Supercooling of Silver Nano Composite PCM Microcapsules

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Abstract: Supercooling effects of novel Phase Change Materials microcapsules incorporated with silver nano particles (NC-MicroPCMs) and conventional PCM microcapsules (MicroPCMs) are compared and evaluated systematically. Melting and crystallization behaviors of microcapsules with different processing parameters are investigated mainly by DSC measurements. Combinations of processing parameters are determined by a full factorial experimental design. The influences of processing parameters are discussed and analyzed by statistical softwares of SPSS and Minitab. The results have shown that the formation of nano composite structure can reduce the effect of supercooling. The possible mechanisms have also been explored.

Keywords: phase Change Materials, Microencapsulation, Silver Nano Composite, Supercooling

1. Introduction

Supercooling is one of the common features of Phase Change Materials (PCMs) whenever it undergoes a phase change from liquid to solid. Higher degree of supercooling has an adverse effect on thermal performance when PCMs crystallize from liquid to solid as energy releasing would be retarded during the process. Therefore, thermal regulation functions cannot be fully utilized.

Decreasing Supercooling for PCMs and MicroPCMs are crucial for the applications of energy storage, researches on them are active. Increasing thermal capacity and decreasing supercooling are main purposes of these researches.

A number of methods and apparatuses are available for determining the degree of supercooling (ΔT) and a number of reports in the literature have generally focused on the thermal features of MicroPCMs. These methods generally involve Differential Scanning Calorimetry (DSC) techniques, by which the degree of supercooling (ΔT) can be measured directly by a thermograph (M.N.A. Hawladera 2003; Mucha 2003; Alvarado 2006).

Yamagishi et al measured latent heat of fusion (ΔH), melting and crystallization temperature points of microencapsulated n-dodecane and n-tetradecane as a function of microcapsule size. The results indicated that the degree of supercooling increases accordingly when the microcapsule size decreases (Yamagishi Y 1996) (B. BOH 2005). That also means that larger microcapsules often have a better performance in depression of supercooling. Yamagishi believed the reason causing the differences in supercooling between the microcapsules with different sizes may be due to the differences of number of nuclei in the capsule core, and the number of nuclei decreases as size reduces. The crystallization inside a microcapsule starts from the generation of small crystalline nuclei (Yamagishi 1996).

Nucleating materials selections are hot research topics in the area of depressing supercooling. Mucha and Krolikowski carefully studied the impact of several nucleating agents or fillers on the crystallization kinetics of polypropylene (Mucha 2003). Avella et al discussed that CaCO3 nano particles at 3 wt% addition could act as an efficient nucleating agent in isotactic polypropylene (Avella 2005). Fan used and tested sodium chloride (3%) (Y.F. Fan. 2004), and X.X. Zhang applied 9 wt%

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octadecanol as nucleating agent in microencapsulated n-octadecane. These approaches have been reported efficiently in decreasing supercooling. However, such amount of nucleating agents have adverse effects on thermal capacity (Alvarado 2006).

There is little information available presently on the effect of processing parameters affecting supercooling during a microencapsulation process. Moreover, MicroPCMs with nano composite structure is a novel thermal storage functional materials. Their properties, especially the relationships between nano composite structures and thermal features, as well as processing parameters, need to be fully investigated and characterized..

In this study, MicroPCMs incorporated with silver nano particles were fabricated with a complex composite structures, where many silver nano particles are found dispersing on a shell and within a core. Silver nano particles may influence the behaviour of melting/crystallization due to the fact that these nano particles are distributed within the structure of the PCM microcapsules.

To fill these knowledge gaps, this paper investigates the effects of processing parameters on the thermal properties of supercooling. NC-MicroPCMs incorporated with silver nano particles and conventional MicroPCMs are compared systematically in terms of a degree of supercooling (ΔT). The possible mechanisms of the nano composite structure are explored.

12 groups of microcapsule were fabricated according to a full experimental design, including 8 groups with silver nano particles addition and 4 groups of conventional types. The sizes of these microcapsules of the 12 groups are in the range around 3.78 μm. There are no significant differences in size and distribution among the 12 groups. Therefore, the influences of microcapsule size on thermal property can be excluded.

We have found that a positive effect of supercooling depression for MicroPCMs with nano composite structures, in which the crystallization process may have been affected as the nano particles may exert a function of nucleating agents in the microcapsule structure.

2. Experimental

2.1 Sample Preparation

Microcapsules with different parameters were prepared according to a 23 experimental design, in which three variables of core/shell ratio (C/S), F/M molar ratio (F/M) and silver nano material addition (ADD %) are the main affecting parameters, which were determined by pre-screening experiments. Surface morphology observation using the 12 MicroPCMs groups were carried out by JSM 6335F (Japan).

The SEM images of the silver nano particles and some of the 12 samples are displayed in Figures. 1, 2 and 3.

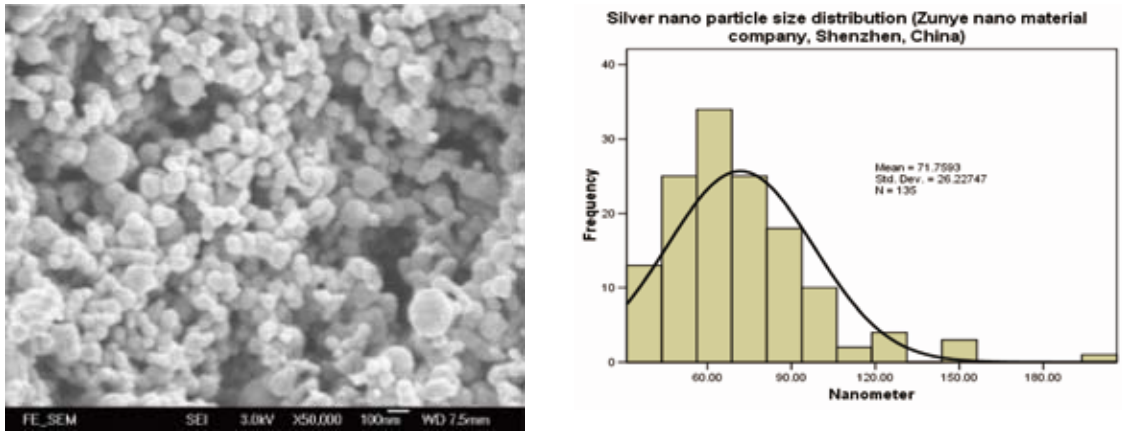


Figure 1 SEM image and size distribution of silver nano particles

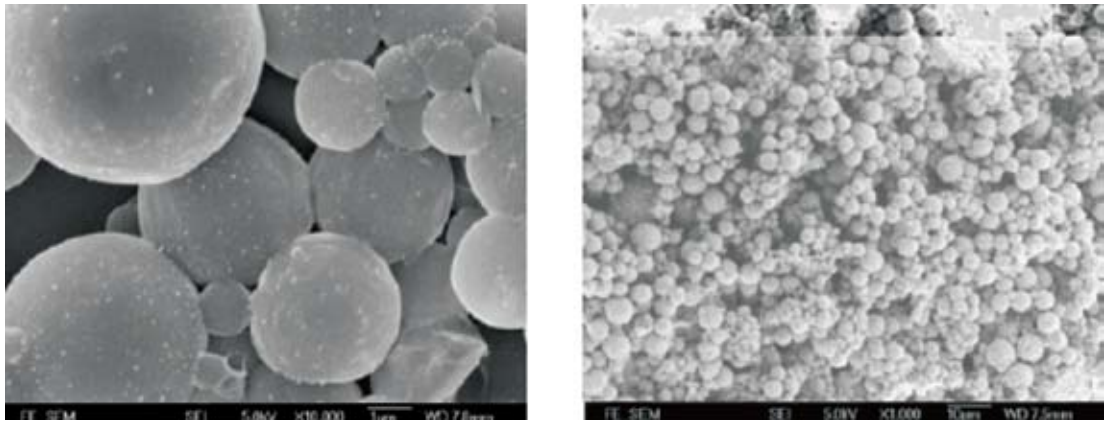


Figure 2 Conventional PCM microcapsules with core/shell ratio 5 and F/M molar ratio 2.3 (mean size 3.68μm with Std.Dev 1.42, coded as 5 0% 2.3.)

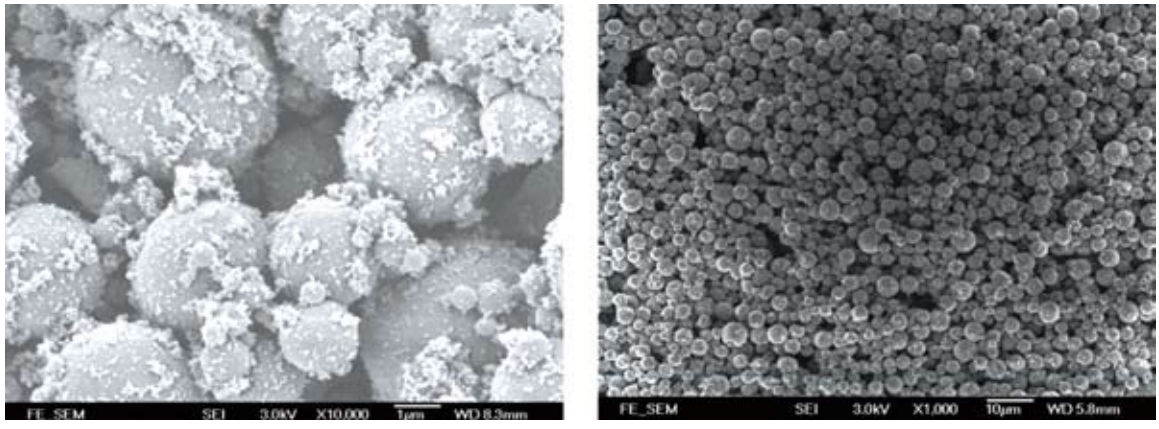


Figure 3 Microcapsules coded as Ag 7 3% 1.8 (mean size 3.66μm with Std.Dev 1.05)

2.2 Characterization

Supercoolings (ΔT) of the 12 samples were measured by the apparatus of Perkin Elmer DSC7 with a working temperature ranging from -50°C to 450°C. The degree of Supercooling of a specimen can be calculated by a thermograph from the data recorded by DSC as shown in Figure 4

$$\Delta T = T_m^0 - T_c$$

Where, T_m^0 is onset melting point and is the onset crystallization temperature.

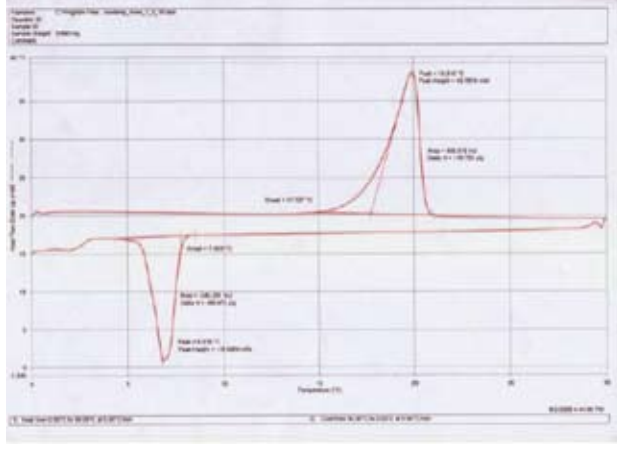


Figure 4 A typical DSC thermal graph of PCM microcapsule, showing thermal properties of onset melting / crystallization temperature and enthalpy.

During the DSC test (Perkin Elmer DSC7), 5~10mg sample were heated from -10ºC to 35ºC at a scanning velocity of 5ºC/min, and maintained at that temperature for 5 minutes, then cooled down to -10ºC, as one measure circle was finished. Argon atmosphere was maintained during the whole process. Three parallel measurements were taken for each sample.

3. Result and Discussion

3.1 SEM observation

Through the morphology and surface observations in Figures 2 and 3, the two groups are significantly different. Many silver nano particles can be spotted on the surface of microcapsules with silver nano composite structure. Almost no coacervations are observed on SEM images. On the contrary, the most significant feature of the conventional MicroPCMs groups is that all the microcapsules are provided with smooth surfaces.

3.2 Statistical Analysis on Supercooling

All the results of the twelve experimental runs with different parameter combinations for the responses of supercooling are shown in Table 1, including the data of bulk bromo-hexadecane. It provides a descriptive statistics (mean, standard deviation and number of measurements) for the variables to be compared. These experiments are prepared according to a full factorial experimental design, which allows the study of the effect that several factors and their interactions.

By comparing the data in Table 1, supercooling varies from 7.38 (sample coded as Ag 7 3% 2.3) to 10.39 (ºC) (Con 7 0% 1.8), and the data for the bulk sample is 6.15. These differences indicate that the processing parameters do have effects on supercooling.

Tables 2 and 3 are the results of variance analysis run by using Minitab 14.0 statistical software, in which the main effect of variables and their interactions are displayed.In the study, the response at 95% confidence level is applied, and “p” value less than 0.05 implies the factor has a significant influence on the value of the response.

As shown in Tables 2 and 3, the factors of C/S, F/M do not show any significant effect (P>0.05). However, the main effect of ADD (%) and the two/three way interactions of C/S×Add (wt%), Add (wt%)×F/M , C/S×F/M, C/S×F/M×Add (wt%) are statistically significant ($p<0.05$).The R2 (adj)=0.88 means that the general linear model for supercooling is relatively reliable, which can illustrate the influence of the variables on the response.

3.3 Effects of variables in the Process

The influence of processing factors of F/M, core/shell ratio (C/S) and the addition level of silver nano particles Add (wt%) and their interactions are investigated. Figure 5 shows parato plots that illustrate the most significant parameters or interactions that affect supercooling graphically. The addition of silver nano powders has shown a significant influence on supercooling. Although C/S and F/M do not show any significant effect on supercooling, their interactions have significant effects.

The plots shown in Figure 6 suggest the main effects of C/S, F/M and Add (wt%), in that Add(wt%) is negative and has a greater influence compared with the other two.The main effects of C/S and F/M are not strong.

The interaction plots are shown in Figure.7. Significant effects in the interactions between the C/S× F/M and C/S ×Add (wt%) are found.

Table 1 The descriptive statistics of supercooling (ΔT) of samples with different parameter combinations

C/S	F/M	Add %	Supercooling ΔT (ºC)	Std. Deviation
5	1.8	0	9.03	0.40
5	1.8	1	8.39	0.16
5	1.8	3	8.30	0.08
5	2.3	0	10.18	0.68
5	2.3	1	9.26	0.27
5	2.3	3	8.62	0.37
7	1.8	0	10.39	0.31
7	1.8	1	9.13	0.39
7	1.8	3	8.57	0.31
7	2.3	0	10.22	0.34
7	2.3	1	9.91	0.23
7	2.3	3	7.38	1.78
Bulk bromo-hexadecane			6.15	0.48

Table 2 Estimated Effects and Coefficients for supercooling

Term	Effect	Coef	SE Coef	T	P
Constant		8.72	0.052	165.83	0.000
C/S	0.18	0.09	0.052	1.73	0.104
F/M	0.10	0.05	0.052	0.97	0.348
ADD(%)	-0.97	-0.48	0.052	-9.30	0.000
C/S*F/M	-0.37	-0.18	0.052	-3.56	0.003
C/S*ADD(%)	-0.65	-0.32	0.052	-6.26	**0.000**
F/M*ADD(%)	-0.57	-0.28	0.052	-5.43	**0.000**
C/S*F/M*ADD	-0.38	-0.19	0.052	-3.66	**0.002**

S = 0.257779 R-Sq = 92.04% R-Sq(adj) = 88.56%

Table 3 Variance Analysis on supercooling

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	6.00	6.00	2.00	30.11	0.000
2-Way Interactions	3	5.40	5.40	1.80	27.11	0.000
3-Way Interactions	1	0.88	0.88	0.88	13.38	0.002
Residual Error	16	1.06	1.06	0.06		
Pure Error	16	1.06	1.06	0.06		
Total	23	13.36				

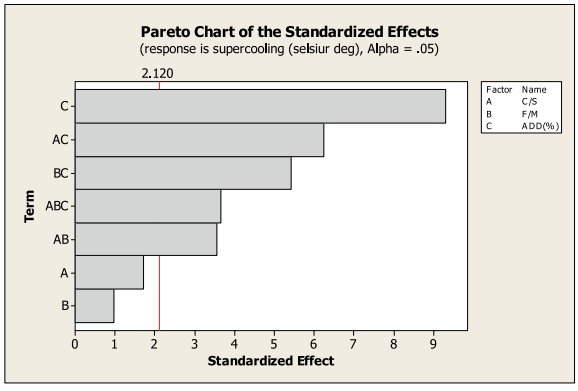


Figure 5 Parato charts of the effect on supercooling

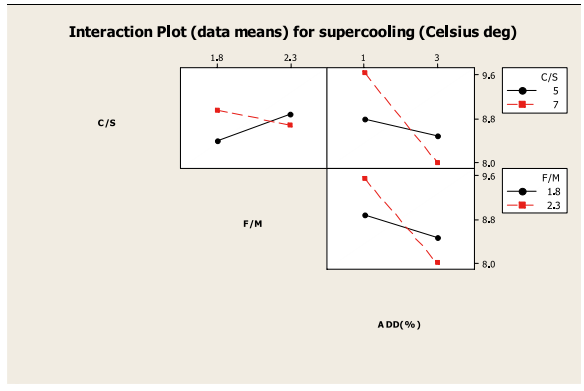


Figure 7 Interaction plots on supercooling

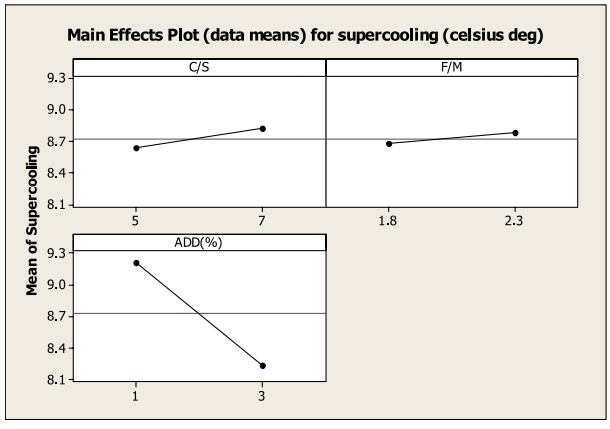


Figure 6 Main effect plots on supercooling

3.4 Response Optimization

The relationships between the response and variables can be visualized by a response surface or contour plot; (1) to see a relative influence of these factors, (2) to find an optimum parameter combination and (3) to predict experimental result for other parameter combinations. Figure 8 displays a contour plot for supercooling (Δ°C) with a fixed value of F/M 2.3. From the chart, the regions between 7-8 (C/S) and 4~5wt% (Add %) fit the demand value of a lower supercooling (5~6°C).

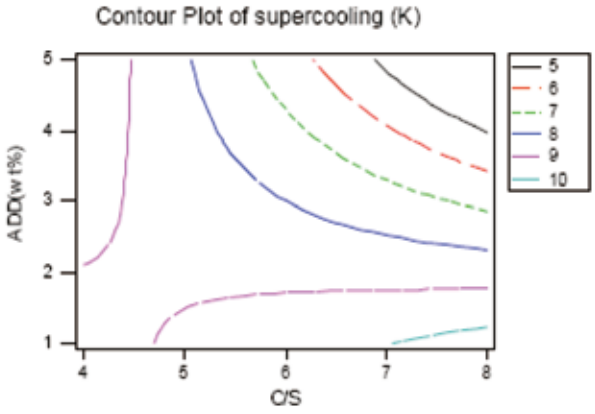


Figure 8 Contour Plot of the Response of Supercooling

3.5 The Influence of Nano Composite Structure on Thermal Properties of Supercooling

By the data analysis discussed previously, the formation of nano composite structures have a profound influence on thermal properties of supercooling. The reasons and possible mechanisms are being explored in the section;

3.6 The Influence on Thermal Behaviors during Melting

Figure 9 illustrates the thermographs of the 12 groups of microcapsules with different parameter combinations during the stages of heating in DSC testing process.

The melting and crystallization temperatures of the bulk paraffin depend on the number of carbon atoms and bulk paraffin also crystallizes with a supercooling behavior. The onset melting temperatures for the 12 samples MicroPCMs are in a range from 14.5 to 15ºC, and end at the range of 17.6 to 18.5ºC. Only one peak is observed from DSC heating curves for all the 12 samples. The enclosed peak areas (mJ) between the onset and ending temperature represent the thermal capacity of a sample. A larger peak area represents higher latent heat of the material.

As shown in Figure 9, the 12 samples have different peak areas, implying a different melting enthalpy they have absorbed and stored. Despite of the different peak areas, all the 12 samples have a similar melting behavior in that each sample only has one endothermic peak, and melt at almost the same temperature.

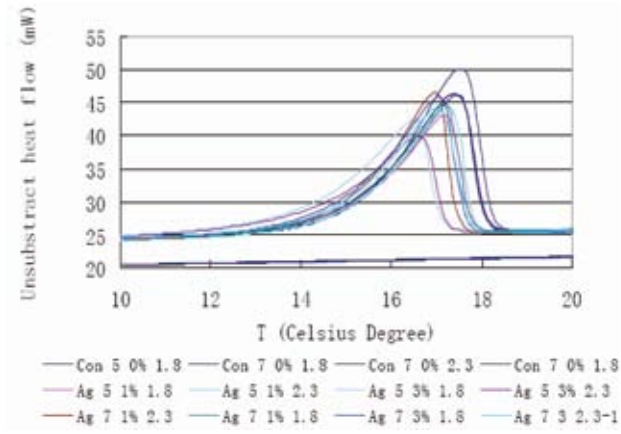


Figure 9 DSC thermal graphs of the 12 groups of microcapsules with different parameters in the heating process (-10~30ºC, 5˚C/min)

The Influence on Thermal Behaviors during Cooling.

However, the crystallization behavior of the 12 microcapsule samples do not freeze at the point of temperature melting. The phenomenon of supercooling is observed, in which the crystallization temperature point is decreased for each sample. Furthermore, two exothermic peaks (multiple crystallization peaks) appear in all the 12 samples as shown in Figure 10 The first exothermic peak starts at the temperature approximately 9 to 6ºC, and the other begins at the temperature of -3 to -5ºC. This feature suggestes that these MicroPCMs undergo two phase change stages during cooling process and the stored energy do not release at one time.

Many researchers have also observed the crystallization behaviors of phase change materials. This phenomenon is believed to be related with the behavior of nucleating manner in MicroPCMs in the process of cooling. Cooling leads to a transition of a disordered liquid phase to an ordered solid structure, and a substantial time is needed to finish the transition. Hence, the degree of supercooling is believed to be related with a cooling rate of the crystallization process. The first exothermic

peak is called as “peak alpha”, corresponding to a heterogeneously nucleated liquid-rotator phase transition.The second exothermic peak is called as “peak beta”, corresponding to the homogeneously nucleated rotator-crystal transition.

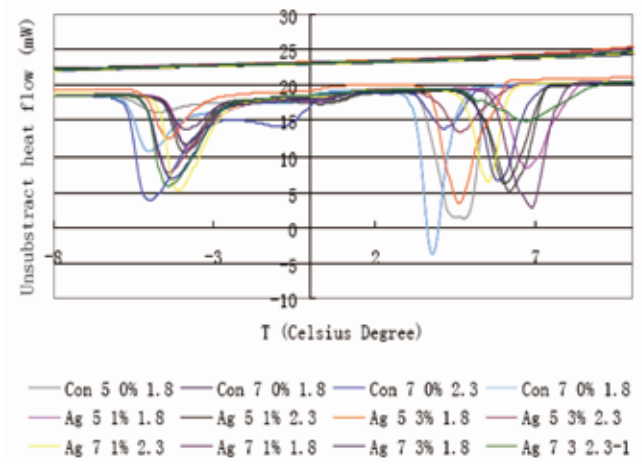


Figure 10 DSC thermal graphs of the 12 groups of microcapsules in the cooling stage (30~-10ºC, 5˚C/min)

MicroPCMs crystallization mechanisms

MicroPCMs are the PCMs that enclosed by a polymer shell. It was hypothized that a shell material has no interference with core PCMs and has no contributions to thermal capacity. The physical properties of liquid PCM (Bromo-hexadecane) in a very small droplet, e.g., microencapsulated PCM, can be significantly different from those in bulk phase. During a crystallization process, a large number of independent nucleation sites should be created in the MicroPCMs. The crystal growth is governed and limited by the size of microcapsule after nucleation, and crystallization process is stopped when the shell area is reached as each MicroPCMs must be nucleated separately (M.J. OLIVER 1975) (Bennema 1993). (S. CHAROENREIN 1989) (J. Pak 2000).

The nucleating mechanism for MicroPCMs with tiny volume is shifted from heterogeneous to homogeneous nucleation (R.Montenegro 2003). The reason for the shifting in the crystallization mechanism could be associated with the number of foreign nuclei that usually cause heterogeneous nucleation in bulk phase and are now distributed among a large number of isolated tiny Microcapsules. The heterogeneous nucleation for MicroPCMs is reduced because only a small number of nuclei contained in a microcapsule. Therefore, the crystallization process can not be finished at one time, and the energy has to be released at several stages at different temperatures rather than one time(Keumnam Cho 2000).

Figure. 11 elucidates the DSC result of the samples 5 3% 1.8, 5 0% 1.8 and bulk PCM during crystallinition stage. It reveals different crystallization behaviors of bulk PCM, conventional MicroPCMs and NC-MicroPCM with a similar processing parameter. The result agrees well with the observations made by Xing-Xiang Zhang and Keumnam. Meanwhile, these three samples have different degree of supercooling, in that MicroPCMs with nano particle addition (Ag 5 3% 1.8) has a lower supercooling compared with its rival (5 0% 1.8) , and bulk PCM has the lowest supercooling.

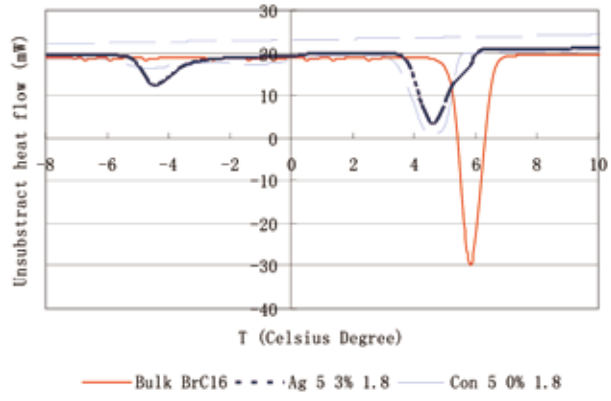


Figure 11 Supercooling behavior of bulk PCMs, conventional microPCMs and its rival sample with nano composite structure (size 3 to 4μm).

Note: The onset freezing temperature of the sample with nano composite structure is 0.7ºC higher than its rival sample. Bulk PCMs freeze 0.5ºC higher than the two MicroPCMs and release heat in a thorough manner at one time.

As shown in Table 1, supercooling can be depressed to about 1ºC to 3ºC for the MicroPCMs with nano composite structure. The degree of the depression of each sample depends on the addition of nano materials mainly. This phenomenon may attribute to the formation of the nano composite structure.

In summary, silver nano particles in the core may probably act as extra foreign nucleus in a crystallization stage, as heterogeneous nucleation is still the main mechanism in crystallization. Silver nano particles are also excellent materials with high thermal conductivity, in which heat can be transferred with a higher efficiency during cooling process. The rough shell appearance of the NC-MicroPCMs can increase the contact area between MicroPCMs and surrounding greatly. This feature may also regard as a reason to explain the depression of supercooling. Therefore, silver nano particles dispersing on the shell and in the core may probably provide an enhancing effect in crystallization process. All these actions originated from silver nano particles may cause a depression effect on supercooling.

4. Conclusion

To summary these research findings on thermal properties of supercooling for the MicroPCMs and NC-MicroPCMs, it has been discovered that processing variables of C/S and F/M do not show a very significant effect on depressing supercooling. However, adding silver nano particle to the MicroPCMs and the formation of nano composite structures can perform a profound influence on supercooling to an extent of 2-3˚C.

Two crystallization peaks are observed in the 12 MicroPCMs samples. The mechanisms of the depression have been explored in that silver nano particles may act as extra nucleis and the metal nano particles have the ability to enhance thermal conductivity in core PCMs during cooling process, as well as the effect of increased surface area. The manner of crystallization of MicroPCMs may shift. The heterogeneous nucleation for MicroPCMs is reduced due to the Small Volume Retardant Effect, and both the heterogeneous and homogeneous nucleation mechanisms take place in a MicroPCMs during a cooling stage.

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