], the binary system of paraffin and butyl stearate with different weight ratio was introduced in the micro-PCMs as the core materials. The micro-PCMs with polyurea/polyurethane shell or acrylate-based polymer shell have been studied, and the thermal properties of the micro-PCMs with the binary core were investigated as well. 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 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. In this research work, ester PCMs like octadecyl methacrylate and dodecyl 2-methylacrylate were respectively introduced to constitute binary or ternary systems with paraffin and butyl stearate, and the phase change properties of these systems were studied. Furthermore, microspheres were prepared by introducing the above-mentioned phase change systems, methyl methacrylate (MMA) and divinylbenzene (DVB), thermal properties and thermal reliabilities of these as-prepared microspheres were also investigated. All the results indicated that these microspheres have a good potential as thermal energy storage materials.

2. Experimental

2.1. Materials
Paraffin (Nanyang Paraffin Fine Chemical Factory, China), butyl stearate (BS), octadecyl methacrylate (OM), dodecyl 2-methylacrylate (DM) were selected as PCMs. 2,2’-azobisisobutyronitrile (AIBN) was chosen as initiator. Monomers were methyl methacrylate (MMA) and divinylbenzene (DVB). Sodium salt of styrene-maleic anhydride copolymer was selected as stabilizer. The chemical structures were schematically displayed in Fig. 1.

![Fig.1. The scheme of microencapsulated process of microspheres.](image)

2.2. Preparation of microspheres
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.
3. Results and discussion

3.1. Morphology of microspheres

The morphologies of the microspheres with different co-polymer shells were shown in Figure 2.

OM and DM was not only excellent PCMs as their own, but they could co-polymerize with MMA and DVB for their vinyl group. Therefore, the resultants were microspheres rather than microcapsules. In the case of the absence of BS, when the amount of paraffin and OM was 5.00 g, micro-PO-1 had very smooth and compact surface with spherical profiles and no dimples. When the amount of paraffin and OM increased to 8.00 g, micro-PO-2 became rougher and individual fragments appeared. Moreover, when the amount of paraffin and DM was 5.00 g, micro-PD-1 also had very smooth and compact surface with spherical profiles and no dimples. At the same time, when the amount of paraffin and DM increased into 8.00 g, micro-PD-2 still kept excellent morphology. This result indicated that compared with OM, DM copolymerized more synergistically with MMA and DVB. In order to observe the inner structure of these samples, micro-PO-1 and micro-PD-1 were broken. As seen that all these “matrix encapsulation” in which the core materials was distributed homogeneously into the shell materials. It was because OM and DM could react with MMA and DVB due to their vinyl group which led to the appearance of solid microspheres instead of core-shell structure. Thus, the microcapsule structure grew into microsphere entire integrity structure. This microsphere morphology might reduce the possibility of the shell deformation during contracting process. With the participation of BS in the co-polymerization system, there were no microspheres could be synthesized. When MMA was replaced by DVB, and with DVB increased from 2.50 g to 3.00 g, the microspheres turned more and more smooth and spherical without coagulation. Additionally, after 500 times thermal cycling test, micro-PBO-3 remained excellent morphology without broken fragments. If the dosage of paraffin and BS respectively was 2.50 g, no microspheres could be obtained when MMA was introduced into the co-polymerization system like micro-PBD-1 or the weight ratio of DVB to DM was too low like micro-PBD-5. Additionally, with the same amount of paraffin and BS both was 2.50 g, compared micro-PBD-2, the surface of micro-PBD-2 were rougher due to the relatively low weight ratio of DVB to DM, suggesting that increasing amount of DVB could help to form more smooth surface of microspheres. Meanwhile, in comparison with micro-PBD-2, micro-PBD-6 and micro-PBD-7 which all had the same weight ratio 1.00:1.00 of DVB to DM, the most desirable microspheres could be synthesized when the weight ratio of paraffin to BS was 1.00:1.00 (micro-PBD-2). Besides, when the amount of BS was 1.00 g or 4.00 g and paraffin correspondingly was 4.00 g or 1.00 g, these as-prepared microspheres became more fragile with many breakages (micro-PBD-1 and micro-PBD-7). When the weight ratio of paraffin: BS: DM was 1.00:1.00:1.00, the best microspheres could be prepared. Furthermore, with the increasing dosage of BS, the long chain of BS would increase the viscosity of the reaction system and impair the polymerization process leading to bad morphologies of these samples. Moreover, when the amount of PB-1 increased from 5.00 g to 7.00 g, micro-PBD-3 still kept good morphology with little broken surface. In addition, micro-PBO-3 and micro-PBD-2 both remained good thermal reliabilities after 500 times thermal cycling, but micro-PBD series became more fragile than micro-PBO series after 500 times thermal cycling test.
3.2. Thermal performances of microspheres

Phase change properties of these as-prepared microspheres were listed in Table 1, and Figure 3. The phase change temperature of these microspheres was in the range of 26 °C to 33 °C.

These as-prepared microspheres were divided into two sets. The first set was the microspheres prepared without the participation of BS, which were series of micro-PO and micro-PD. Micro-PBO and micro-PBD were the second set. For the first set, when using the same amount of paraffin, MMA and DVB, the melting enthalpy of micro-PO-1 was about 10 J/g higher than that of micro-PD-1. Besides, when the dosage of the binary systems (PO or PD) increased from 5.00 g to 8.00 g, the melting enthalpy of micro-PO series increased by 25.65 J/g (for micro-PO-2, \( \Delta H_m = 64.85 \) J/g). But for the micro-PD series, the melting enthalpy almost did not change (for micro-PD-2, \( \Delta H_m = 29.74 \) J/g). This result indicated that though DM react more synergistically with MMA and DVB than OM did, it did not contribute to the phase change performance within about 30 °C as much as OM did. For the second set, no microspheres could be obtained if MMA joined in the co-polymerization process. In addition, if the dosage of paraffin, BS and DVB were all 2.50 g, when the amount of DM was 2.50 g, the melting enthalpy of micro-PBD-2 was 46.62 J/g, but no microspheres could be gotten when using
OM instead of DM. Besides, when the dosage of OM and DVB was respectively 2.00 g and 3.00 g, microspheres could be prepared and the melting enthalpy of micro-PBO-3 was 59.60 J/g. Furthermore, for the micro-PBD series, when the amount of DVB increased from 2.50 g to 4.00 g, the melting enthalpy of these microspheres increased by 10.58 J/g (micro-PBD-2 and micro-PBD-4). When the weight ratio of paraffin to BS decreased, the melting enthalpy of the microspheres decreased because the melting enthalpy of BS was lower than that of paraffin. Besides, when the amount of PB-1 increasing from 5.00 g to 7.00 g, the melting enthalpy of the microspheres increased by 16.16 J/g (micro-PBD-2 and micro-PBD-3). After 500 times melting-freezing thermal cycling test, they kept excellent thermal reliability that the melting enthalpy of these microspheres almost did not change. For example, the melting enthalpy of micro-PBO-3 was 59.08 J/g after 500-times thermal cycling test and the melting enthalpy for the original sample was 59.60 J/g.

Table 1. Basic compositions and thermal performances of the microspheres.

| NO.       | Paraffin (g) | BS (g) | MMA (g) | DVB (g) | OM (g) | DM (g) | $T_{pm}^{*}$ (°C) | $\Delta H_m^*$ (J/g) |
|-----------|--------------|--------|---------|---------|--------|--------|-----------------|------------------|
| Micro-PO-1| 2.50         | -      | 2.50    | 2.50    | 2.50   | -      | 28.37           | 39.20            |
| Micro-PO-2| 4.00         | -      | 2.50    | 2.50    | 4.00   | -      | 33.05           | 64.85            |
| Micro-PBO-1| 2.50       | 2.50   | 2.50    | -       | 2.50   | -      | No microspheres |                  |
| Micro-PBO-2| 2.50       | 2.50   | -       | 2.50    | 2.50   | -      | No microspheres |                  |
| Micro-PBO-3| 2.50       | 2.50   | -       | 3.00    | 2.00   | -      | 29.52           | 59.60            |
| Micro-PD-1| 2.50         | -      | 2.50    | 2.50    | -      | 2.50   | 27.35           | 29.38            |
| Micro-PD-2| 4.00         | -      | 2.50    | 2.50    | -      | 4.00   | 28.80           | 29.74            |
| Micro-PBD-1| 2.50       | 2.50   | 2.50    | -       | -      | 2.50   | No microspheres |                  |
| Micro-PBD-2| 2.50       | 2.50   | -       | 2.50    | -      | 2.50   | 26.68           | 46.62            |
| Micro-PBD-3| 3.50       | 3.50   | -       | 2.50    | -      | 2.50   | 26.36           | 62.78            |
| Micro-PBD-4| 2.50       | 2.50   | -       | 4.00    | -      | 1.00   | 29.22           | 57.20            |
| Micro-PBD-5| 2.50       | 2.50   | -       | 1.00    | -      | 4.00   | No microspheres |                  |
| Micro-PBD-6| 4.00         | 1.00   | -       | 2.50    | -      | 2.50   | 29.19           | 57.97            |
| Micro-PBD-7| 1.00         | 4.00   | -       | 2.50    | -      | 2.50   | 25.99           | 35.70            |

Figure 3. DSC curves of the microspheres
4. Conclusions
Using suspension-like polymerization method, the microencapsulation ratio of these as-prepared microspheres was in a high range of 46 wt% to 68 wt%. The melting enthalpy of the microspheres containing OM was relatively higher than that of DM. Moreover, after the treatments of 500 times thermal-cycling test, the microspheres still keep excellent reliability.

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