# Crystallization and Melting Behavior of Nano-$CaCO_3$/Polypropylene Composites Modified by Acrylic Acid

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**ABSTRACT:** Nano-$CaCO_3$/polypropylene (PP) composites modified with polypropylene grafted with acrylic acid (PP-*g*-AA) or acrylic acid with and without dicumyl peroxide (DCP) were prepared by a twin-screw extruder. The crystallization and melting behavior of PP in the composites were investigated by DSC. The experimental results showed that the crystallization temperature of PP in the composites increased with increasing nano-$CaCO_3$ content. Addition of PP-*g*-AA further increased the crystallization temperatures of PP in the composites. It is suggested that PP-*g*-AA could improve the nucleation effect of nano-$CaCO_3$. However, the improvement in the nucleation effect of nano-$CaCO_3$ would be saturated when the PP-*g*-AA content of 5 phf (parts per hundred based on weight of filler) was used. The increase in the crystallization temperature of PP was observed by adding AA into the composites and the crystallization temperature of the composites increased with increasing AA content. It is suggested that the AA reacted with nano-$CaCO_3$ and the formation of $Ca(AA)_2$ promoted the nucleation of PP. In the presence of DCP, the increment of the AA content had no significant influence on the crystallization temperature of PP in the composites. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2443–2453, 2004

**Key words:** poly(propylene) (PP); nanocomposites; crystallization; DSC; graft copolymers

## INTRODUCTION

Polypropylene (PP) has been widely used for its good processing properties, high rigidity, and excellent mechanical properties. However, to meet various applications, further increased-use temperature and improved mechanical properties still constitute the main focus of PP modification. The incorporation of fillers into PP can lead to changes in crystallization and melting behavior of PP. According to the nucleation ability of the filler for the crystallization of PP, the fillers can be classified into two kinds, active and inactive. The nucleating effect of $CaCO_3$ on PP is drastically disputed, which relates to the crystal form, surface topography, and dispersion of $CaCO_3$. The addition of $CaCO_3$ with different crystal form and surface topography into PP results in various changes in the crystallization morphology, the proportion of crystallization phase to amorphous phase, and the distribution of these two phases, which accordingly affects the mechanical properties of $CaCO_3$/PP composites. Therefore, many studies on the crystallization and melting behavior of $CaCO_3$/PP composites have been reported.

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There were reports that the addition of $CaCO_3$ markedly improved the nucleation effect and the crystallization temperature of PP attributed to the heterogeneous nucleation effect of $CaCO_3$.[1,2] The increase in crystallization temperature was related to the particle size and content of $CaCO_3$: the smaller the size,[3] the larger the amount of $CaCO_3$[4] and the more significant the improvement in crystallization behavior. Khare et al.[5] found that the incorporation of $CaCO_3$ increased the crystallization rate of PP and decreased the spherulite size with the increase of the $CaCO_3$ content. The decreased crystallization half-time was observed with the increase of the $CaCO_3$ content, and was related to crystallization temperature. At high crystallization temperature, a greater decreased crystallization half-time was observed. Although the incorporation of $CaCO_3$ had no influence on the mechanism of crystallization nucleation, the crystallization temperature, crystallization rate, and Ozawa exponent of PP depended on the $CaCO_3$ content.[6]

The surface treatment of $CaCO_3$ with coupling agents, such as silane and titanate, could change the heterogeneous nucleation effect of $CaCO_3$ on PP. Albano et al.[7] found that addition of $CaCO_3$ treated with and without titanate coupling agents increased the crystallization temperature of PP by about 7°C. $CaCO_3$ treated with silicone was more effective in increasing the crystallization degree of PP than that treated with titanate.[8] The nucleation ability and the crystallization

**TABLE I**
**Composition of Nano-$CaCO_3$/PP Composites**

| Sample | PP (wt %) | CC (wt %) | AA (phf)[a] | DCP (phf) | FPP (phf) |
|---|---|---|---|---|---|
| PP | 100 | — | — | — | — |
| CC2 | 98 | 2 | — | — | — |
| CC5 | 95 | 5 | — | — | — |
| CC10 | 90 | 10 | — | — | — |
| CC40 | 60 | 40 | — | — | — |
| CC40F5 | 60 | 40 | — | — | 5 |
| CC40F10 | 60 | 40 | — | — | 10 |
| CC40AA2 | 60 | 40 | 2 | — | — |
| CC40AA4 | 60 | 40 | 4 | — | — |
| CC40AA6 | 60 | 40 | 6 | — | — |
| CC40AA2D | 60 | 40 | 2 | 0.1 | — |
| CC40AA4D | 60 | 40 | 4 | 0.1 | — |
| CC40AA6D | 60 | 40 | 6 | 0.1 | — |

[a] phf denotes parts per hundred based on weight of filler.

temperature decreased as PP was filled with $CaCO_3$ treated with oligomer of ethylene oxide.[1] Mitsuishi et al.[4] studied the crystallization behavior of PP filled with $CaCO_3$ modified with alkyl dihydrogen phosphate and found that the shape and temperature of the crystallization peak of PP depended on the particle size of $CaCO_3$. For the $CaCO_3$ with particle sizes of 1 and 4.5 $\mu$m, double crystallization peaks of PP were observed. However, only a single peak was observed when the particle size was 30 $\mu$m. For the untreated $CaCO_3$, the crystallization temperature of PP increased with the increase of volume fraction of $CaCO_3$. $CaCO_3$ modified with plasma-polymerized acetylene did not obviously change the crystallization and melting behavior of PP. However, the heat of fusion of PP filled with untreated $CaCO_3$ decreased with increase of the filler content and depended on the surface modification methods of $CaCO_3$. It was believed that the increase of the filler content distorted the crystalline structure and led to the change of microcrystalline orientation.[9]

In recent years, functionalized macromolecular coupling agents have been used to improve the interface interaction between $CaCO_3$ and PP. Rahma and Fellahi[10] investigated the effect of the concentration of peroxide on the crystallization behavior of $CaCO_3$/PP

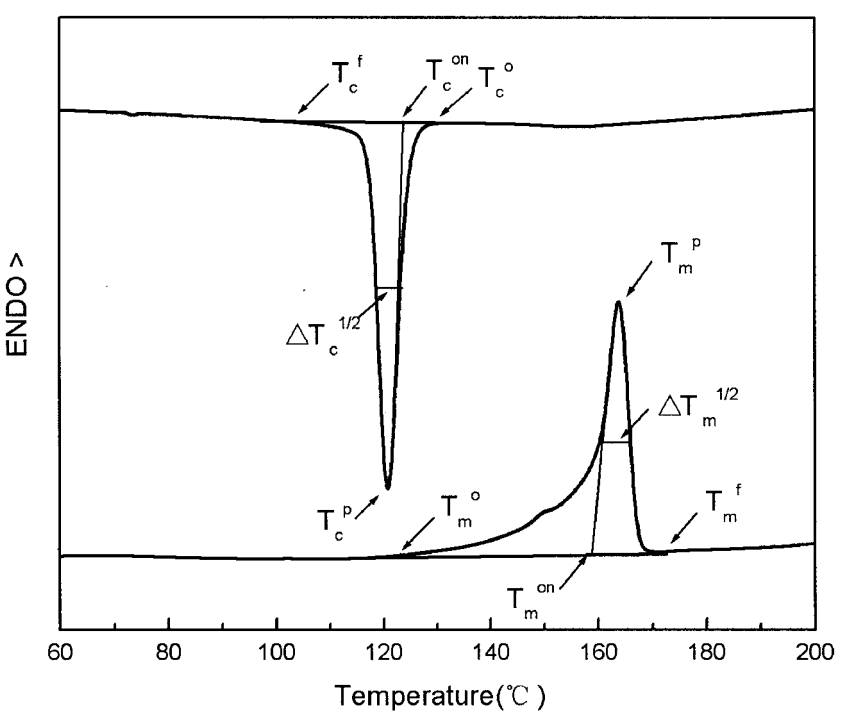


**Figure 1** Determination of the crystallization and melting parameters.

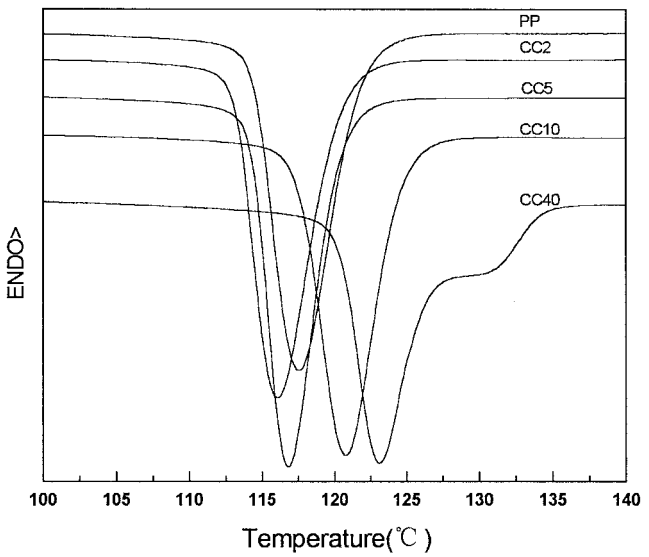


**Figure 2** DSC crystallization curves of PP and nano-$CaCO_3$/PP.

composites modified by polypropylene grafted with acrylic acid (PP-*g*-AA). The result showed that the melting point of PP decreased rapidly with peroxide content initially, but then leveled off at peroxide content of 0.6 phr (parts per hundred based on weight of resin) because of the degradation of PP. This phenomenon was attributed to two competitive effects: (1) $\beta$-chain scission produced short chains and increased the crystallization rate; (2) the increase in the free radicals produced by high content of peroxide increased the chance of chain termination and the molecular weight and thus decreased the crystallization rate. Tabtiang and Venables[2] also investigated the effect of the content of AA, dicumyl peroxide (DCP), and the stabilizer TMP on the crystallization behavior of $CaCO_3$/PP. The result suggested that the increase of the content of DCP and TMP decreased the crystallization temperature of PP, but the crystallization temperature increased with increasing AA content. It was suggested that the TMP with a weak nucleation ability covered the fringe nucleation sites of $CaCO_3$ crystal and decreased the heterogeneous nucleation effects of $CaCO_3$. On the contrary, an increased crystallization temperature of PP was observed as the AA and DCP were added together, which was attributed to the nucleation of $Ca(AA)_2$ formed in the process of material preparation. Both AA and TMP reacted competitively with polymeric PP free radicals initiated by DCP as the AA, TMP, and DCP were all added to PP. The increase in the concentrations of TMP and DCP decreased the crystallization temperature of PP. Moreover, the increase in the AA content increased the crystallization temperature of PP because of the formation of the higher nucleation ability of $Ca(AA)_2$.

Tabtiang and Venables[11] further investigated the performance of several unsaturated acids and acid anhydrides of varying molecular weight for $CaCO_3$ filler in PP. The modified $CaCO_3$ were then compounded with polypropylene, both in the presence and absence of an initiator, through twin-screw extrusion to give compounds containing 75 phr of $CaCO_3$. Infrared analyses showed that reaction between each coating and the $CaCO_3$ surface led to the formation of carboxylate salts. The occurrence of peroxide initiated transfer grafting between the alkenyl chains of the coatings and the PP matrix during compounding was inferred from extraction studies and from physical test data. Extensive grafting was evident for the AA-coated filler, but much less so for coatings with longer alkenyl chains. In the presence of peroxide the melt flow rates of each compound increased because of the reduction of molecular weight of the matrix polymer as a consequence of free radical–induced grafting and degradation reactions. This led to the reduction in toughness and ductility of compounds with surface coatings that possessed alkenyl chains with fewer than 17 carbon atoms. For those with chains lengths of 17 or greater, toughness was substantially improved as a result of the release of matrix constraint around the filler particles that counteracted the effects of degradation.

With the development of nanotechnology, new polymeric composites filled with nanofillers have been rapidly developed.[12–26] The mechanical properties of

**TABLE II**
**DSC Crystallization Results of PP and Nano-$CaCO_3$/PP[a]**

| Sample | $T_c^0$ (°C) | $T_c^p$ (°C) | $T_c^f$ (°C) | $T_c^{on}$ (°C) | $\Delta H_c$ (J/g) | $\Delta T_c^1$ (°C) | $\Delta T_c^2$ (°C) | $\Delta T_c^{1/2}$ (°C) |
|---|---|---|---|---|---|---|---|---|
| PP | 128.2 | 117.5 | 99.3 | 121.9 | 101.1 | 28.9 | 4.3 | 4.5 |
| CC2 | 127.9 | 116.1 | 97.3 | 120.4 | 99.5 | 30.5 | 4.4 | 4.3 |
| CC5 | 126.8 | 116.8 | 95.7 | 120.4 | 103.2 | 31.1 | 3.6 | 3.5 |
| CC10 | 129.6 | 120.8 | 103.2 | 124.6 | 97.7 | 26.4 | 3.8 | 4.3 |
| CC40 | 137.5 | 123.1 | 98.2 | 127.1 | 111.5 | 39.3 | 4.0 | 4.3 |

[a] $T_c^0$, the temperature at which crystallization curve deviates from the baseline; $T_c^p$, the peak temperature of crystallization; $T_c^f$, the temperature at the completion of crystallization; $T_c^{on}$, the temperature at the onset of crystallization; $\Delta T_c^1 = T_c^0 - T_c^f$, the width of the crystallization peak; $\Delta T_c^2 = T_c^{on} - T_c^p$, the width of the crystallization peak in the high temperature region; $\Delta T_c^{1/2}$, the half-height width of crystallization peak; $\Delta H_c$, the heat of crystallization.

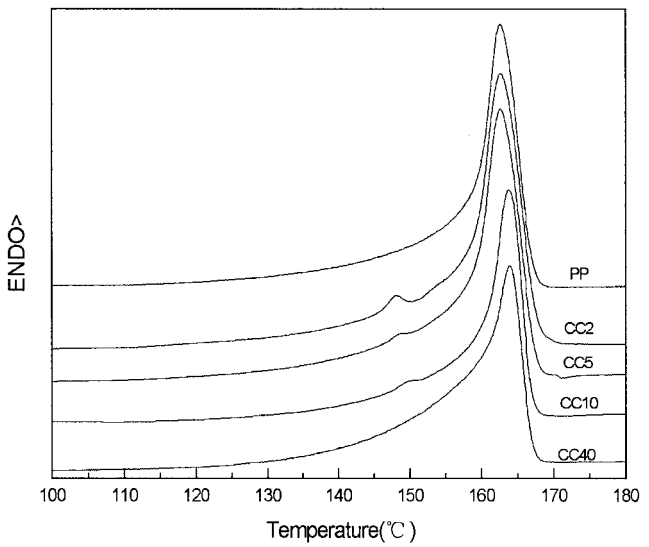


**Figure 3** DSC melting curves of PP and nano-$CaCO_3$/PP.

polymeric materials depend on the crystallization behavior of the polymeric matrix, so there were some reports on the crystallization behavior of PP filled with nanomaterials. Xu et al.[27] studied the nonisothermal crystallization kinetics of polypropylene/montmorillonite (MMT) nanocomposites. The result showed that the crystallization temperature shifted to a higher temperature. At the same cooling rate, the crystallization temperature of the PP nanocomposite was higher than that of pure PP, and the Avrami exponent of the nanocomposite was less than that of pure PP. The incorporation of the organic MMT decreased the crystallization activation energy of PP. It was believed that nano-MMT had a heterogeneous nucleation effect during the crystallization process of PP. Studies[28,29] on the isothermal crystallization kinetics of the PP/MMT nanocomposite also indicated that MMT had an obvious heterogeneous nucleation effect on PP and markedly increased the crystallization rate of PP. The Avrami exponent was ≅3.0. It was suggested that the crystallization of PP nanocomposites occurred on the typical mechanism of heterogeneous nucleation.

The effect of nanoparticles on the crystallization behavior of PP was also investigated. Addition of nano-$SiO_2$ significantly increased the crystallization temperature of PP in PP/EPDM composites because of the heterogeneous nucleation effect of nano-$SiO_2$.[30] The nucleation effect of nanoparticles was related to the particle size.[31] In the system of PP/nano-$Ca_3(PO_4)_2$, the decrease in particle size and the increase in the active surface area increased the heterogeneous nucleation effect and the crystallization rate of PP.

Nano-$CaCO_3$ significantly improved the nucleation of PP, which is different with micro-$CaCO_3$. Wang and Huang[32] studied the effect of nano-$CaCO_3$ on the crystallization property of PP. The onset crystallization temperature of PP was increased slightly with increasing nano-$CaCO_3$ content and the heat of fusion initially increased and then fell. For the nano-$CaCO_3$ content below 3.5 wt %, nano-$CaCO_3$ dispersed well in the PP matrix and reinforced the interface interaction between matrix and nano-$CaCO_3$, which significantly induced the heterogeneous nucleation of PP and increased the degree of crystallization. For the nano-$CaCO_3$ content above 3.5 wt %, the heterogeneous nucleation effect and the degree of crystallization of PP decreased because of the severe aggregation of nano-$CaCO_3$. The heat of fusion of PP in its composites filled with nano-$CaCO_3$ was higher than that of the composites filled with micro-$CaCO_3$ as a result of the high heterogeneous nucleation effect of nano-$CaCO_3$. The melting behavior of nano-$CaCO_3$/PP composite was also investigated by Ren.[33] For the pure PP, a melting peak of the $\alpha$-crystal was observed. For nano-$CaCO_3$/PP, there was not only a melting peak of the $\alpha$-crystal at 165°C, but also a small peak at 150.6°C, which corresponded to the $\beta$-crystal. It was suggested that the nano-$CaCO_3$ induced the formation of a few $\beta$-crystals of PP. The smaller the nanoparticles, the greater the heterogeneous nucleation effect of $\beta$-crystallization.

To develop polymeric composites modified with nanomaterials, it is most important to resolve some problems, such as dispersion of nanomaterials in the

**TABLE III**
**DSC Melting Results of PP and Nano-$CaCO_3$/PP[a]**

| Sample | $T_m^0$ (°C) | $T_m^p$ (°C) | $T_m^f$ (°C) | $T_{on}^{on}$ (°C) | $\Delta H_m$ (J/g) | $\Delta T_m$ (°C) | $\Delta T_m^{1/2}$ (°C) |
|---|---|---|---|---|---|---|---|
| PP | 110.0 | 162.7 | 170.9 | 158.9 | 101.0 | 60.9 | 5.1 |
| CC2 | 112.7 | 162.7 | 171.8 | 158.1 | 98.7 | 59.1 | 5.9 |
| CC5 | 112.1 | 162.7 | 171.4 | 158.3 | 104.1 | 59.1 | 5.9 |
| CC10 | 116.1 | 163.9 | 172.1 | 159.6 | 90.8 | 56.0 | 4.5 |
| CC40 | 113.2 | 164.0 | 169.8 | 158.6 | 106.8 | 56.6 | 6.7 |

[a] $T_m^0$, the temperature at which melting curve deviates from the baseline; $T_m^p$, the peak temperature of melting curve; $T_m^f$, the temperature at the completion of melting; $T_m^{on}$, the temperature at the onset of melting curve; $\Delta T_m = T_m^f - T_m^0$, the width of the melting peak; $\Delta T_m^{1/2}$, the half-height width of melting peak; $\Delta H_m$, the heat of fusion.

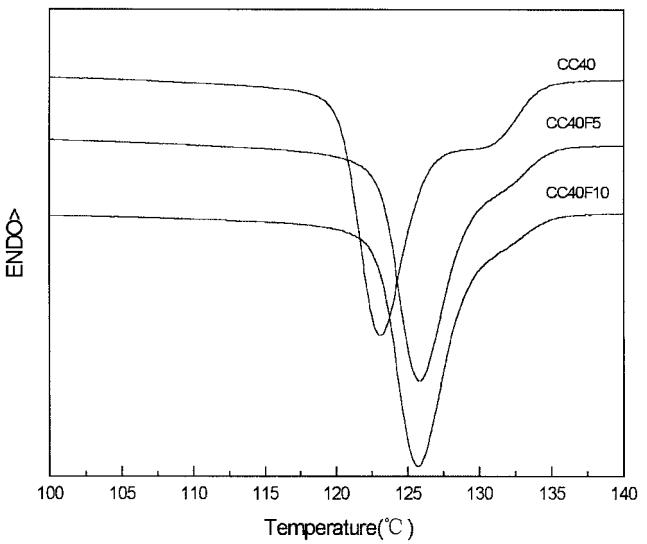


**Figure 4** DSC crystallization curves of nano-$CaCO_3$/PP modified with FPP.

matrix and interface adhesion between nanoparticles and matrix or interface adhesion between particles in the aggregation. Although traditional organic coupling agents improved the dispersion of the filler in the matrix, the improved interface adhesion between the filler and the matrix or between the filler and the filler is limited because the organic chains are short and unreactive. Use of reactive polar monomers, such as acrylic acid, to cover the surface of the filler, and then *in situ* synthesize functionalized macromolecular coupling agent in the preparation process of materials are more effective methods to improve the interface adhesion between filler and matrix.[1,11,34,45] The macromolecular coupling agent not only can improve the dispersion of the filler in the polymeric matrix, but also strengthen the adhesion between the filler and the polymer matrix. However, there is still no report on nano-$CaCO_3$/PP composites modified with functionalized macromolecular coupling agents. In our laboratory, the nano-$CaCO_3$/PP composites modified by AA were prepared by melt mixing in a twin-screw extruder. The nanodispersion of nano-$CaCO_3$ in PP matrix and improved physical and mechanical properties have been observed.[46] Physical and mechanical properties of PP composites depend on crystalline morphology of PP, which relates to crystallization behavior of PP. Therefore, the effects of additive functionalized PP and *in situ* formed functionalized PP on the crystallization and melting behavior of the nano-$CaCO_3$/PP composite are investigated in this article.

## EXPERIMENTAL

### Materials

Pelletized PP (CTS-700) and powdered PP (F-401) were the products of Yinzhu Polypropylene Co. (Guangzhou, China). Nano-calcium carbonate ($CaCO_3$; particle diameter between 40 and 60 nm; pH 9.6; BET surface area 23.24 $m^2/g$) was obtained from Guangping Chemical Industry Co., China. Chemical-grade acrylic acid (AA), used as the reactive monomer, was purchased form Fushan Chemical Factory, China. Chemical-grade dicumyl peroxide (DCP), used as an initiator for the grafting reaction, was a commercial product of Shanhai Chemical Reagent Factory, China. Premade PP-*g*-AA (FPP) with grafting yield of 0.56 mol % was synthesized in our laboratory according to the method described in an earlier report.[34]

### Preparation of the PP composite filled with nano-$CaCO_3$

The composition of nanocomposites is shown in Table I. The AA and DCP were added when nano-$CaCO_3$ and PP were blended in a GH-10 high-speed mixing machine (Beijing Plastic Machine Factory, China). The mixture was then extruded by a SHJN-20 twin-screw extruder (screw diameter = 25 mm; L/D = 30; Xinli Plastic Machine Factory, Nanjing Aviation University, China) at temperatures of 180–220°C, with the screw speed set at 60 rpm.

### DSC analyses

Differential scanning calorimetry (DSC) was performed with a Perkin–Elmer DSC-7 differential scanning calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT) under a nitrogen atmosphere. The samples were heated from 50 to 220°C at a rate of 100°C/min, held at that temperature for 5 min, then cooled to 50°C at a rate of 10°C/min, and finally heated again to 220°C at the same rate. The crystallization and melting parameters were recorded from the cooling and re-

**TABLE IV**
**DSC Crystallization Results of Nano-$CaCO_3$/PP Modified with Premade PP-*g*-AA**

| Sample | $T_c^0$ (°C) | $T_c^p$ (°C) | $T_c^f$ (°C) | $T_c^{on}$ (°C) | $\Delta H_c$ (J/g) | $\Delta T_c^1$ (°C) | $\Delta T_c^2$ (°C) | $\Delta T_c^{1/2}$ (°C) |
|---|---|---|---|---|---|---|---|---|
| CC40 | 137.5 | 123.1 | 98.2 | 127.1 | 111.5 | 39.3 | 4.0 | 4.3 |
| CC40F5 | 140.4 | 125.9 | 100.9 | 130.0 | 104.8 | 39.5 | 4.2 | 4.3 |
| CC40F10 | 139.1 | 125.7 | 101.4 | 129.7 | 97.0 | 37.7 | 4.0 | 4.0 |

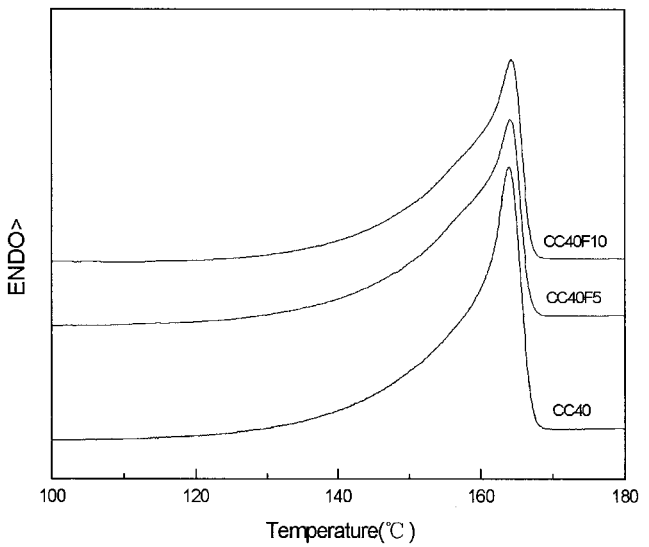


**Figure 5** DSC melting curves of nano-$CaCO_3$/PP modified with FPP.

heating scans. The crystallization and melting parameters were determined according to the method described in Figure 1.

## RESULTS AND DISCUSSION

### Crystallization and melting behavior of nano-$CaCO_3$/PP

DSC crystallization curves and data of pure PP and nano-$CaCO_3$/PP composites are shown in Figure 2 and Table II, respectively. For pure PP, the temperature at which the crystallization curve deviates from the baseline ($T_c^0$), the peak temperature of crystallization ($T_c^P$), and the temperature at the onset of crystallization ($T_c^{on}$) are 128.2, 117.5, and 121.9°C, respectively. When a small amount of nano-$CaCO_3$ (≤5 wt %) is added to PP, the $T_c^0$, $T_c^P$, and $T_c^{on}$ of the nano-$CaCO_3$/PP (CC2 and CC5) are lower than that of pure PP. When the nano-$CaCO_3$ is above 10 wt %, the $T_c^0$, $T_c^P$, and $T_c^{on}$ are increased with values much higher than those of pure PP. The increase in the crystallization temperature of PP is more significant with increasing nano-$CaCO_3$ content. Incorporation of nano-$CaCO_3$ can cause the width of crystallization peak ($\Delta T_c^2$) in the high temperature region and the half-height width ($\Delta T_c^{1/2}$) of the crystallization peak to narrow lightly, especially for the system containing 5 wt % nano-$CaCO_3$. It is suggested that the incorporation of nano-$CaCO_3$ increases the crystallization rate of PP. The nano-$CaCO_3$ has only a slight influence on the heat of crystallization of PP ($\Delta H_c$) when the content of nano-$CaCO_3$ is lower than 10 wt %; on the contrary, the nano-$CaCO_3$ of 40 wt % increases the $\Delta H_c$.

It is suggested that the high content of nano-$CaCO_3$ induced a greater heterogeneous nucleation effect and increased the crystallization degree of PP. Moreover, there is a shoulder peak at 129.6°C in the crystallization curve of PP when the content of nano-$CaCO_3$ is 40 wt %. Evidently, nano-$CaCO_3$ with high content can greatly change the crystallization behavior of PP. Mitsuishi et al.[4] also found that there was a shoulder peak or double peak in the DSC curve of $CaCO_3$/PP composites. They thought that the interaction between polymer and filler changed the crystallization rate of the matrix on the surface of fillers, and accordingly affected the crystallization behavior of PP. After $CaCO_3$ was treated by alkyl dihydrogen phosphate, the double peak disappeared. They believed that the surface of treated $CaCO_3$ was covered by treating agents, and therefore decreased the heterogeneous nucleation effect of $CaCO_3$ on PP. In this study, nano-$CaCO_3$ was treated by stearic acid. For lower contents of nano-$CaCO_3$, the effect of nano-$CaCO_3$ on the melt viscosity of PP is not great, and the friction and shear force during the mixing are too weak to destroy the surfactant covering on the surface of nano-$CaCO_3$. Because the surface of nano-$CaCO_3$, which acts as the heterogeneous nucleation agent of PP, is covered by stearic acid, the crystallization temperature of PP is decreased slightly. However, the incorporation of high nano-$CaCO_3$ contents can increase the melt viscosity of PP, in which the contact probability among nano-$CaCO_3$ particles and the friction are increased. The stearic acid that coated the surface of $CaCO_3$ may have been stripped off, and thus the exposed surface of $CaCO_3$ increases the interfacial interaction between nano-$CaCO_3$ and PP. Therefore PP has a higher crystallization temperature. Addition of nano-$CaCO_3$ not only changed the main crystallization peak but also a shoulder peak was observed, attributed to the heterogeneous nucleation.

Figure 3 presents the DSC melting curves of pure PP and nano-$CaCO_3$ composites and the melting data are

**TABLE V**
**DSC Melting Results of Nano-$CaCO_3$/PP Modified with Premade FPP**

| Sample | $T_m^0$ (°C) | $T_m^p$ (°C) | $T_m^f$ (°C) | $T_m^{on}$ (°C) | $\Delta H_m$ (J/g) | $\Delta T_m$ (°C) | $\Delta T_m^{1/2}$ (°C) |
|---|---|---|---|---|---|---|---|
| CC40 | 113.2 | 164.0 | 169.0 | 158.8 | 106.8 | 56.6 | 6.7 |
| CC40F5 | 118.0 | 164.3 | 169.5 | 157.4 | 98.6 | 51.4 | 9.1 |
| CC40F10 | 118.0 | 164.2 | 170.0 | 157.1 | 93.7 | 52.0 | 9.3 |

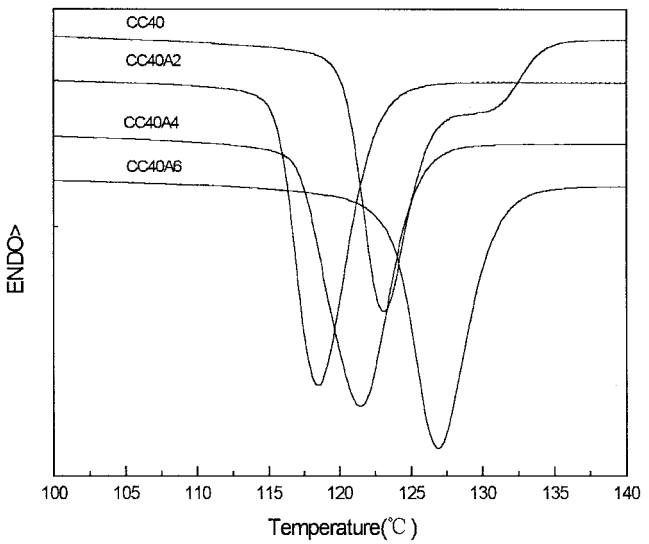


**Figure 6** DSC crystallization curves of nano-$CaCO_3$/PP modified with AA.

shown in Table III. When the content of nano-$CaCO_3$ is lower (≤5 wt %), the melting peak temperature $T_m^P$, the temperature at the melting completion $T_m^f$, and the temperature at the melting onset $T_m^{on}$ do not change significantly compared with pure PP. When the content of nano-$CaCO_3$ is more than 10 wt %, PP filled with nano-$CaCO_3$ has a high $T_m^P$, but the $T_m^{on}$ is scarcely changed. The increase of $T_m^P$ is attributed to formation of a more perfect crystal of PP with high lamellar thickness and high melting point attributed to the heterogeneous nucleation of nano-$CaCO_3$. The incorporation of nano-$CaCO_3$ causes the half-height width of melting peak ($\Delta T_m^{1/2}$) to become wider, which indicates that the size distribution of crystal grains became narrower. As for CC40 with high crystallization temperature and high nano-$CaCO_3$ content, the $\Delta T_m^{1/2}$ becomes wider because of the influence of the change of the shape of melting peak. The incorporation of nano-$CaCO_3$ affects the shape of melting peak of PP. For pure PP, a single melting peak was observed, but the CC2, CC5, and CC10 have a small melting peak at 147.3, 148.2, and 149.7°C, respectively, in the low-temperature region of the main melting peak. As the content of nano-$CaCO_3$ is increased, the small peak would shift to a higher temperature. For CC10 and CC40 with the higher nano-$CaCO_3$ content, this small peak overlaps with the main peak, which makes the $\Delta T_m^{1/2}$ of CC40 much wider. Although Ren[33] found that nano-$CaCO_3$ could induce PP to form β-crystal and there was a melting peak of β-crystal at about 150°C, it is still expected to further confirm by the experiment reported here whether the small melting peak is related to the formation of β-crystal.

### Crystallization and melting behavior of nano-$CaCO_3$/PP modified with premade PP-*g*-AA

DSC crystallization curves of nano-$CaCO_3$/PP composites modified with premade PP-*g*-AA are shown in Figure 4 and the crystallization data are presented in Table IV. For PP filled with 40 wt % nano-$CaCO_3$, the $T_c^0$, $T_c^f$, $T_c^P$, and $T_c^{on}$ are 137.5, 98.2, 123.1, and 127.1°C, respectively. When PP-*g*-AA of 5 and 10 phf was added, all the above values of the samples were increased but $\Delta T_c^1$, $\Delta T_c^2$, and $\Delta T_c^{1/2}$ scarcely changed. Mai et al.[34] found that the PP-*g*-AA can improve the heterogeneous nucleation effect of nano-$CaCO_3$ and further increase the crystallization temperature. However, $\Delta H_c$ decreased with increasing of the PP-*g*-AA content. The $\Delta T_c^{1/2}$ of the crystallization peak does not obviously change, which indicates that the addition of PP-*g*-AA has no evident influence on the size distribution of PP crystal grain.

Our studies on $Al(OH)_3$/PP composites modified with functionalized polypropylene indicated that the PP-*g*-AA can improve the nucleation of PP and increase the crystallization temperature.[35–38] In nano-$CaCO_3$/PP composites modified with PP-*g*-AA, the promoted heterogeneous nucleation effect of nano-$CaCO_3$ by PP-*g*-AA reach a saturation when 5 phf PP-*g*-AA was added into nano-$CaCO_3$/PP. When the content of PP-*g*-AA was increased to 10 phf, the crystallization temperature of PP no longer increases. The incorporation of PP-*g*-AA can also change the shape of the crystallization peak of PP in the nano-$CaCO_3$/PP composite. With the increasing of PP-*g*-AA content, the intensity of the shoulder peak of CC40 at high temperature tends to be weakened. It is suggested that PP-*g*-AA lies in the interface between nano-$CaCO_3$ and PP and produces the interaction of the interface between nano-$CaCO_3$ and PP, thus decreasing the effect of $CaCO_3$ on the PP crystallization behavior and weakening the intensity of the shoulder peak at high temperature.

**TABLE VI**
**DSC Crystallization Results of Nano-$CaCO_3$/PP Modified with AA**

| Sample | $T_c^0$ (°C) | $T_c^P$ (°C) | $T_c^f$ (°C) | $T_c^{on}$ (°C) | $\Delta H_c$ (J/g) | $\Delta T_c^1$ (°C) | $\Delta T_c^2$ (°C) | $\Delta T_c^{1/2}$ (°C) |
|---|---|---|---|---|---|---|---|---|
| CC40 | 137.5 | 123.1 | 98.2 | 127.1 | 111.5 | 39.3 | 4.0 | 4.3 |
| CC40A2 | 128.6 | 118.5 | 101.6 | 122.6 | 96.0 | 27.0 | 4.1 | 4.0 |
| CC40A4 | 132.0 | 121.5 | 100.4 | 125.5 | 104.6 | 31.6 | 4.0 | 5.1 |
| CC40A6 | 137.5 | 126.9 | 100.9 | 130.9 | 102.4 | 36.6 | 4.0 | 4.3 |

Figure 5 presents the DSC melting curves of nano-$CaCO_3$/PP composites modified with premade PP-*g*-AA and the melting data are shown in Table V. Although the addition of PP-*g*-AA and the increase in the PP-*g*-AA content have no significant influence on the $T_m^P$, $T_m^f$, and $T_m^{1/2}$, the $T_m^{on}$ and $\Delta H_m$ are decreased slightly and the $T_m^0$ and $\Delta T_m^{1/2}$ are increased with increasing of the PP-*g*-AA content. It is thought that the addition of PP-*g*-AA is helpful in causing nano-$CaCO_3$/PP composites to form crystals with small crystal lamellae and wide crystal size distribution. However, the incorporation of PP-*g*-AA significantly changes the shape of the melting peak. The intensity of the melting peak in low temperature region is sharply increased.

### Crystallization and melting behavior of nano-$CaCO_3$/PP modified with acrylic acid

DSC crystallization curves of nano-$CaCO_3$/PP composites modified with acrylic acid (AA) are shown in Figure 6 and crystallization data are presented in Table VI. Addition of 2 phf AA decreased the $T_c^0$, $T_c^f$, and $T_c^{on}$ of PP in nano-$CaCO_3$/PP composites. However, the $T_c^0$, $T_c^f$, and $T_c^{on}$ gradually increase with increasing AA content. When the AA content is 6 phf, the $T_c^0$, $T_c^f$, and $T_c^{on}$ are higher than those of unmodified nano-$CaCO_3$/PP composites. For the nano-$CaCO_3$ used here with particle diameter of 40–60 nm, the specific surface area is about 23.24 $m^2/g$. Assuming that the AA tends to orient normal to the surface of the filler with the carboxylic acid group, then one AA molecule should occupy an area of about 0.2 $nm^2$.[47] The surface area of the nano-$CaCO_3$ (i.e., 23.24 $m^2/g$) requires $11.62 \times 10^{19}$ molecules/g or 0.18 mmol/g of AA to form a monolayer coating, which is equivalent to 1.38 phf. Therefore, in other words, the dosage of AA in our work is more than that of the single molecular layer. Tabtiang[2,11] also found that if the dosage of AA was greater than that of the single molecular layer, the reaction of excessive AA with micro-$CaCO_3$ produced $Ca(AA)_2$, which was dissociated in the matrix. In our work, addition of AA with a low content weakened the heterogeneous nucleation effect of nano-$CaCO_3$ and led to a lower crystallization temperature than that of the unmodified composites because the surface of nano-$CaCO_3$ is covered with AA. With increasing of AA, the excessive AA will react with nano-$CaCO_3$ to form $Ca(AA)_2$, which leads to improved heterogeneous nucleation and increased crystallization temperature of PP in nano-$CaCO_3$/PP composites. Addition of AA decreased the $\Delta H_c$ of all samples, although $\Delta T_c^2$ values scarcely changed. The addition of AA also caused the complete disappearance of the shoulder peak in the unmodified sample, the same as with PP-*g*-AA, which indicates that the heterogeneous nucleation effect of nano-$CaCO_3$ on the crystallization of PP is weakened because of the surface coverage of nano-$CaCO_3$ with AA.

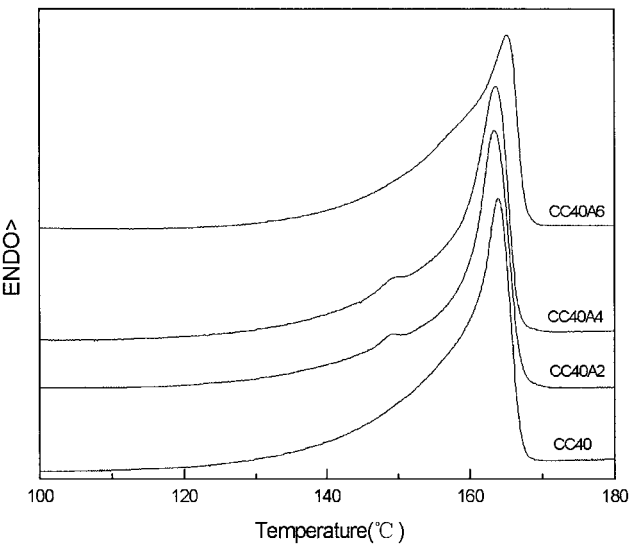


**Figure 7** DSC melting curves of nano-$CaCO_3$/PP modified with AA.

Figure 7 presents the DSC melting curves of samples corresponding to Figure 6 and the melting data are shown in Table VII. The addition of AA slightly decreased the $T_m^P$. However , when AA of 6 phf was added, the $T_m^P$ was higher than that of the sample without AA. It is suggested that the addition of lower content of AA decreases the crystallization temperature of PP in the nano-$CaCO_3$/PP composites and forms crystals with small lamellar thickness and a lower degree of crystallization perfection. In the nano-$CaCO_3$/PP composites modified by 6 phf of AA, the lamellar thickness and $T_m^P$ both increased as a result of the higher crystallization temperature. The $T_m^0$ was

**TABLE VII**
**DSC Melting Results of Nano-$CaCO_3$/PP Modified with AA**

| Sample | $T_m^0$ (°C) | $T_m^p$ (°C) | $T_m^f$ (°C) | $T_m^{on}$ (°C) | $\Delta H_m$ (J/g) | $\Delta T_m$ (°C) | $\Delta T_m^{1/2}$ (°C) |
|---|---|---|---|---|---|---|---|
| CC40 | 113.2 | 164.0 | 169.8 | 158.6 | 106.8 | 56.6 | 6.7 |
| CC40A2 | 115.9 | 163.5 | 171.6 | 158.5 | 96.1 | 55.7 | 5.3 |
| CC40A4 | 116.4 | 163.6 | 171.2 | 157.2 | 101.0 | 54.8 | 5.9 |
| CC40A6 | 121.8 | 165.3 | 170.5 | 157.0 | 97.3 | 48.8 | 9.3 |

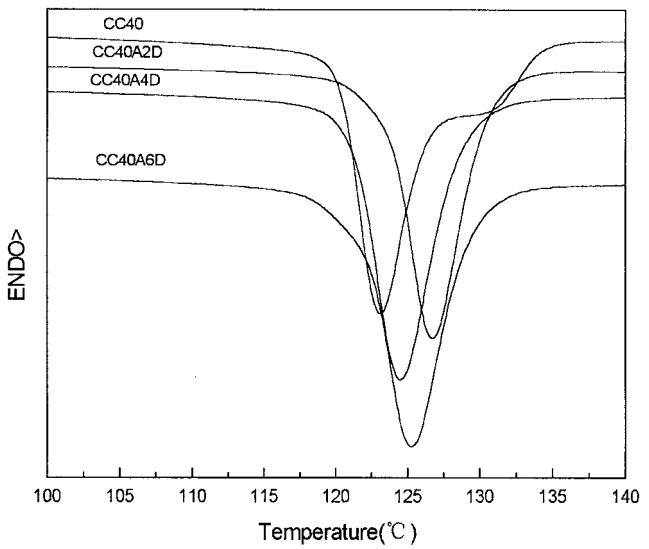


**Figure 8** DSC crystallization curves nano-$CaCO_3$/PP modified with AA in the presence of DCP.

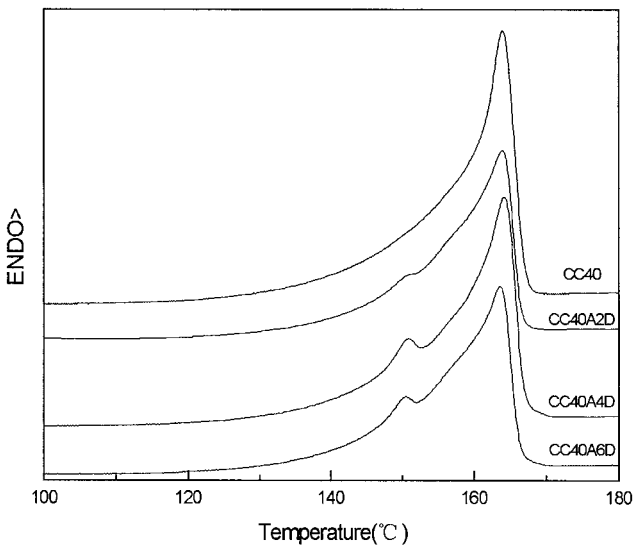


**Figure 9** DSC melting curves of nano-$CaCO_3$/PP modified with AA in the presence of DCP.

increased with increasing AA content. For the 6 phf of AA, the $T_m^0$ was 8.6°C higher than that of the sample without AA. The addition of AA also slightly increased $T_m^f$ compared to that of the unmodified sample. However, the incorporation of AA and increasing of the AA content decreased the $T_m^{on}$ because of the change of the peak shape. The effect of AA content on the $\Delta T_m^{1/2}$ was observed. When either 2 and 4 phf AA was added, the $\Delta T_m^{1/2}$ was lower than that of the sample without AA. Addition of 6 phf AA increased the $\Delta T_m^{1/2}$ and the $\Delta T_m^{1/2}$ was 2.6°C higher than that of the sample without AA. The $\Delta T_m^{1/2}$ is related to the change of the peak shape. Compared to the sample without AA, a small peak appeared at temperatures of 148.8 or 149.2°C in the nano-$CaCO_3$/PP composites modified by 2 and 4 phf AA, respectively. However, the small peak disappeared again and the area of the low-temperature region of the melting peak increased in the nano-$CaCO_3$/PP composites modified with 6 phf AA. The small melting peak is probably related to the $\beta$-crystal of PP, which is expected to be further confirmed by experiments.

### Crystallization and melting behavior of nano-$CaCO_3$/PP modified with AA in the presence of dcp

DSC crystallization curves of nano-$CaCO_3$/PP composites modified with AA in the presence of DCP are shown in Figure 8 and the crystallization data are presented in Table VIII. For the composites containing DCP the objective was to promote coupling through grafting between AA and PP. Compared with Figure 6, the temperature of the crystallization peak of PP in nano-$CaCO_3$/PP composites modified with AA in the presence of DCP is much higher than that of nano-$CaCO_3$/PP composites modified only with AA. The $T_c^0$, $T_c^P$, $T_c^f$, and $T_c^{on}$ of composites modified with 2 phf AA in the presence of DCP are 7.8, 8.2, 5.0, and 3.5°C higher than those of the composites without DCP. As for the composites without DCP, the $T_c^0$, $T_c^P$, and $T_c^{on}$ are increased with increasing AA content. After DCP was added, however, the effect of the AA content on the crystallization temperature decreased. On one hand, the nucleation effect of the formatiion of *in situ* formed PP-*g*-AA increases the crystallization rate; on the other hand, the polarity of PP-*g*-AA hinders the growth of PP crystal. If the effect of $CaCO_3$ on the PP crystallization is ascertained by increasing the temperature of the crystallization peak, the incorporation of AA with a high content can increase the crystallization peak temperature of PP without DCP; in the presence of DCP, however, only with the content of 2 phf AA can PP obtain a higher crystallization peak temperature. In the meantime, the shape of the crystallization peak also changes and the shoulder peak of

**TABLE VIII**
**DSC Crystallization Results of Nano-$CaCO_3$/PP Modified with AA in the Presence of DCP**

| Sample | $T_c^0$ (°C) | $T_c^p$ (°C) | $T_c^f$ (°C) | $T_c^{on}$ (°C) | $\Delta H_c$ (J/g) | $\Delta T_c^1$ (°C) | $\Delta T_c^2$ (°C) | $\Delta T_c^{1/2}$ (°C) |
|---|---|---|---|---|---|---|---|---|
| CC40 | 137.5 | 123.1 | 98.2 | 127.1 | 111.5 | 39.3 | 4.0 | 4.3 |
| CC40A2D | 136.4 | 126.7 | 103.2 | 130.6 | 100.4 | 33.2 | 3.8 | 3.7 |
| CC40A4D | 135.7 | 124.5 | 103.2 | 128.8 | 111.5 | 32.5 | 4.3 | 4.5 |
| CC40A6D | 137.1 | 125.3 | 104.1 | 129.5 | 99.5 | 33.0 | 4.2 | 4.5 |

**TABLE IX**
**DSC Melting Results of Nano-$CaCO_3$/PP Modified with AA in the Presence of DCP**

| Sample | $T_m^0$ (°C) | $T_m^p$ (°C) | $T_m^f$ (°C) | $T_m^{on}$ (°C) | $\Delta H_m$ (J/g) | $\Delta T_m$ (°C) | $\Delta T_m^{1/2}$ (°C) |
|---|---|---|---|---|---|---|---|
| CC40 | 113.2 | 164.0 | 169.8 | 158.6 | 106.8 | 56.6 | 6.7 |
| CC40A2D | 111.8 | 164.0 | 169.3 | 154.3 | 93.8 | 57.5 | 9.1 |
| CC40A4D | 120.7 | 164.2 | 171.6 | 157.3 | 108.9 | 50.9 | 8.0 |
| CC40A6D | 120.7 | 163.7 | 170.5 | 155.1 | 93.8 | 49.8 | 9.3 |

CC40 disappears. In the presence of DCP, the effect modified with AA is similar to that modified with PP-*g*-AA. The formation of *in situ* formed PP-*g*-AA lies in the interface between nano-$CaCO_3$ and PP, which affects the crystallization behavior of nano-$CaCO_3$–filled PP.

Figure 9 presents the DSC melting curves of samples corresponding to Figure 8 and the melting data are shown in Table IX. In the presence of DCP, the $T_m^p$, $T_m^f$, $T_m^{on}$, and $\Delta H_m$ scarcely change but $\Delta T_m^{1/2}$ is widened. The formation of *in situ* formed PP-*g*-AA in the presence of DCP promotes the nucleation and accelerates the crystallization of PP, although the polarity interaction of PP-*g*-AA hinders the growth of PP crystal and widens the size distribution of crystal lamellae. From Figure 8, a small peak at about 150°C, which is not affected by the content of AA, may be observed that may be related to the $\beta$-crystal of PP. For the same content of AA, the intensity of the small melting peak of PP increases in the composites modified with AA in the presence of DCP. It is suggested that the scission of PP chains in the presence of DCP decreases the molecular weight and increases the ability to produce $\beta$-crystal.

## CONCLUSIONS

A low content of nano-$CaCO_3$ did not exert a nucleation effect on PP to increase the crystallization temperature of PP because of the coating of stearic acid. With a high content of nano-$CaCO_3$, however, the coating of stearic acid was stripped off during the preparation of nano-$CaCO_3$/PP composites in the extruder; the exposed surface of nano-$CaCO_3$ exerted a heterogeneous nucleation effect on PP, leading to an increase of crystallization temperature. With the increased content of AA, the crystallization temperature of nano-$CaCO_3$/PP composites modified by acylic acid (AA) was increased because of the formation of $Ca(AA)_2$. In the presence of DCP, the nano-$CaCO_3$/PP modified by AA also had a higher crystallization temperature because of the formation of PP-*g*-AA. According to the change of crystallization and melting behavior, we deduced that the modification of AA with and without DCP mainly existed on the interface and led to the change of interface interaction between nano-$CaCO_3$ and PP, consequently influencing the other important properties, thus providing a compelling basis for further investigation.

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