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Super-cooling prevention of microencapsulated phase change material

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Abstract

The microcapsules comprising *n*-octadecane and nucleating agents encapsulated in melamine-formaldehyde resin shell with about 1 μm in average diameter were prepared through in situ polymerization. The effects of nucleating agents, i.e. sodium chloride, 1-octadecnol and paraffin, on the crystallization properties, morphology and dispersibility of microcapsules were investigated using SEM, DSC and XRD. The super-cooling was prevented by adding about 6 wt.% sodium chloride to the emulsion, however, the microcapsules were worse dispersed and their surfaces were rough. Adding approximately 9 wt.% 1-octadecanol in core material was found to prevent microcapsules from super-cooling, but the microcapsules were easily conglomerated and their surfaces were extraordinarily rough. Microcapsules with approximately 20 wt.% paraffin in core material were free from super-cooling, and paraffin had no influence on the morphology and dispersibility of microcapsules.

Keywords: Microcapsules; Phase change material; Super-cooling; Nucleating agents

1. Introduction

Microencapsulated phase change materials (MicroPCMs) were studied in the late 1970s after phase change material (PCM) had long been employed as the thermal storage and control materials [1]. Along with Lane's effort which was made to incorporate PCM directly in structural materials in order to enhance the energy storage of the materials [2], Mehalick investigated MicroPCMs as a heat transfer fluid to enhance both heat transport characteristics and energy storage properties in 1979 [1]. From then on, MicroPCMs have been widely applied to fabrics [3–7], and suspensions for heat transfer [8], solar and nuclear heat storage systems [9] and packed bed heat exchangers [10]. Furthermore, MicroPCMs are hopefully employed in the microclimate environmental control on vegetation and seeds [11].

Although MicroPCMs are widely used in many fields, the super-cooling is still an important obstacle to the industrial application of MicroPCMs. Yamagishi et al. demonstrated that the crystallization temperature of MicroPCMs with 5–100 μm in diameters lowered as their sizes decreased [12]. Kishimoto et al. found that 1-pentadecanol was able to prevent the super-cooling of *n*-pentadecane in MicroPCMs [13]. Yamagishi selected 1-tetradecanol (2 wt.% by weight of the core material) as a nucleating agent for super-cooling prevention of *n*-tetradecane in MicroPCMs (microcapsule diameters 110–300 μm) [12]. Mamoru also synthesized MicroPCMs with the core material consisted of *n*-alkanol and *n*-paraffin without super-cooling [14]. Lee considered that the derivatives of *n*-paraffin, such as 1-octadecylamine, 1-octadecanol, were suitable for preventing PCM from super-cooling and were used appropriately within a range of about 1–6 wt.% with respect to the weight of PCM [15]. However, the influence of nucleating agents on the enthalpies of MicroPCMs except super-cooling have not been studied. In addition, the morphology and dispersibility of microcapsules with PCM and nucleating agents have been investigated.

In this paper, the effects of the nucleating agents, including sodium chloride, 1-octadecanol and paraffin, on the melting and crystallization behavior, morphology, and dispersibility were studied.

2. Experimental

2.1. Materials

Melamine (Tianjin Resin Factory) and Formaldehyde (37 wt.% aqueous solution, A.R., Tianjin Chemical

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Table 1
Contents of 1-octadecanol in raw materials

	Control	B_1	B_2	B_3	B_4	B_5	B_6	B_7	B_8	B_9
1-Octadecanol mass W_2 (g)	0	1.0	2.0	2.5	3.0	4.0	5.0	6.0	7.0	8.0
1-Octadecanol concentration in core C_2 (wt.%)	0	2.4	4.8	5.9	7.0	9.1	11.1	13.0	14.9	16.7
n-Octadecane (g)					40.0					
Formaldehyde (37% aqueous solution) (ml)					19.5					
Melamine (g)					10					
TA (19 wt.% aqueous solution) (g)					20					

Table 2
Contents of paraffin in raw materials

	Control	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
Paraffin mass W_3 (g)	0	2.0	4.0	6.0	8.0	10.0	12.0	16.0	20.0
Paraffin concentration in core C_3 (wt.%)	0	5.0	10.0	15.0	20.0	25.0	30.0	40.0	50.0
n-Octadecane (g)	40.0	38.0	36.0	34.0	32.0	30.0	28.0	24.0	20.0
Formaldehyde (37% aqueous solution) (ml)					19.5				
Melamine (g)					10				
TA (19 wt.% aqueous solution) (g)					20				

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 Works) was used as an emulsifier.

2.2. Fabrication of microcapsules

An organic solution of *n*-octadecane and various amounts of 1-octadecanol or paraffin (Tables 1 and 2) was prepared. About 20 g TA was dissolved in 300 ml distilled water to form an emulsion. The organic solution was added to the emulsion and the mixture was emulsified mechanically with a stirring speed of 8000 rpm for 90 min to form an oil-in-water system in a 1000 ml reactor equipped with circulated cooling water. Simultaneously, the prepolymerization was carried out in a 250 ml three-neck round-bottomed flask equipped with a mechanical stirrer. About 19.5 ml formaldehyde, 10 g melamine and 20 ml distilled water were added to the flask, respectively. 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 1000 ml 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 180 min. The resultant microcapsules were filtered and washed with boiling distilled water 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 3). Other processes were just the same as those of microcapsules with 1-octadecanol or paraffin.

2.3. 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 microcapsules with *n*-octadecane and different nucleating agents were observed through a scanning

Table 3
Contents of sodium chloride in raw materials

	Control	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9
Sodium chloride mass W_1 (g)	0	6.0	12.0	18.0	20.0	21.0	24.0	30.0	36.0	48.0
Sodium chloride concentration in water C_1 (wt.%)	0	1.9	3.0	4.7	5.0	5.4	6.0	7.5	8.8	10.6
n-Octadecane (g)					40.0					
Formaldehyde (37% aqueous solution) (ml)					19.5					
Melamine (g)					10					
TA (19 wt.% aqueous solution) (g)					20					

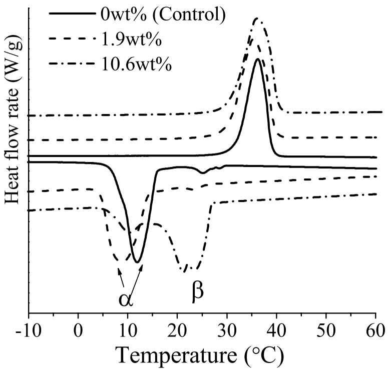


Fig. 1. DSC curves of MicroPCMs feeding sodium chloride of various concentration in water (C_1).

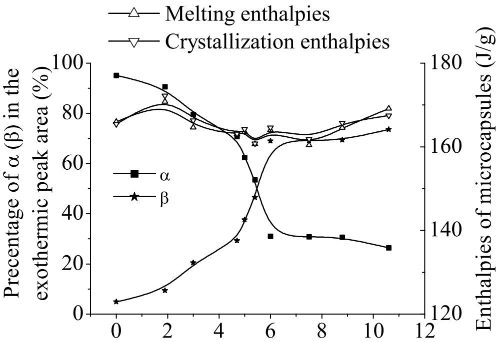


Fig. 2. Relation between percentage of α (β) in the exothermic peak area or enthalpies of microcapsules and concentration of sodium chloride in water (C_1).

electronic microscopy (SEM) (KYKY-2800, China Zhongke Scientific Instrument Inc.).

The thermal properties of microcapsules were measured using a differential scanning calorimetry (DSC) (Perkin-Elmer, DSC7) at a heating or cooling rate of 10 °C/min under a nitrogen (N_2) atmosphere, and the multi peaks were separated by the "Peaksep" program of NETZSCH-TA4.

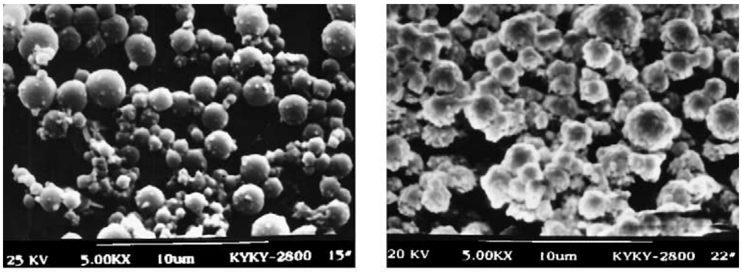
X-ray diffraction patterns were obtained on X-ray diffractometer (Rigaku D Max) using Cu Kα_1 radiation ($\lambda = 1.5406$ Å).

3. Results and discussion

3.1. Effects of sodium chloride on the properties of MicroPCMs

Sodium chloride inducing heterogeneous nucleation is in general justified but not in the case of the 1.9 wt.%. 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 drastically on the exothermic peaks as compared to the control. Two exothermic peaks due to different nucleation mechanisms 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 [12]. When sodium chloride concentration (C_1) is 10.6 wt.%, the peak β shifts to the higher temperature, and the integrated area of the 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 their diameters [12]. The crystallization of *n*-octadecane inside MicroPCMs starts from the generation of small crystalline nuclei. While the impurity, sodium chloride is added into the emulsion, it is inevitably mixed into the film of microcapsules [16]. The DSC results indicate that, sodium chloride, as the nucleating agent, promotes the heterogeneous nucleation of *n*-octadecane.

Relation between the percentage of α (β) in the exothermic peak area or enthalpies of microcapsules and concentration (C_1) of sodium chloride in water is shown in Fig. 2. As sodium chloride concentration (C_1) increases, the melting enthalpies and crystallization ones of the core material fluctuate between 160 and 170 J/g because the feed amount of *n*-octadecane is not changed, as indicated in Table 3. The percentage of α in the exothermic peaks increases rapidly and accordingly that of α decreases promptly, however. When sodium chloride concentration (C_1) is 6.0 wt.%, the percentage of α in the exothermic peaks is approximately 70%. However, it does not change sharply as the concentration (C_1) exceeds 6.0 wt.%. It is demonstrated that microcapsules can be prevented from super-cooling when the concentration of sodium chloride in water exceeds 6.0 wt.%.



(a) (b)

Fig. 3. SEM photographs of microcapsules. (a) 0 wt.% (control); (b) 6.0 wt.% sodium chloride in water.

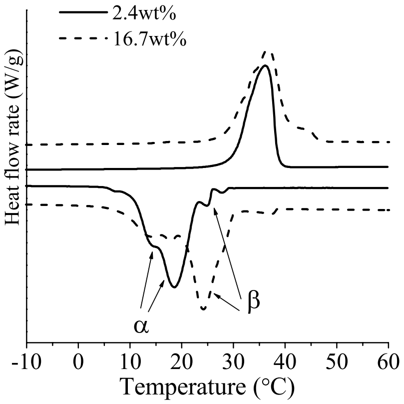


Fig. 4. DSC curves of MicroPCMs with 1-octadecanol of various concentration in core material (C_2).

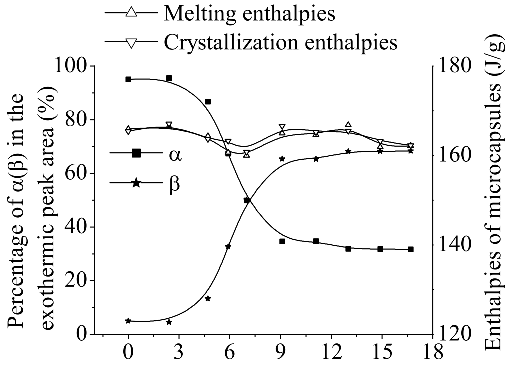


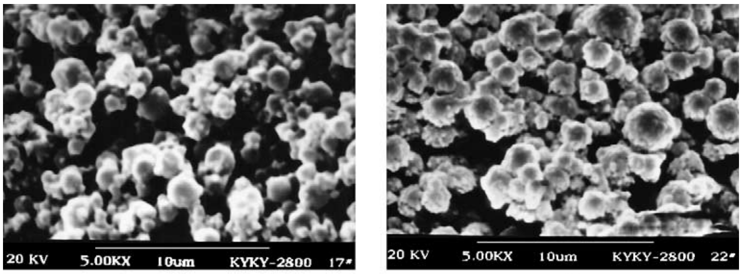
Fig. 5. Relation between percentage of α (β) in the exothermic peak area or enthalpies of microcapsules and concentration of 1-octadecanol in core material (C_2).

Fig. 3 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, as is indicated by the control of Fig. 1. In contrast, the surfaces of microcapsules feeding 6.0 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 [16].

3.2. Effects of 1-octadecanol on the properties of MicroPCMs

Fig. 4 shows the DSC curves of microcapsules with various concentration (C_2) of 1-octadecanol in core material. Both the endothermic peak and the exothermic peaks of microcapsules with 2.4 wt.% 1-octadecanol are similar to those of the control, as illustrated in Figs. 1 and 4. When the concentration (C_2) is 16.7 wt.%, their melting behavior was still changeless, but the exothermic peaks shift to the higher temperature and the onset point (28.4 °C) of the integrated exothermic peak is close to that of the endothermic peak (30.0 °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. Based on the Domanska's experimental results, the solubility of 1-octadecanol in *n*-octadecane reduces quickly from the melting point of 1-octadecanol to the melting point of *n*-octadecane [17].

The exothermic peaks are also divided into the homogeneous nucleation peak α and the heterogeneous nucleation peak β. Relation between the percentage of α (β) in the exothermic peak area or enthalpies of microcapsules and concentration (C_2) of 1-octadecanol in core material is shown in Fig. 5. As a result of the constant feed amount of *n*-octadecane, the melting enthalpies and crystallization ones of microcapsules with 1-cotadecanol are located within the range of 160–170 J/g and vary slightly with 1-octadecanol concentration (C_2) increasing. As the concentration (C_2) increases, the percentage of β in the exothermic peaks rose rapidly and accordingly that of α reduces sharply. The peak β of microcapsules with 9.1 wt.% 1-octadecanol is about 65% of the exothermic peak area, however, it increases very slowly thereafter. It shows that the insoluble 1-octadecanol is enough as the nuclei to prevent *n*-octadecane in microcapsules from super-cooling. It is inconsistent with Lee's results that the nucleating agent is preferred to be used within a range of about 1–6 wt.% [15].About 9.1 wt.% 1-octadecanol in *n*-octadecane has effect on the morphology and dispersibility of microcapsules, as shown in Fig. 6. Compared to microcapsules without 1-octadecanol, which are illustrated with the control of Fig. 3, microcapsules with 2.4 wt.% 1-octadecanol in core material still have smooth surfaces and these microcapsules are slightly stuck



(a) (b)

Fig. 6. SEM photographs of microcapsules with 1-octadecanol of various concentration (C_2) in core material. (a) 2.4 wt.%, (b) 9.1 wt.%.

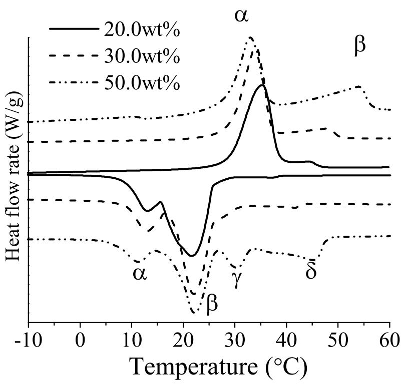


Fig. 7. DSC curves of MicroPCMs with paraffin of various concentration in core material (C_3).

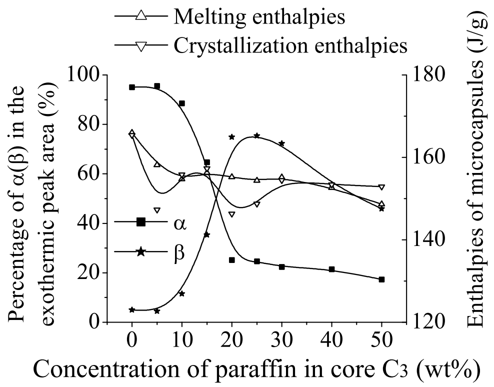


Fig. 8. Relation between percentage of α (β) in the exothermic peak area or enthalpies of microcapsules and concentration of paraffin in core material (C_3).

together. However, the surfaces of microcapsules with 9.1 wt.% 1-octadecanol are extraordinarily rough and the dispersibility is too bad to observe an intact microcapsule through SEM, as shown in Fig. 6. 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.

3.3. *Effects of paraffin on the properties of MicroPCMs*

Fig. 7 illustrates the DSC curves of microcapsules with different concentration (C_3) of paraffin in core material. Compared to microcapsules without paraffin, which is indicated by the control of Fig. 1, two endothermic peaks due to *n*-octadecane melting (α) and paraffin melting (β) are shown in the DSC heating curves of microcapsules with more than 20.0 wt.% paraffin. The peak α in the endothermic peaks broadens and shifts to the higher temperature as paraffin concentration (C_3) increases.

For microcapsules with less than 30.0 wt.% paraffin, two exothermic peaks (α, homogeneous nucleation; and β, heterogeneous nucleation) appear in the cooling curves. Triclinic crystal existing in even *n*-alkane [18,19] of paraffin is more beneficial to promote the formation of triclinic crystal in *n*-octadecane due to the same crystal structures. For microcapsules with 50.0 wt.% paraffin, however, four exothermic peaks are shown in Fig. 7. γ and δ thereof are attributed to paraffin crystallization. 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.

Relation between the percentage 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 with various concentration (C_3) of paraffin, as shown in Fig. 8. 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.

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, as indicated in Fig. 8. As paraffin concentration (C_3) exceeds 20.0 wt.%, the variation trend is not remarkable and the β percentage decreases owing to the emergence of γ and δ in the exothermic peaks. For microcapsules with 20.0 wt.% paraffin, the α percentage was about 75%, and the super-cooling was considered to being prevented.

Fig. 9 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 50.0 wt.%. So paraffin has no effect on the morphology and dispersibility of the

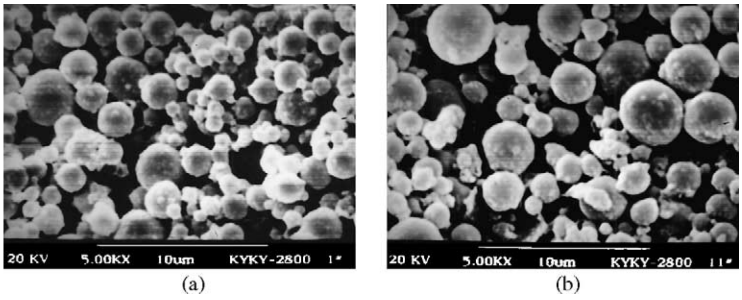


Fig. 9. SEM photographs of microcapsules with paraffin of various concentration (C_3) in core material. (a) 20.0 wt.%, (b) 50.0 wt.%.

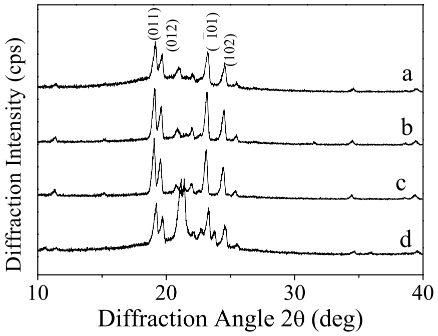


Fig. 10. X-ray diffraction patterns of microcapsules with different nucleating agents. (a) Control, (b) 6.0 wt.% sodium chloride, (c) 9.1 wt.% 1-octadecanol, (d) 20.0 wt.% paraffin.

microcapsules. It differs from the influence of sodium chloride or 1-octadecanol on the morphology and dispersibility of the microcapsules. Therefore, the preferred paraffin concentration (C_3) is approximately 20 wt.%.

3.4. Crystallographic system of MicroPCMs with different nucleating agents

The crystallographic system of microencapsulated PCM is usually obtained using X-ray diffraction (XRD) measurements. Melamine-formaldehyde resin made of microcapsule shell is amorphous, so it is convenient to analyze the crystallographic forms of encapsulated *n*-octadecane feeding the nucleating agents. X-ray diffraction patterns of microcapsules with different nucleating agents of appropriate amounts are shown in Fig. 10. Intense reflections in the range of 10–40° (2θ) indicate that microencapsulated *n*-octadecane without any nucleating agent is triclinic, as is indicated by the control of Fig. 10. The X-ray diffraction pattern of microcapsules with 9.1 wt.% 1-octadecanol is similar to that of the control, and the diffraction peaks (i.e. 21.66° (2θ)) characteristic of 1-octadecanol have not appeared in Fig. 10. Similar results have been obtained for microcapsules feeding 6.0 wt.% sodium chloride. The distinct peak attributed to sodium chloride does not appear at 31.69° (2θ). It demonstrates that 1-octadecanol and sodium chloride have no influence on the crystallographic system of *n*-octadecane. For microcapsules with 20.0 wt.% paraffin, the diffraction peaks attributed to paraffin crystallization appear at 21.32° (2θ) and 23.69° (2θ) in Fig. 10, and simultaneously the distinct (i.e. (0 1 1), (0 1 2), (1 0 1), (1 0 2)) peaks of *n*-octadecane still exist, which indicate that *n*-octadecane belongs to the triclinic system. Thus paraffin does not make *n*-octadecane change its crystallographic system.

Generally, the three nucleating agents do not affect the crystallographic system of *n*-octadecane, but they change its unit cell parameters slightly. Consequently, the variation of DSC curves of microcapsules with the nucleating agents is not attributed to the transition of *n*-octadecane crystallographic system, but to the nucleating agents inducing heterogeneous nucleation of *n*-octadecane.

4. Conclusions

Addition of sodium chloride, 1-octadecanol and paraffin has effect on the melting and crystallization behaviors, morphology and dispersibility of the microencapsulated *n*-octadecane. The super-cooling was prevented by feeding about 6 wt.% sodium chloride in the emulsion, but the surfaces of microcapsules were very rough and their dispersibility was worse. The super-cooling can also be prevented by feeding about 9 wt.% 1-octadecanol in core material, however, the surfaces of microcapsules were extraordinarily rough and the microcapsules were easily conglomerate. Differing from sodium chloride and 1-octadecanol, addition of approximately 20 wt.% paraffin in core material was able to prevent *n*-octadecane from super-cooling, and had no effect on the morphology and dispersibility of microcapsules. The three nucleating agents did not affect the crystallographic system of *n*-octadecane, but they induced heterogeneous nucleation of *n*-octadecane.

Acknowledgements

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References

[1] D.P. Colvin, Advances in Heat and Mass Transfer in Biotechnology, ASME HTD-Vol. 363/BED-Vol. 44 (1999) 199.
[2] G.A. Lane, D.N. Glew, In: Proceedings of Workshop on Solar Energy Storage Systems for the Heating and Cooling of Buildings, Charlottesville, VA, 1975, p. 43.
[3] D.C. Hittle, T.L. André, ASHRAS 4509 (2002) 175.
[4] Y.G. Bryant, D.P. Colvin, US Patent 5,366,801 (1994).
[5] M.E. Holman, Advances in Heat and Mass Transfer in Biotechnology, ASME HTD-Vol. 363/BED-Vol. 44 (1999) 235.
[6] M.L. Nuckols, Ocean Eng. 26 (1999) 547.
[7] J. Kim, G. Cho, Textile Res. J. 72 (2002) 1093.
[8] S.K. Roy, S. Sengupta, Int. Comm. Heat Mass Transfer 18 (1986) 495.
[9] P. Chaurasia, Res. Ind. 26 (1981) 159.
[10] M.N.A. Hawlader, M.S. Uddin, H.J. Zhu, Int. J. Energy Res. 26 (2002) 159.
[11] D.P. Colvin, D.K. Cartwright, US Patent 6,057,266 (2000).
[12] Y. Yamagishi, T. Sugeno, T. Ishige, IEEE 96082 (1996) 2077.
[13] A. Kishimoto, T. Setoguchi, M. Yoshikawa, T. Nakahira, In: Proceedings of 16th Japan Symposium on Thermophysical Properties, Hiroshima, 1995, p. 233.
[14] I. Mamoru, JP Patent 8-259932 (1996).
[15] W.M. Lee, WO Patent 02/053370 A1 (2002).
[16] Z.Q. Liang, Microencapsulation Technology and Its Application, Light industry press, Beijing, 1999 (in Chinese).
[17] U. Domanska, J. Rolinska, Fluid Phase Equilib. 86 (1993) 233.
[18] S.Y. Chazhenginaa, E.N. Kotelnikovab, I.V. Filippovab, S.K. Filatov, J. Mol. Struct. 646 (2002) 243–257.
[19] E.B. Sirota, A.B. Herhold, Science 283 (1999) 529.

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