Preparation of Silica Microcapsules Containing Octadecane as Temperature-adjusting Powder

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Spherical microcapsules of silica-shelled octadecane are prepared in the presence of polyvinyl alcohol in an O/W emulsion. The silica shell forms via hydrolysis and condensation from tetraethyl silicate with acetatic acid as catalyst. The thermogravimetric curves show that the microcapsules have thermal stability superior to that of octadecane. The latent heat and the melting point of microcapsule are 162 J·g^{-1} and 30 °C, respectively.

During recent decades, phase-change materials (PCMs) have attracted considerable interest in the fields of energy storage.[1–3] Generally, there are two key problems that play negative roles on the applications of some PCMs: (i) during crystallizing process, working substance (WS)[4] freezes on the inner wall of container, leading to the increase of thermal resistance; (ii) WS is corrosive to container, resulting in the leakage of WS. In order to solve the two problems, preparing composite PCMs by capsulating or loading WS using inorganic or organic host materials are generally considered. For example, polyurea-capsulated *n*-hexadecane,[5] expanded graphite loaded with paraffin,[6] silica-coated paraffin/polyethylene[7] have been reported.

As versatile host materials,[8] hollow silica spheres are usually obtained using oil droplet as template.[9,10] Thus, it is probable to prepare microcapsules of silica-shelled hydrophobic WS. Moreover, the PCM microcapsules with silica as shell possess the following features: (i) hydrophilic surface can be obtained conveniently; (ii) the antioxidization property is improved; (iii) using silica as shells can avoid some toxic remainders in the final products, such as toluene diisocyanate[11] and formaldehyde used as monomers for preparing shells of some PCM microcapsules.

This paper reports spherical microcapsules of silica-shelled octadecane, prepared from an O/W emulsion in the presence of polyvinyl alcohol (PVA) as stabilizer,[12] and sorbitan monooleate (Span80) and polyoxyethylene(20) sorbitan monooleate (Tween80) as emulsifiers.

A typical microencapsulation procedure was carried out as follows: (i) 1.0 g of PVA was dissolved in 49.0 mL of distilled water; (ii) An organic solution of 4.6 g of octadecane (99 mass %) and 1.5 g of mixed surfactants (45.0 mass % Span 80 and 55.0 mass % Tween 80) was prepared; (iii) The aqueous PVA solution was added to the organic solution, and the mixture was emulsified mechanically at stirring rates of 600 rpm to form an O/W emulsion; (iv) While stirring, 1.0 g of sodium chloride solution (2.5 M) was added into the emulsion; (v) After stirring for 30 min, 7.5 g of tetraethyl silicate (TEOS) and 0.1 g of acetate acid solution (10.0 mass %) were slowly added into the emulsion system to start the hydrolysis and condensation of TEOS; (vi) After the addition, the reaction mixture was heated to 55.0 °C for 3 h. The resultant microcapsules (denoted as sample-1) were filtered, washed with distilled water, and dried at 55.0 °C in oven for 24 h.

The concentration of PVA is found to have important role on the morphology and size of microcapsule. The SEM micrographs of the microcapsules prepared from emulsions with different concentrations of PVA (0, 0.5, and 1.5 mass %) are presented in Figures 1a–1c.[13] Microcapsules have not been obtained without using PVA (in Figure 1a). Using 0.5 mass % PVA, product with irregular morphology formed (in Figure 1b). When the concentration of PVA is 1.5 mass %, most of microcapsules in sample-1 are regular micrometer-sized spheres with smooth surface (in Figure 1c), the diameter (D_{50}) of which is 6 μm by a laser particle size analyzer. However, elevating the concentration of PVA to 2.3 mass % resulted in a white viscous sol product, instead of solid product. The SEM micrograph (Figure 1d) of the ground, broken and deformed sample-1 indicates that the spherical microcapsules (shown in Figure 1c) possess a hollow structure.

The thermogravimetry (TG) curves (Figure 2a) show that the temperature corresponding to initial weight loss (5 mass %) of octadecane is 128 °C, while that of sample-1 is 141 °C, suggesting that sample-1 has a higher thermal stability than that of octadecane. The weight loss of octadecane ends at 220 °C, and the maximum weight loss of sample-1 is 55 mass % at 225 °C, indicating that the content of octadecane in sample-1 is about 55 mass %.

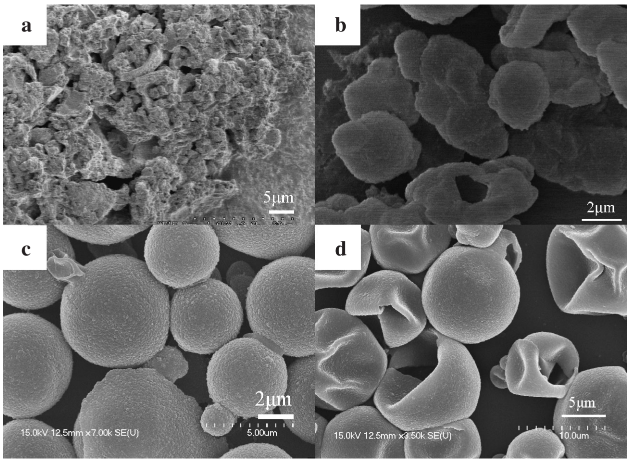

Figure 1. SEM micrographs of microcapsules from emulsions containing PVA: (a) 0 mass %; (b) 0.5 mass %; (c) 1.5 mass %, and (d) the micrograph of broken and deformed shell.

Besides the TG analysis, the content of octadecane in sample-1 was further calculated based on differential scanning

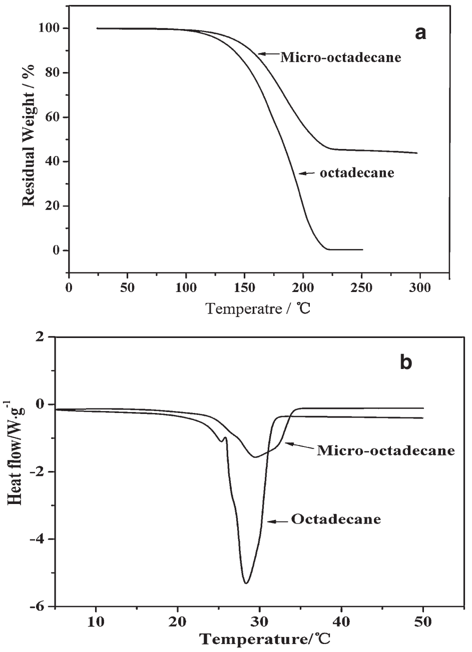

Figure 2. (a) TG curves of sample-1 and octadecane at heating rate of 10 °C·min^{-1} under nitrogen atmosphere and (b) DSC curves of sample-1 and octadecane at heating rate of 5 °C·min^{-1}.

Table 1. Synthesis conditions and ΔH_f of microcapsules

Sample	Oct/g[a]	T_m/°C	ΔH_f/J·g^{-1}	Content/% by ΔH_f
1	4.6	30	119	50.4
2	3.1	32	61	25.8
3	3.9	31	80	33.9
4	6.2	30	162	68.6
5	b	29	236	100

[a]Oct: octadecane. [b]Octadecane without shell.

calorimetry (DSC).[14] DSC curves (Figure 2b) show that the temperature range of phase change (fusion range) of sample-1 is similar to that of octadecane. The ΔH_f of octadecane is 236 J·g^{-1} and its melting point temperature (T_m) is 29 °C; The ΔH_f of sample-1 is 118 J·g^{-1} and its T_m is 30 °C. Accordingly, the content of octadecane in sample-1 is about 50 mass %, which is basically in accordance to result of TG.

A series of microcapsules (listed in Table 1) have been obtained by varying the feed amount of octadecane (the content of PVA equaling 1.5 mass %). With the increase of the feed amount of octadecane, the ΔH_f increases, and the T_m decreases slightly and approaches that of octadecane. The core content and ΔH_f of sample-4 are 68.6 mass % and 162 J·g^{-1} respectively, indicating a relatively higher energy storage capacity.

In order to measure the property of adaptable temperature, heating-up experiments on the cloth coated with sample-4 has been performed (Figure 3). Firstly, a piece of cloth coated with the mixture (75 mass % sample-4 and 25 mass % binder)[15] on one side was cooled to 18 °C and then placed in the environment of 34 °C. Subsequently the heating-up curve on the temperature of coating surface vs. time was recorded using infrared radiation thermometer. It spent 4 min for cloth coated with sample-4 to reach thermal balance. However, the heating-up time of control sample, a piece of cloth coated with equal weight of silica and binder, is only 30 s. The result indicates that the sample-4 possesses a significant property of adaptable temperature.

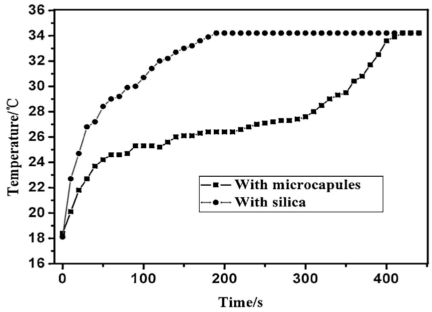

Figure 3. Heating curves of the two pieces of coated cloth.

In summary, the spherical microcapsules of silica-shelled octadecane were prepared. This microcapsule has a relatively higher energy storage capacity of 162 J·g^{-1} and a proper mean diameter of 5–7 µm within the scale (at least smaller than 10 µm) desirable for textile coatings.[16]

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4 For clearly discussing, the working substance (WS) denotes material that undergoes phase transition, instead of container or coating materials.

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