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Effects of Nucleating Agents on the Properties of Microencapsulated Phase Change Material

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The microcapsules containing *n*-octadecane and nucleating agents with about 1 μm in average diameter were prepared through *in situ* polymerization. The effects of nucleating agents, *i.e.* sodium chloride, 1-octadecanol and paraffin, on the crystallization properties, morphology and dispersibility of microcapsules were investigated by using SEM and DSC. The super-cooling was prevented by adding sodium chloride to the emulsion, however, the surfaces of the microcapsules were rough and the microcapsules were worse dispersed. Adding 1-octadecanol in core material was found to prevent microcapsules from super-cooling, but the surfaces of the microcapsules were rough and the microcapsules were easily conglomerated. Microcapsules containing 20 wt % paraffin in core material were free from super-cooling. And paraffin had no influence on the morphology and dispersibility of microcapsules.

Key Words: Microcapsules, Phase change material, Super-cooling, Nucleating agent, Sodium chloride, 1-Octadecanol, Paraffin.

INTRODUCTION

Since Mehalick and Tweedie[1] investigated microencapsulated phase change materials as a heat transfer fluid to enhance both heat transport characteristics and energy storage properties in 1979, MicroPCMs have been widely applied to fabrics[2,3] and suspensions for the heat transfer. Furthermore, MicroPCMs are hopefully employed in microclimate environmental control on vegetation and seeds. Especially, Bryant and Colvin[4] incorporated MicroPCMs into fibers to prepare the fiber with reversible enhanced thermal storage properties. Subsequently, Bryant[5] prepared an acrylonitrile/vinyl acetate (AN/VA) copolymer fiber with 30 wt % MicroPCMs by wet spinning. Due to the enormous commercial potential of melt-spun fibers, Bryant[6] tried to yield polypropylene (PP) and polybutylene terephthalate (PBT) fibers containing 3 wt % MicroPCMs by melt spinning.

Although MicroPCMs are widely used in many fields, the super-cooling is still an important obstacle to the industrial application of MicroPCMs[7]. Yamagishi *et al.*[8] demonstrated that the crystallization temperatures of MicroPCMs with 5-100 mm in diameters lowered as their sizes decreased. Kishimoto *et al.*[9] found that 1-pentadecanol was able to prevent the super-cooling of *n*-paraffin (*e.g.* pentadecane) in MicroPCMs.

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Yamagishi *et al.*[8] selected 1-tetradecanol (2 wt % by weight of the core material) as the nucleating agent for super-cooling prevention of *n*-tetradecane in MicroPCMs (microcapsules diameters 110-300 mm). Mamoru[10] also synthesized MicroPCMs consisted of *n*-alkanol and *n*-paraffin without super-cooling. Lee[11] considered that the derivatives of *n*-paraffin, such as 1-octadecylamine, 1-octadecanol, were suitable for prevention of super-cooling of the phase change material (PCM) and were used appropriately within a range of about 1 wt % to 6 wt % with respect to the weight of the PCM. However, the influence of the nucleating agents on the enthalpies of the MicroPCMs except the super-cooling was not studied. In addition, sodium salts and compounds are often employed as an additive in the process of MicroPCMs preparation[12]. Sodium chloride may partially remain in MicroPCMs and affect on the crystallization of PCM and the other properties of MicroPCMs. However, the effect of sodium chloride on the crystallization of PCM has not been reported.

In this paper, the effects of sodium chloride, 1-octadecanol and paraffin on the melting and crystallization behaviours, morphology and dispersibility have been studied.

EXPERIMENTAL

Melamine (Tianjin Resin Factory) and formaldehyde (37 wt % aqueous solution, A.R., Tianjin Chemical Reagent Factory) were used as shell-forming monomers; N-octadecane (purity 99 %, Union Lab. Supplies Limited, Hong Kong) was used as core material. Sodium chloride (A.R., Tianjin Tanggu Chemistry Reagent Factory), 1-octadecanol (A.R., Beijing Chemistry Industry Factory) and paraffin (melting point 60-65 °C, Shanghai Hualing Chemical Factory) were used as the nucleating agents for preventing *n*-octadecane in MicroPCMs from super-cooling, respectively. Anionic surfactant, TA (styrene-maleic anhydride copolymer, 19 wt % aqueous solution, Shanghai Leather Chemical Auxiliary Plant) was used as an emulsifier.

Preparation of microcapsules: A solution of *n*-octadecane and various amounts of 1-octadecanol or paraffin (Tables 2 and 3) was prepared. 20 g of TA was dissolved in distilled water to form an emulsion. The solution was added to the emulsion and the mixture was emulsified mechanically with a stirring speed of 8000 rpm for 1.5 h to form an oil-in-water system in a reactor equipped with circulated cooling water. Simultaneously, the prepolymerization was carried out in a three-neck round-bottomed flask equipped with a mechanical stirrer. 19.5 mL of formaldehyde, 10 g of melamine and 20 mL of distilled water were added to the flask. The pH of the mixture was regulated to 8-9 with triethanolamine. The prepolymer was prepared at 70 °C with a stirring speed of 250 rpm until the mixture became transparent. The emulsion was shifted to a three-neck round-bottomed flask after the pH was regulated to 4-5. Then the prepolymer was slowly added into the emulsion system to start *in situ* polymerization at 70 °C with a stirring speed of 100 rpm. After the prepolymer was added, the reaction continued with a stirring speed of 600 rpm for 3 h. The resultant microcapsules were filtered and washed with boiling distilled water for twice to remove remaining reactants and TA and then dried in an oven at 100 °C.

Sodium chloride was added into the emulsion system and the microcapsules were prepared (Table-1). The processes were just the same as those of microcapsules containing 1-octadecanol or paraffin.

TABLE-1
CONTENTS OF SODIUM CHLORIDE IN RAW MATERIALS

Samples		Control	A_1	A_2	A_3	A_4	A_5	A_6
Sodium chloride	Mass W_1 (g)	0	6	18	21	24	36	48
	Concentration in water C_1 (wt %)	0	1.88	4.74	5.38	6.00	8.78	10.55
n-Octadecane/g					40.0			
Formaldehyde (37 % aqueous solution) (mL)					19.5			
Melamine (g)					10.0			
TA (19 % wt aqueous solution) (g)					20.0			

TABLE-2
CONTENTS OF 1-OCTADECANOL IN RAW MATERIALS

Samples		Control	B_1	B_2	B_3	B_4	B_5
1-Octadecanol	Mass W_2 (g)	0	1	2	3	4	6
	Concentration in core C_2 (wt %)	0	2.44	4.76	6.98	9.09	13.04
n-Octadecane (g)					40.0		
Formaldehyde (37% aqueous solution) (mL)					19.5		
Melamine (g)					10.0		
TA (19 % wt aqueous solution) (g)					20.0		

TABLE-3
CONTENTS OF PARAFFIN IN RAW MATERIALS

Samples		Control	C_1	C_2	C_3	C_4	C_5
Paraffin	Mass W_3 (g)	0	2	4	8	12	20
	Concentration in core C_3 wt (%)	0	5	10	20	30	50
n-Octadecane (g)		40	38	36	32	28	20
Formaldehyde (37 % aqueous solution) (mL)				19.5			
Melamine (g)				10			
TA (19 % wt aqueous solution) (g)				20			

Characterization of the microcapsules: A drop of the microcapsule dispersion to be investigated was dripped on a stainless steel SEM stub and air-dried overnight and then silver-coated. The morphology and dispersibility of the microcapsules containing *n*-octadecane and nucleating agents were observed through scanning electronic microscopy (SEM) (KYKY-2800, China Zhongke Scientific Instrument Inc.).

The thermal properties of the microcapsules were measured using differential scanning calorimetry (DSC) (Perkin-Elmer, DSC7) at a heating or cooling rate of 10 °C/min under a nitrogen atmosphere and the multi peaks were separated by the "Peaksep" program of NETZSCH - TA4.

RESULTS AND DISCUSSION

Effect of sodium chloride on the properties of MicroPCMs: Fig. 1 shows the DSC curves of MicroPCMs adding various concentration (C_1) of sodium chloride. Sodium chloride has no effect on the endothermic peak, but affects remarkably on the exothermic peaks as compared to control. Two exothermic peaks due to different nucleation mechanism are shown in the DSC cooling curves. Based on Yamagishi's results, the peak α is attributed to the homogeneous nucleation of *n*-octadecane and its heterogeneous nucleation leads to the peak β[8]. When sodium chloride concentration (C_1) is 6.00 wt %, the peak β shifts to the higher temperature and the integrated area of peak β increases. The number of nuclei in each droplet decreases as the droplet size reduces. As a result, the crystallization temperature of microcapsules lowers with reducing the size[8]. The DSC results indicate that, sodium chloride, as the nucleating agent, promotes the heterogeneous nucleation of *n*-octadecane. In addition, based on the DSC data, the melting enthalpies and the crystallization ones of microcapsules fluctuate between 160 J/g and 170 J/g as sodium chloride concentration (C_1) increasing, because the feed amount of *n*-octadecane is not changed (Table-1).

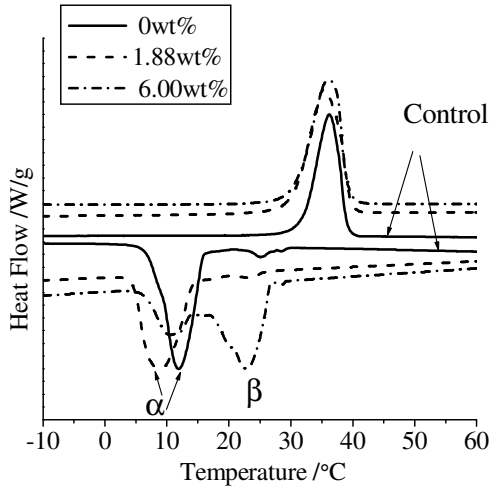
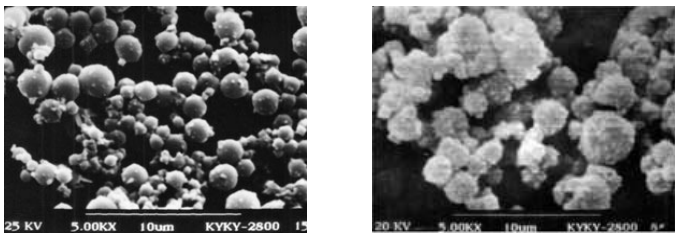


Fig. 1. DSC curves of MicroPCMs feeding sodium chloride of various concentration in water (C_1)

Fig. 2 shows that sodium chloride has great effect on the morphology and dispersibility of microcapsules. The surfaces of microcapsules without sodium chloride are smooth and the dispersibility is fine. By contraries, the surfaces of microcapsules feeding 6.00 wt % sodium chloride are rough and the microcapsules are stuck together. It can be explained by sodium chloride causing anion electrolyte TA to occur coacervation[13].



(a) (b)

Fig. 2. SEM photographs of microcapsules: (a) Control; (b) 6.00 wt % sodium chloride in water

Effect of 1-octadecanol on the properties of MicroPCMs: Fig. 3 shows the DSC curves of microcapsules containing various concentration (C_2) of 1-octadecanol in core material. Both the endothermic peak and the exothermic peaks of microcapsules with 2.44 wt % 1-octadecanol are similar to those of control (Fig. 1). When the concentration (C_2) is 9.09 wt %, its endothermic behaviour is still not change, but its exothermic peaks shift to the higher temperature and the onset point (28.40 °C) is close to that of the endothermic peak (30.04 °C). It shows that excessive 1-octadecanol can prevent the microcapsules with *n*-octadecane as core material from super-cooling, which is associated with the precipitation of redundant 1-octadecanol in *n*-octadecane near the melting point of *n*-octadecane. The solubility of 1-octadecanol in hexadecane reduces quickly from the melting point of 1-octadecanol to the melting point of hexadecane[14], so does its solubility vary in *n*-octadecane. Similar to microcapsules feeding sodium chloride, the melting enthalpies and crystallization ones of microcapsules containing 1-octadecanol are located within the range of 160 to170 J/g and vary slightly with 1-octadecanol concentration (C_2) increasing due to the constant feeding amount of *n*-octadecane.

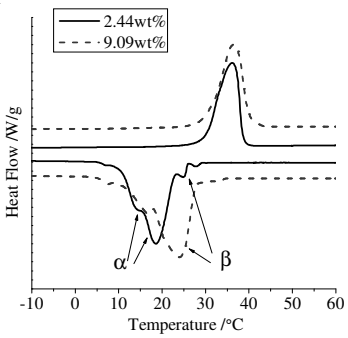
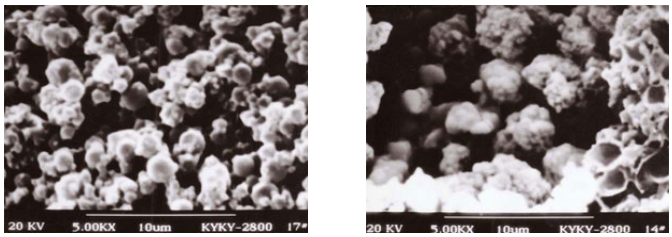


Fig. 3. DSC curves of MicroPCMs containing 1-octadecanol of various concentration in core material (C_2)

9.09 wt % 1-Octadecanol in *n*-octadecane has effect on the morphology and dispersibility of microcapsules (Fig. 4). Compared to microcapsules without 1-octadecanol (Fig. 2a), microcapsules with 2.44 wt % 1-octadecanol in core material

still have smooth surfaces and these microcapsules are slightly stuck together. However, the surfaces of microcapsules with 9.09 wt % 1-octadecanol are extraordinarily rough and the dispersibility is too bad to observe an intact microcapsule through SEM (Fig. 4b). It can be explained by the reactions between hydroxyl group (-OH) of 1-octadecanol and the groups in melamine-formaldehyde polycondensate, including amino group ($-NH_2$), imino group (-NH) and hydroxyl group (-OH). Such a result limits the application of 1-octadecanol as the nucleating agent in this system.



(a) (b)

Fig. 4. SEM photographs of microcapsules containing 1-octadecanol of various concentration in core material: (a) 2.44 wt %; (b) 9.09 wt %

Effect of paraffin on the properties of MicroPCMs: Fig. 5 illustrates the DSC curves of microcapsules with different concentration (C_3) of paraffin in core material. Compared to microcapsules without paraffin (Fig. 1), two endothermic peaks due to *n*-octadecane melting (α) and paraffin melting (β) are shown in the DSC heating curves of microcapsules containing more than 20 wt % paraffin. The peak β in the endothermic peak broadens and shifts to higher temperature as paraffin concentration (C_3) increasing.

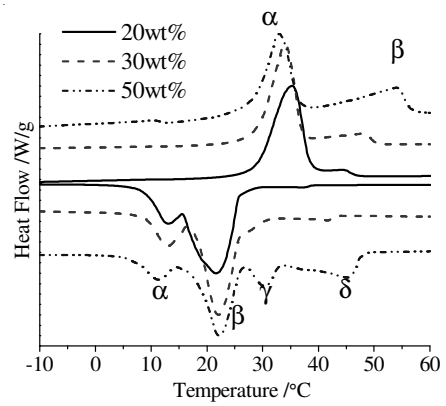


Fig. 5. DSC curves of MicroPCMs containing paraffin of various concentration in core material (C_3)

For microcapsules containing less than 30 wt % paraffin, two exothermic peaks (α-the homogeneous nucleation and β-the heterogeneous nucleation) appear in the

cooling curves. Triclinic crystal existing in even *n*-alkane[15,16] of paraffin is more beneficial to promote the formation of triclinic crystal in *n*-octadecane due to the same crystal structures. For microcapsules containing 50 wt % paraffin, however, four exothermic peaks are shown (Fig. 5) γ and δ thereof are attributed to the crystallization of paraffin. The enthalpy of crystallization is released in a wide temperature range by the multiple exothermic peaks. Therefore, it is not suitable to add too much paraffin into core material.

The relation between percentages of α (β) in the exothermic peaks or enthalpies of microcapsules and paraffin concentration (C_3) can be obtained from the DSC data of microcapsules containing various concentration (C_3) of paraffin (Fig. 6). Due to the amount of *n*-octadecane in core material decreasing, both the melting enthalpies and the crystallization ones of microcapsules with paraffin are lower than those of microcapsules without paraffin.

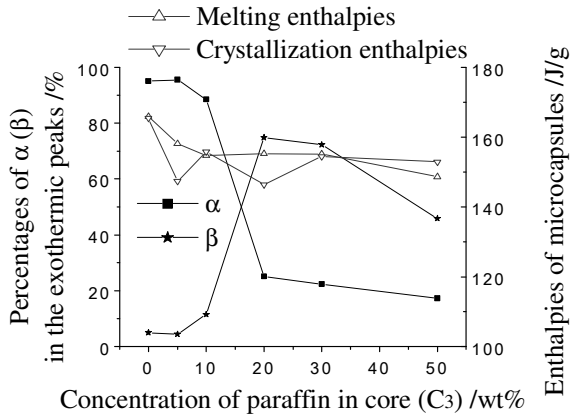
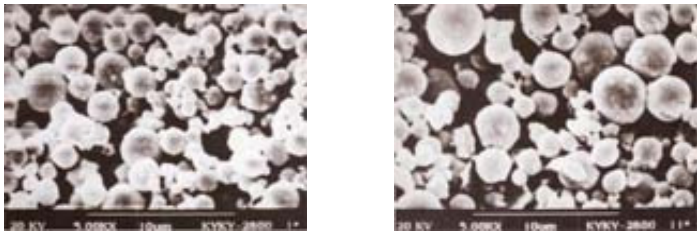


Fig. 6. Relation between percentages of α (β) in the exothermic peaks or enthalpies of microcapsules and concentration of paraffin in core material (C_3)

Obviously, the percentage of α in the exothermic peaks decreases sharply and accordingly that of β goes up rapidly as paraffin concentration (C_3) increasing (Fig. 6). As paraffin concentration (C_3) exceeds 20 wt %, the variation trend is not remarkable and the percentage of β decreases owing to the emergence of γ and δ in the exothermic peaks. For microcapsules containing 20 wt % of paraffin, the β percentage of microcapsules is about 75 % and the super-cooling is considered to being prevented.

Fig. 7 shows the SEM photographs of microcapsules with paraffin. The surfaces of microcapsules with paraffin are very smooth and the microcapsules are well dispersed, even when paraffin concentration (C_3) reaches 50 wt %. So the feeding of paraffin has no effect on the morphology and dispersibility of the microcapsules. It differs from the influence of sodium chloride or 1-octadecanol on that of microcapsules. Therefore, the preferred paraffin concentration (C_3) is 20 wt %.



(a) (b)

Fig. 7. SEM photographs of microcapsules containing paraffin of various concentration in core material: (a) 20 wt %; (b) 50 wt %

Conclusion

Addition of sodium chloride, 1-octadecanol and paraffin has effect on the melting and crystallization behaviours, morphology and dispersibility of microencapsulated *n*-octadecane. The super-cooling was prevented by feeding sodium chloride in the emulsion, but the surfaces of the microcapsules were very rough and the dispersibility was worse. The super-cooling could also be prevented by feeding 1-octadecanol in core material, however, the surfaces of the microcapsules were rough and the microcapsules were easily conglomerate. Differing from sodium chloride and 1-octadecanol, addition of 20 wt % paraffin in core material could prevent *n*-octadecane from super-cooling and have no effect on the morphology and dispersibility of microcapsules.

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