Crystallization and Melt Behavior of $Mg(OH)_2$/PP Composites Modified by Functionalized Polypropylene

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ABSTRACT: The crystallization and melting behavior of $Mg(OH)_2$/PP composites modified by the addition of functionalized polypropylene (FPP) or acrylic acid (AA) and the formation of *in situ* FPP were investigated by DSC. The results indicated that addition of FPP increased the crystallization temperatures of PP because of the nucleation effect of FPP. The formation of *in situ* FPP resulted in a reduced crystallization rate, melting point, and degree of crystallization attributed to the decreased regularity of the PP chain. For $Mg(OH)_2$/PP composites, the addition of $Mg(OH)_2$ increased the crystallization temperatures of PP resulting from a heterogeneous nucleation effect of $Mg(OH)_2$. The addition of FPP into $Mg(OH)_2$/PP composites further enhanced the crystallization temperatures of PP. It is suggested that there is an activation of FPP to the heterogeneous nucleation effect on the $Mg(OH)_2$ surface. The addition of AA also increased the crystallization temperatures of PP in $Mg(OH)_2$/PP composites, although the crystallization temperature of PP was not influenced by the AA content, which is explained by the heterogeneous nucleation effect of the $Mg(OH)_2$ surface activated by FPP and AA. A synergistic effect on the crystallization of PP in $Mg(OH)_2$/PP composites further increased the crystallization temperatures of PP. However, The crystallization temperatures of $Mg(OH)_2$/PP composites modified by *in situ* FPP were lower than those of $Mg(OH)_2$/PP composites modified by addition of either FPP or AA. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3610–3621, 2004

Key words: crystallization; nucleation; composites; functionalized polypropylene (FPP); melting point

INTRODUCTION

Polypropylene (PP) is a kind of general plastic with excellent comprehensive characteristics. However, the high flammability of PP has limited its usefulness. Presently, halogen-antimony trioxide synergistic fire retardant and intumescent fire retardant based on phosphorous-containing materials are mainly used to reduce the inherent flammability of PP. In recent years, inorganic fire-retardants such as aluminum hydroxide $[Al(OH)_3]$ and magnesium hydroxide $[Mg(OH)_2]$ have attracted great attention because they are acid and halogen free. However, to be effective, high filler loadings are necessary, resulting in a significant loss in mechanical properties, especially in strength and toughness.

PP composites filled by $Mg(OH)_2$ have been widely studied. Hornsby and Watson[1] investigated the mechanical properties of $Mg(OH)_2$/PP composites. Because of the differences in surface polarity, the addition of $Mg(OH)_2$ resulted in a significant deterioration to mechanical properties of PP, particularly impact strength. Although surface treatment of $Mg(OH)_2$ improved the mechanical properties of PP composites, different surface treatments on $Mg(OH)_2$ have had various effects on the mechanical properties of $Mg(OH)_2$/PP composites.[2,3] Slight improvements in flexural strength and flexural modulus for silane coupling–agent treated composites and some increase in impact strength for titanate coupling–agent treated composites were observed. The addition of $Mg(OH)_2$ treated by fatty acid derivatives resulted in a marked improvement in impact strength of $Mg(OH)_2$/PP composites. This significant improvement was attributed to a modification of the polymer deformation mechanism in the vicinity of the filler particles, resulting in localized voiding, manifested as stress whitening.

The morphology,[4,5] size,[6] and dispersion[7] of $Mg(OH)_2$ also influenced the mechanical properties of $Mg(OH)_2$/PP composites. The mechanical properties of PP filled by $Mg(OH)_2$ needles was higher than that of PP filled by $Mg(OH)_2$ platelets because of the larger surface area of $Mg(OH)_2$ needles, leading to an increased effective contact with matrix and enhanced interaction between filler and matrix.[4] The addition of microporous filler particles with irregular surface promoted the interfacial interaction between particles and

matrix, leading to an increased flexural strength, although platelet filler tended to introduce crack, resulting in a decreased impact strength.[5] For PP filled by smaller-size particles, the flexural modulus was higher than that of PP filled by larger-size particles.[6] Usually the better the dispersion, the higher the tensile, flexural, and impact strengths.[7] On the other hand, the fire-retardant property of $Mg(OH)_2$/PP composites depended on the content of $Mg(OH)_2$.[8–10] With increased $Mg(OH)_2$ content, an improved fire-retardant property was observed. Besides $Mg(OH)_2$ content, the fire-retardant property of $Mg(OH)_2$/PP composites was also relative to the dispersion[7] and surface treatment of $Mg(OH)_2$.[11] It was found that $Mg(OH)_2$ treated by magnesium stearate coupling agent markedly enhanced the flammability of $Mg(OH)_2$/PP composites, attributed to increasing the filler content and lowering the viscosity of the PP by addition of magnesium stearate. The synergistic effect of $Mg(OH)_2$ with other fire retardants was reported, such as intumescent fire retardant,[12] red phosphorous and $Al(OH)_3$,[13] KCl and Na_2SnO_3,[14] and so on.

Although surface modification of $Mg(OH)_2$ treated by organic coupling agents enhances the mechanical properties of $Mg(OH)_2$/PP composites, the use of functionalized polymer to improve compatibility, interfacial interaction, and mechanical properties of PP blends and PP composites has been widely investigated in recent years, such as $CaCO_3$/PP,[4,15,16] mica/PP,[17] talc/PP,[18] halogen-antimony trioxide/PP,[19] $Al(OH)_3$/PP,[20–24] glass fiber/PP,[25] and natural fiber/PP[26,27] composites. However, few studies[2,3] on the effect of functionalized PP (FPP) in $Mg(OH)_2$/PP composites were reported, in particular the $Mg(OH)_2$/PP composites modified by addition of FPP and the formation of *in situ* FPP.

The physical and mechanical properties of PP composites depend on crystalline morphologies of PP, which are relative to crystallization behavior of PP. Few studies on crystallization behavior of $Mg(OH)_2$/PP composites have been reported. The crystallization behavior of PP composites filled by $Mg(OH)_2$ with two kinds of morphology were investigated by Cook and Harper.[5,6] They found that, like mica[28] and $CaCO_3$,[29] $Mg(OH)_2$ had a heterogeneous nucleation effect on PP, leading to an increase in the crystallization temperatures by 5–10°C and a higher degree of crystallization. The smaller size of $Mg(OH)_2$ has a more significant effect on the crystallization of PP. It was found that $Mg(OH)_2$ treated by ammonium stearate led to a further improved nucleation rate and narrowed the crystallization distribution, although too much modifier had the opposite effect on PP crystallization, resulting in a maximum degree of crystallization appearing at 3 wt % modifier content. However, the effect of FPP on crystallization behavior and melt behavior of $Mg(OH)_2$/PP composites has not yet

been reported. Because of the location of additive FPP and *in situ* FPP on the interface between $Mg(OH)_2$ and PP, the interaction of FPP with $Mg(OH)_2$ surface will modify the $Mg(OH)_2$ surface properties, accordingly changing the nucleation effect of $Mg(OH)_2$ on the crystallization behavior of PP. In this article, the effect of additive FPP and *in situ* FPP on crystallization behavior and melt behavior of $Mg(OH)_2$/PP composites were studied and discussed.

EXPERIMENTAL

Materials

Powdered PP (F401) and pelletized PP (CTS-700, melt flow index = 13 g/min) were commercial products of Guangzhou Yinzhu PP (China). Chemical-grade AA was purchased from Shanghai Feida Industrial Trade (China) and used without further purification. Chemical-grade dicumyl peroxide(DCP), used as an initiator for the AA grafting reaction, was a commercial product of Shanghai Chemical Reagent Stocking and Providing Station Pool Enterprise Central Factory (China). $Mg(OH)_2$ was obtained from Zhejiang Chemical Plant (China). The solvent acetone was obtained from Guangzhou Chemical Reagent Factory (China).

Preparation of composites

Functionalized polypropylene (FPP)

The DCP and AA were dissolved in acetone and thoroughly blended with powdered PP in a GH-10 high-speed mixing machine (Beijing Plastic Machine Shop, China). After the solvent acetone had completely evaporated, the mixture of AA and DCP was coated onto the surface of the powdered PP, and the pretreated PP was prepared. The pretreated PP was then extruded by a SHJ-53 twin-screw extruder (Nanjing Aviation Institute Xinli Plastic Machine Shop, China) at temperatures of 185–190°C, with the screw speed set at 60 rpm. The extruded products of functionalized polypropylene (FPP) were frozen in-line in a water bath, dried, and granulated.

Mg(OH)₂/PP composites modified by FPP

Mg(OH)₂/PP composites modified by in situ *FPP.* $Mg(OH)_2$, DCP, AA, and pelletized PP were thoroughly blended with a high-speed mixing machine and the mixtures were then extruded by a twin-screw extruder at temperatures of 185–190°C, with the screw speed set at 60 rpm. The extruded products were granulated and designated as $Mg(OH)_2$/PP composites modified by *in situ* FPP.

Mg(OH)₂/PP composites modified by addition of FPP. $Mg(OH)_2$, premade FPP, and pelletized PP were thoroughly blended with a high-speed mixing machine
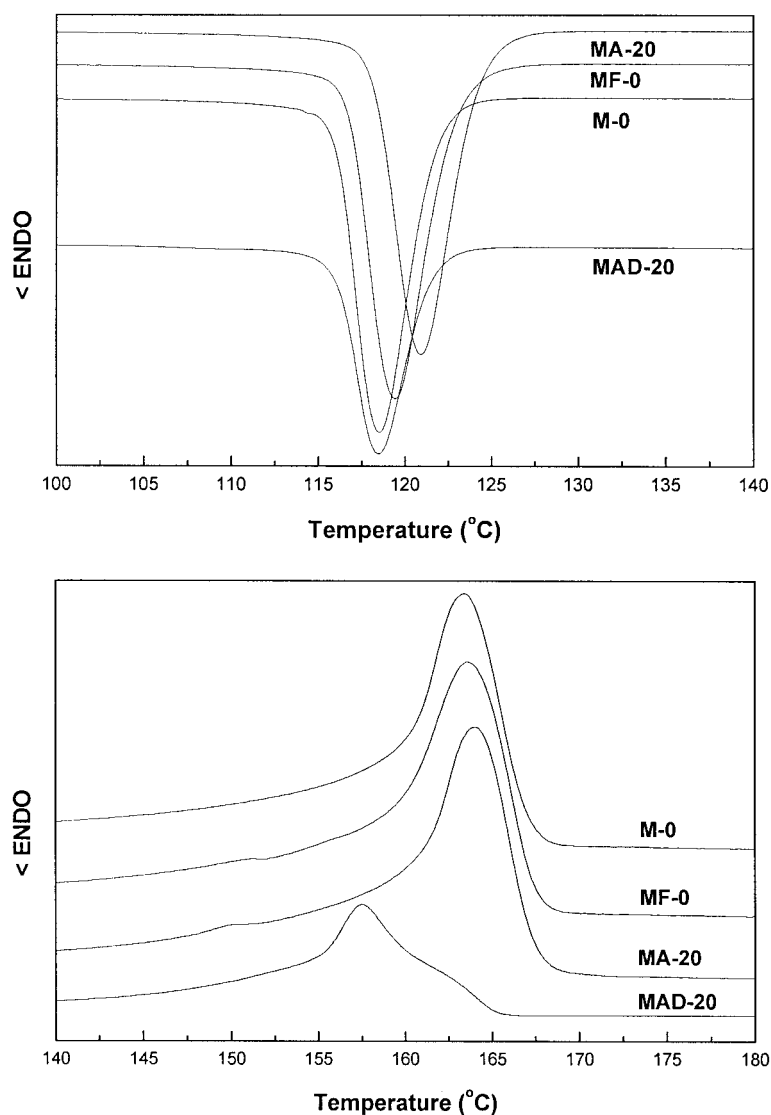
Figure 1   DSC crystallization and melting curves of PP modified by AA or FPP.

and the mixtures were then extruded by a twin-screw extruder at temperatures of 185–190°C, with the screw speed set at 60 rpm. The extruded products were granulated and designated as $Mg(OH)_2/PP$ composites modified by additive FPP.

DSC measurements

DSC measurements were made on a Perkin–Elmer DSC-7 thermal system (Perkin Elmer Cetus Instruments, Norwalk, CT) under nitrogen atmosphere with heating and cooling rates of 10°C/min. The samples were heated from 50 to 220°C, held at that temperature for 3 min, and then cooled to 50°C, followed by reheating to 220°C for the second heating run. The crystallization and melting parameters were recorded from the cooling and reheating scans.

RESULTS AND DISCUSSION

Crystallization and melting behavior of PP and PP modified by FPP

Figure 1 depicts DSC cooling and heating curves of PP modified by additive FPP and PP modified by *in situ* FPP, and the crystallization and melting parameters are presented in Tables I and II. Studies on functionalized PP[20–24] have established that the temperature at which the crystallization curve deviates from the baseline (T_c^o) and the peak temperature of crystallization (T_c^p) of FPP were 125.4 and 116.4°C, respectively, both lower than those of pure PP (M-0). However, it can be seen from Table I that temperature at the onset of crystallization (T_c^{on}) and the T_c^p of MF-0 prepared from PP modified by addition of 5 phr FPP were higher than those of M-0, indicating that even a small amount

TABLE I
DSC Crystallization Results of $Mg(OH)_2$/PP Composites[a]

Sample	T_c° (°C)	T_c^p (°C)	T_c^f (°C)	T_c^{on} (°C)	ΔT_c (°C)	$\Delta T_c^{1/2}$ (°C)	ΔH_c (J/g)
M-0	127.1	118.6	106.3	121.9	20.8	3.4	98.7
MF-0	128.3	119.5	106.3	123.0	22.1	3.8	98.5
MA-20	129.6	121.0	106.6	124.4	17.0	3.8	99.0
MAD-20	127.5	119.0	106.3	121.9	21.2	3.1	96.5
M-2	131.2	123.3	108.8	127.2	23.7	3.8	92.2
M-4	129.4	121.4	112.5	124.8	19.2	3.1	90.7
M-6	131.7	123.6	109.6	127.0	22.1	4.4	97.5
MA-26	138.1	130.7	122.7	135.0	15.4	4.1	93.0
MA-46	137.7	130.7	121.9	134.8	15.8	4.4	75.0
MF-2	133.3	124.9	111.0	128.6	22.3	3.8	104.6
MF-4	134.3	126.6	112.5	130.2	21.9	3.4	104.8
MF-6	134.2	126.9	113.8	130.4	22.4	3.8	96.0
MAD-22	129.4	120.0	112.7	123.8	16.7	3.4	90.0
MAD-24	132.1	122.0	113.8	127.3	18.3	3.8	94.3
MAD-26	131.7	123.9	116.3	127.5	15.4	3.4	96.3
MAD-44	130.6	122.2	114.4	126.3	16.3	3.8	87.0
MAD-46	130.8	123.3	117.1	127.5	18.3	3.8	93.0

[a] T_c°, the temperature in 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; $\Delta T_c = T_c^\circ T_c^f$; $\Delta T_c^{1/2}$, the half-height width of crystallization peak; ΔH_c, the heat of crystallization.

of FPP had a nucleation effect on PP. A broadening of the width of the crystallization peak (ΔT_c) and the width at half-height of the crystallization peak ($\Delta T_c^{1/2}$) of MF-0 were observed. However, the degree of crystallization essentially had not been influenced. For MA-20 prepared from PP modified by addition of 2 phr AA, more significantly increased values of T_c^{on} and T_c^p were obtained, 124.4 and 121.0°C, respectively. The

ΔT_c was suppressed. The $\Delta T_c^{1/2}$ and ΔH_c were basically identical to those of MF-0. These experimental results indicated that the addition of AA into PP could also accelerate the crystallization of PP. During the preparation process of MA-20 by melting extrusion, possibly one part of AA homopolymerized and formed a homopolymer (PAA), whereas the other part of AA reacted with macroradical produced by degra-

TABLE II
DSC Melting Results of $Mg(OH)_2$/PP Composites

Sample	T_m° (°C)	T_m^p (°C)	T_m^f (°C)	T_m^{on} (°C)	ΔT_m (°C)	$\Delta T_m^{1/2}$ (°C)	ΔH_m (J/g)
M-0	124.8	163.2	169.6	159.0	44.8	4.1	95.0
MF-0	123.1	163.5	170.0	158.1	46.9	5.6	97.2
MA-20	124.6	163.9	171.6	159.4	47.1	5.0	95.7
MAD-20	126.7	157.4	167.1	153.6	40.4	6.3	86.4
M-2	126.3	163.5	168.8	157.5	40.0	4.4	92.6
M-4	127.5	163.6	168.0	159.0	37.5	4.1	95.2
M-6	128.5	164.5	168.7	158.0	40.2	6.9	95.9
MA-26	135.4	165.5	169.6	154.0	34.2	10.0	96.3
MA-46	135.0	165.6	169.6	150.0	34.6	10.3	79.3
MF-2	127.3	164.6	169.2	159.2	41.9	5.9	103.5
MF-4	130.0	164.5	169.0	159.2	39.0	6.3	96.2
MF-6	128.5	164.0	168.7	158.0	40.2	6.9	97.0
MAD-22	132.5	158.3	167.1	155.0	34.6	5.0	85.1
MAD-24	129.2	159.1	166.7	154.7	37.5	7.2	92.2
MAD-26	130.4	159.0	165.6	152.6	35.2	8.1	93.8
MAD-44	134.8	158.4	166.0	154.1	31.3	7.2	81.3
MAD-46	137.7	159.3	166.2	153.9	28.5	7.5	85.8

[a] T_m°, the temperature in 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; $\Delta T_m = T_m = T_m^\circ$, the melting peak width; $\Delta T_m^{1/2}$, the half-height width of melting peak; ΔH_m, the heat of fusion.

dation of PP during the melt extrusion process, grafting onto PP, and forming *in situ* FPP. Both FPP and PAA may exert a nucleation effect on PP, consequently accelerating the crystallization of PP and increasing the crystallization temperature. Rao et al.[30] investigated the thermodynamics of PP grafted with AA and found that the AA homopolymer in PP acted as a nucleating agent.

To facilitate the formation of macroradical for PP, PP modified by AA in the presence of 0.5 phr DCP, MAD-20, was prepared. Compared to MA-20, a decrease in the T_c^{on} and T_c^p, an increased width of crystallization peak, a decrease of $\Delta T_c^{1/2}$, and a reduced ΔH_c of MAD-20 were observed. These phenomena may be attributed to two reasons. On one hand, the DCP produced a large amount of free radicals, resulting in AA grafting onto PP and the formation of *in situ* FPP, thus accelerating crystallization of PP. On the other hand, the grafting of AA onto PP destroyed the regularity of the PP chain, leading to reduced crystallizability of PP. The crystallization of PP depends on the balance of these two interactions. Compared to pure PP (M-0), the high T_c^{on} and T_c^p of MAD-20 were observed. Obviously, AA grafting onto PP exerts a nucleation effect on PP, leading to a shift of crystallization peak to high temperature.

The addition of FPP and the formation of *in situ* FPP not only affected the crystallization behavior of PP, but also influenced the melting behavior of PP. The DSC melting results of PP modified by additive PP and *in situ* FPP are presented in Table II. Studies on functionalized PP[20–24] have shown that the T_m^{on} and T_m^p of FPP were 147.8 and 153.0°C, respectively, both values of which were lower than those of M-0, 159.1 and 163.2°C, respectively. The ΔH_m (74.7 J/g) of FPP was also much less than that of MF-0 (95.0 J/g). In the MF-0 prepared by addition of 5 phr FPP into PP, except for the increased half-height width of melting peak ($\Delta T_m^{1/2}$), the T_m^{on}, T_m^p, and ΔH_m were close to those of M-0, indicating that the addition of FPP in PP does not significantly influence the melting behavior of PP. For MA-20 prepared from PP modified by the addition of 2 phr AA in the absence of DCP, the T_m^{on}, T_m^p, and ΔH_m basically remained unchanged. For MAD-20 prepared from PP modified by the addition of 2 phr AA in the presence of DCP, however, the T_m^{on}, T_m^p, and ΔH_m were all lower than those of M-0, MF-0, and MA-20. It is suggested that the addition of DCP led to the degradation of PP and the production of numerous free radicals, in which the AA grafted onto PP and formed FPP. Although the formation of FPP exhibited an improved nucleation effect on crystallization of PP, the formation of FPP by grafting reaction resulted in a decrease in the regularity of the PP chain, which in turn led to reduced nucleation and growth rate, the formation of crystal with low crystalline perfection, and the suppression in melting point and degree of crystallization of PP.

Crystallization and melting behavior of Mg(OH)₂/PP composites

Figure 2 depicts DSC cooling and heating curves of PP filled with different contents of $Mg(OH)_2$, and the crystallization and melting parameters are presented in Tables I and II, respectively. The addition of different amounts of $Mg(OH)_2$ led to an increase in T_c^{on} and T_c^p of PP. The crystallization temperature of M-2 with 20 wt % $Mg(OH)_2$ was much higher than that of M-0, and a broadened crystallization peak was observed, attributed to the heterogeneous nucleation effect of the $Mg(OH)_2$ surface. However, by increasing the $Mg(OH)_2$ content, the crystallization parameters of PP changed only slightly, possibly because of the fact that there would be a critical surface area for the heterogeneous nucleation effect of the $Mg(OH)_2$ surface for the crystallization of PP in $Mg(OH)_2$/PP composites. It can be seen from DSC crystallization curves that when the loading of $Mg(OH)_2$ was below 40 wt % (M-4), symmetry of the crystallization peak is preferable. However, when the loading of $Mg(OH)_2$ was up to 60 wt % (M-6), the area in the lower-temperature region of crystallization peak increased significantly, suggesting that too much $Mg(OH)_2$ would retard the crystal growth of PP, leading to crystallization in the lower temperature. Compared to pure PP (M-0), however, no matter what the $Mg(OH)_2$ content was, a higher crystallization temperature of PP was observed as a result of the heterogeneous nucleation of the $Mg(OH)_2$ surface.

The addition of $Mg(OH)_2$ basically had no effect on the melting behavior of PP, but a shift to high temperature of T_m° and a broadened half-height width of melting peak were observed, especially for PP filled with 60 wt % $Mg(OH)_2$. It can be seen from the melting curves that the area in the low-temperature region of melting peak increased. It is suggested that the large content of $Mg(OH)_2$ in M-6 hindered the crystallization of PP, resulting in poor crystalline perfection and lower melting point of PP.

Crystallization and melting behavior of Mg(OH)₂/PP composites modified by AA

Figure 3 depicts DSC cooling and heating curves of $Mg(OH)_2$/PP composites modified by AA containing 60 wt % $Mg(OH)_2$, and the crystallization and melting parameters are shown in Tables I and II, respectively. It can be seen that the addition of 2 phr AA into $Mg(OH)_2$/PP composites resulted in an increased T_c°, T_c^p, T_c^f, and T_c^{on}, and a reduced ΔT_c, indicating that the addition of AA further enhanced the heterogeneous nucleation effect on PP in $Mg(OH)_2$/PP composites
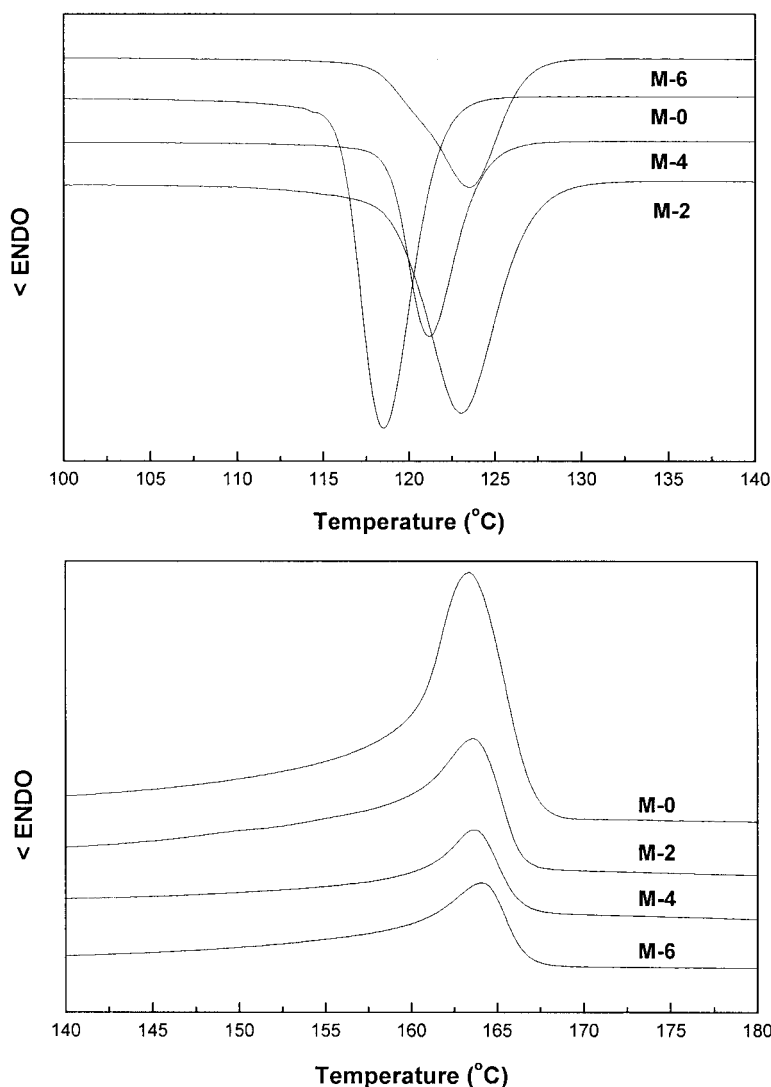
Figure 2 DSC crystallization and melting curves of magnesium hydroxide/PP composites filled with different magnesium hydroxide content.

and led to nucleation and crystallization at higher temperatures. Because of the crystallization at high temperature, the crystallization rate was slowed, leading to an increased width of the high-temperature region of crystallization peak compared to that of M-6, and a distinct decrease in the crystallization peak width. With increasing the AA content up to 4 phr, all parameters remained unchanged except for a decrease in the ΔH_c, which indicated that the increase in the AA content scarcely influenced the crystallization behavior of PP in Mg(OH)₂/PP composites.

The above experimental results indicated that the addition of AA or Mg(OH)₂ led to an increased crystallization temperature of PP. The former resulted from the nucleation effect of the homogeneous polymer of AA, PAA, or *in situ* FPP. The latter was mainly attributed to heterogeneous nucleation of the Mg(OH)₂ surface. The simultaneous addition of AA

and Mg(OH)₂ into PP had a synergetic effect on the crystallization of PP, leading to a further increase in crystallization temperature. Because there is a critical content of PAA or FPP acting as a nucleating agent, too much AA would form a thick interface layer between PP and Mg(OH)₂. The greater the content of AA, the larger the grafting amount and the greater the change in the regularity of the PP chain, leading to a decreased crystallizability of PP. As a result, a reduced heat of crystallization was obtained.

From the melting results (Table II), it can be seen that the T_m^{on} and T_m^p of MA-26 and MA-46 modified with AA were higher than those of M-6 unmodified with AA. This outcome was attributed to the crystallization of PP at high temperature and the formation of crystals with a larger size of lamellae and better crystalline perfection. A narrowed melting peak (small ΔT_m) and a broadened half-height width (large
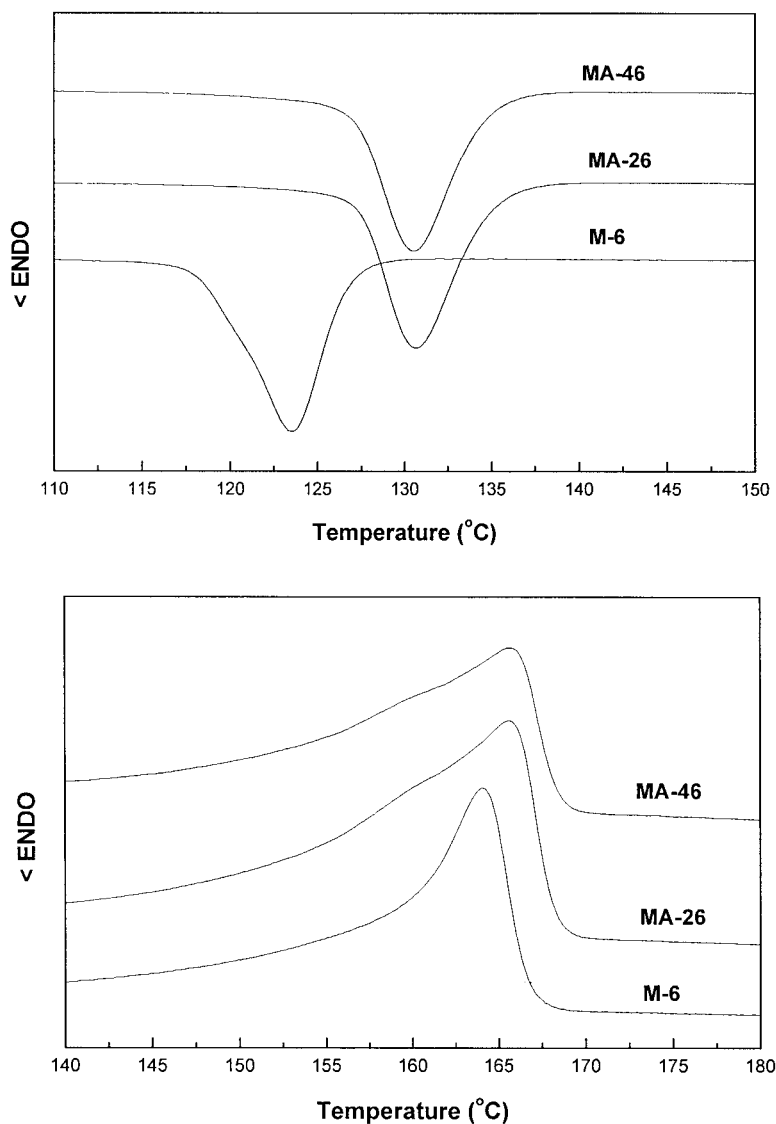
Figure 3 DSC crystallization and melting curves of magnesium hydroxide (60%)/PP composites modified by AA.

$\Delta T_m^{1/2}$) were observed. A decreased T_m^{on} was attributed to the peak's change of shape. The increase in the AA content resulted in a decrease in heat of fusion. A shoulder peak was observed at 160°C in the melting curve, The shoulder could possibly be attributed to a family of smaller α-crystals, or to a melting–recrystallization–melting of the α-form, or possibly to the formation of the β-form of PP.

Crystallization and melting behavior of Mg(OH)₂/ PP composites modified by addition of FPP

Figure 4 depicts DSC cooling and heating curves of Mg(OH)₂/PP composites modified by the addition of FPP, and the crystallization and melting parameters are presented in Tables I and II, respectively. It can be seen that the addition of FPP in Mg(OH)₂/PP composites led to a further increase in crystallization temper-

atures (T_c^o, T_c^p, and T_c^{on}), resulting in enhanced T_c^p from 123.3, 121.4, and 136.6°C of M-2, M-4, and M-6, to 124.9, 126.6, and 126.9°C of MF-2, MF-4, and MF-6, respectively. It also suggested that additive FPP functioned as a nucleating agent for the crystallization of PP. The synergetic nucleation effect of FPP and the Mg(OH)₂ surface led to further increased crystallizability of PP. Although the crystallization temperature of PP in Mg(OH)₂/PP composites does not increase with the increased Mg(OH)₂ content, enhanced T_c^p was observed with increasing the Mg(OH)₂ content. In Mg(OH)₂/PP composites modified by addition of FPP, the T_c^p of PP did not decrease, even when the Mg(OH)₂ content was 60 wt %. Compared with M-6, increased crystallization in the low-temperature region in the crystallization peak did not occur. It is suggested that the FPP not only exhibited nucleation
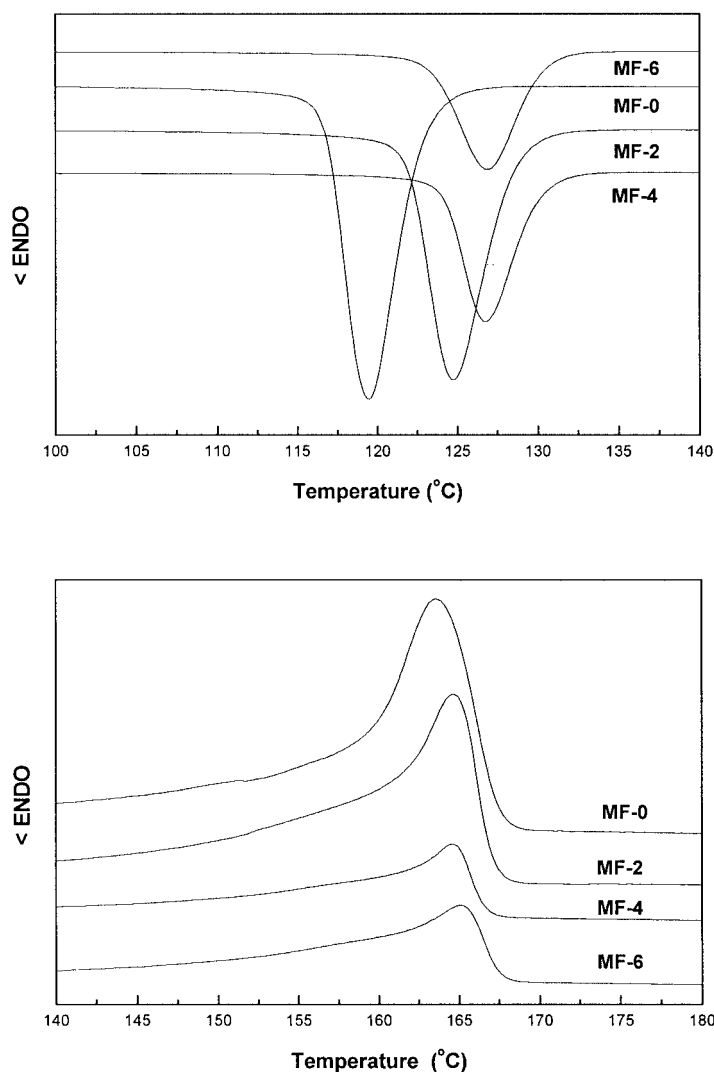
Figure 4 DSC crystallization and melting curves of magnesium hydroxide/PP composites filled with different magnesium hydroxide content and modified by addition of FPP.

effect, but also activated the heterogeneous nucleation effect of the Mg(OH)$_2$ surface, leading to further increased crystallization temperatures of PP in Mg(OH)$_2$/PP composites modified by addition of FPP.

It can be seen from Table II that PP in Mg(OH)$_2$/PP composites modified by addition of FPP exhibits a high T_m^p, indicating that PP can form crystals with high perfection in the presence of FPP. In the case of no FPP, although an increased crystallization temperature was observed, the addition of Mg(OH)$_2$ did not change the temperature of the melting peak. However, in the presence of FPP, the PP in Mg(OH)$_2$/PP composites modified by addition of FPP has a high melting temperature attributed to the effect of FPP. However, the melting temperature of Mg(OH)$_2$/PP composites modified by addition of FPP did not change with the increase in the content of Mg(OH)$_2$.

Crystallization and melting behavior of Mg(OH)$_2$/ PP composites modified by *in situ* FPP

Figure 5 depicts the DSC cooling and heating curves of Mg(OH)$_2$/PP composites modified by the addition of 2 phr AA in the presence of 0.5 phr DCP containing 40 and 60 wt % Mg(OH)$_2$, respectively. The crystallization and melting parameters are shown in Tables I and II, respectively. In the effect of the formation of *in situ* FPP, the T_c^{on}, T_c^p, and ΔH_c of PP in its composites were improved with increased Mg(OH)$_2$ content. Compared with unmodified Mg(OH)$_2$/PP composites (M series) and Mg(OH)$_2$/PP composites modified by addition of FPP (MF series), the improvement in T_c^{on} and T_c^p of Mg(OH)$_2$/PP composites modified by *in situ* FPP (MAD series) was less than those of the MF series, and a lower ΔH_c was obtained. This was attributed to the fact that the addition of DCP resulted in the degrada-
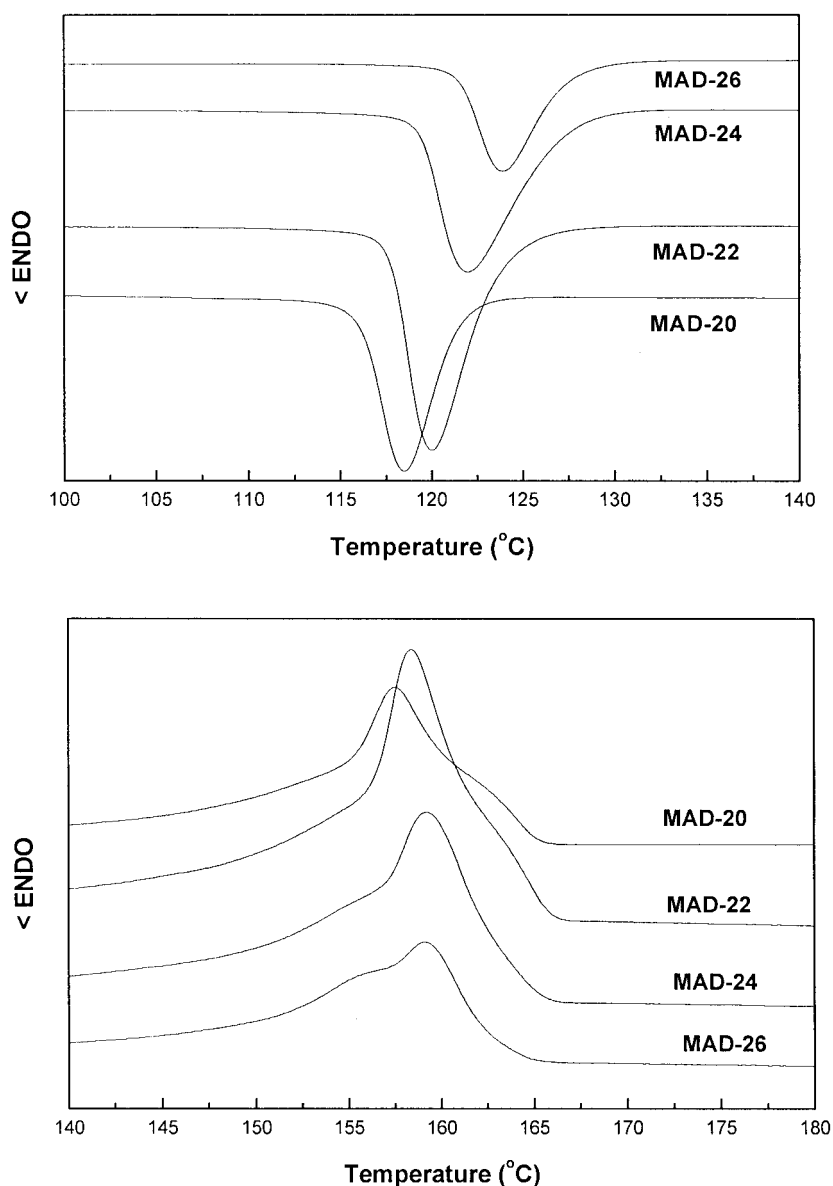
Figure 5 DSC crystallization and melting curves of magnesium hydroxide/PP composites filled with different magnesium hydroxide content and modified by *in situ* FPP.

tion of PP and the formation of free radicals, which initialized the *in situ* grafting of AA onto the PP chain and generated functionalized polymer, FPP. The produced *in situ* FPP was mainly located at the interface between PP and $Mg(OH)_2$, and consequently strong polar or even chemical interaction occurred between the carboxylic group of FPP and $Mg(OH)_2$. The PP chain in FPP was compatible, or cocrystallized with PP matrix, leading to the decreased heterogeneous nucleation effect of the $Mg(OH)_2$ surface. FPP located on the $Mg(OH)_2$ surface did not enter into the PP matrix to induce nucleation effect. Because of the aggregation of DCP and grafting monomer at the interface between $Mg(OH)_2$ and PP, the grafting reaction destroyed the regularity of the PP chain near the $Mg(OH)_2$. There-

fore, the improvement in the T_c^{on} and T_c^p of the MAD series was less significant than that of the MF series.

The formation of *in situ* FPP greatly influenced the T_m^p of PP in its composites. Comparing the sample unfilled with $Mg(OH)_2$ (MAD-20) and pure PP (M-0), the T_m^p was reduced by 6°C. In $Mg(OH)_2$/PP composites modified by *in situ* FPP, the T_m^p slightly increased with increased $Mg(OH)_2$ content from 20 to 60 wt %. The T_m^p of MAD-26 was still lower than that of M-0. A varied shape of melting peak, a decreased intensity of melting peak, and an extended $\Delta T_m^{1/2}$ were observed with increasing the $Mg(OH)_2$ content. During the formation of *in situ* FPP, FPP located between the two phases led to a changed interface. Because of this changed interface, the effect of $Mg(OH)_2$ on PP crys-
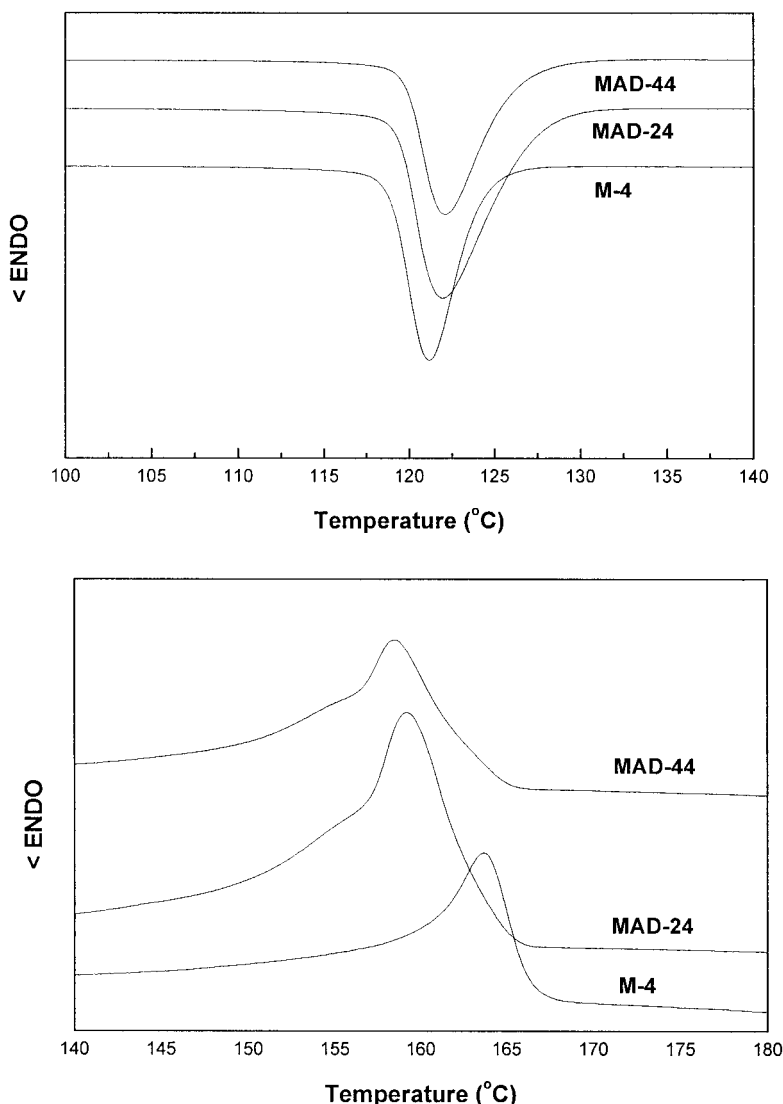
Figure 6 DSC crystallization and melting curves of magnesium hydroxide (40%)/PP composites with different AA content and modified by *in situ* FPP.

tallization was varied, resulting in formation of the non–α-form of PP. Because of this transformation of crystal form during melting, a shoulder peak near 155°C was observed in the melting curves of MAD-26.

Figures 6 and 7, respectively, depict the DSC cooling and heating curves of Mg(OH)$_2$/PP composites modified by the addition of 4 phr AA in the presence of 0.5 phr DCP. The crystallization and melting parameters are presented in Tables I and II, respectively. The addition of 2 phr AA and 0.5 phr DCP in composites containing 40 wt % Mg(OH)$_2$ (MAD-24) led to an increase in T_c^{on} and T_c^p, an extended $\Delta T_c^{1/2}$, and a suppressed ΔH_c. When the AA content was up to 4 phr, the T_c^{on}, T_c^p, and $\Delta T_c^{1/2}$ were basically the same as those of MAD-22 except for a further decreased ΔH_c. This result agrees with the DSC results of the Mg(OH)$_2$/PP composites modified by addition of AA.

An increase in the content of AA did not change the crystallization behavior of PP.

In the composites modified by the addition of AA, with increased AA content, the excessive AA produced a large amount of homopolymer and retarded both the heterogeneous nucleation effect of Mg(OH)$_2$ and the crystallization of PP. However, for the composites in the presence of DCP, the decrease in degree of crystallization was mainly attributed to the fact that most of AA reacted with PP macroradicals initiated by DCP, leading to an increased amount of AA grafting onto the PP chain. A large amount of grafting chain in PP prevented PP chain folding and arraying to form crystals. Hence, a slightly reduced degree of crystallization was observed.

In Mg(OH)$_2$/PP composites modified by *in situ* FPP containing 40 and 60 wt % Mg(OH)$_2$, respectively, the
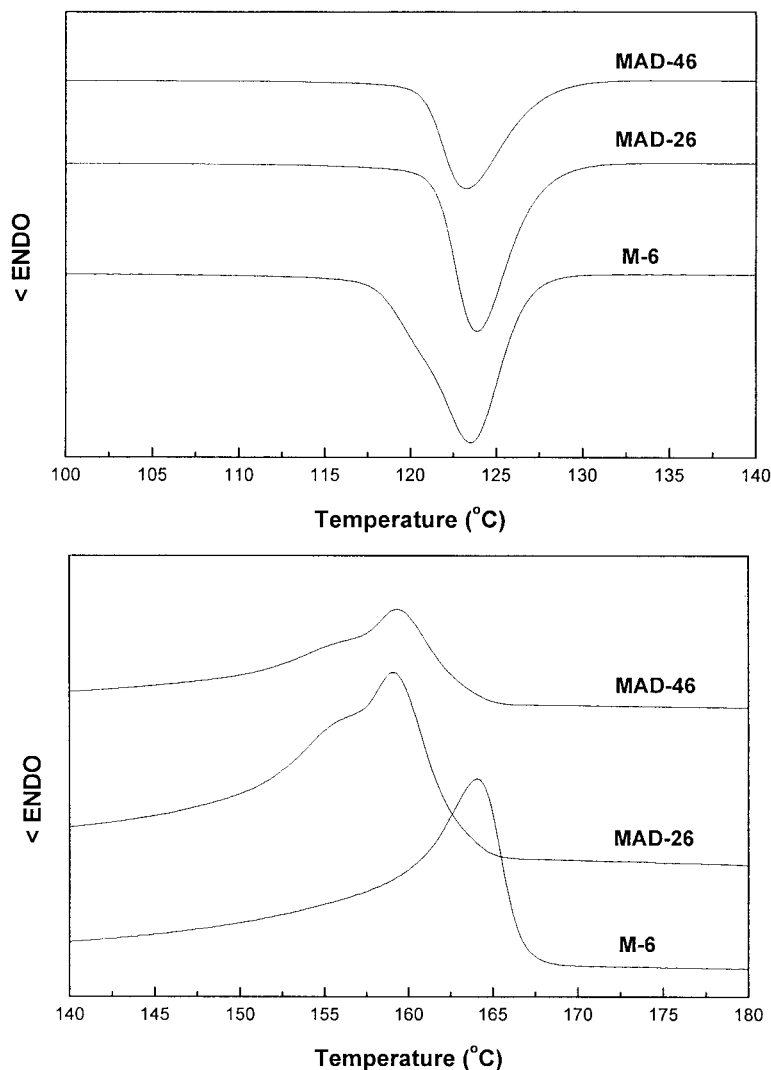
Figure 7 DSC crystallization and melting curves of magnesium hydroxide (60%)/PP composites with different AA content and modified by *in situ* FPP.

addition of the 2 phr AA decreased the T_m^p, T_m^{on}, and ΔT_m, and increased the $\Delta T_m^{1/2}$ compared with those of composites filled with the same loading of $Mg(OH)_2$ in the absence of AA. It can be seen from the melting curves that the increased area in the low-temperature region of the melting peak was also observed. Increasing the AA content up to 4 phr, the T_m^p and T_m^{on} remained unchanged, but the ΔH_m of MAD-44 decreased and the ΔH_m of MAD-46 agreed with that of MAD-26. However, the height of the melting peak was lower than that of the corresponding composites containing 2 phr AA. It is suggested that the 4 phr AA was excessive to composites containing 40 wt % $Mg(OH)_2$, leading to the formation of PAA to decrease the heterogeneous nucleation effect of $Mg(OH)_2$ and resulting in a reduced degree of crystallization. However, for the composites containing 60 wt % $Mg(OH)_2$, the 4 phr of AA was not excessive and resulted in an increased amount of grafting to activate the heteroge-

neous nucleation effect of $Mg(OH)_2$ and an increased content of crystallization in the low-temperature region of the melting peak.

CONCLUSIONS

In conclusion, we report that addition of functionalized polypropylene (FPP) accelerated the crystallization of PP and increased the crystallization temperature of PP attributed to the nucleation effect of FPP. The formation of *in situ* FPP resulted in a reduced crystallization rate, melting point, and degree of crystallization resulting from the decreased regularity of the PP chain. In $Mg(OH)_2$/PP composites, the addition of $Mg(OH)_2$ increased the crystallization temperatures of PP attributed to a heterogeneous nucleation effect of $Mg(OH)_2$. Addition of FPP further enhanced the crystallization temperatures of PP in $Mg(OH)_2$/PP composites. It is suggested that there is an activation

of FPP to the heterogeneous nucleation effect on the Mg(OH)$_2$ surface. The addition of AA also increased the crystallization temperature of PP in Mg(OH)$_2$/PP composites, but the increased AA content had no effect on the crystallization behavior of PP. The above investigated results indicated that FPP and AA exhibited an activated heterogeneous nucleation effect on the Mg(OH)$_2$ surface. Mg(OH)$_2$ and FPP afforded a synergistic effect on the crystallization of PP in Mg(OH)$_2$/PP composites, leading to the further increased crystallization temperatures of PP. However, the crystallization temperatures of Mg(OH)$_2$/PP composites modified by *in situ* FPP were lower than those of Mg(OH)$_2$/PP composites modified by addition of either FPP or AA.

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