Interfacial Interaction in AI(OH)$_3$/Polypropylene Composites Modified by *In Situ*-Functionalized Polypropylene

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ABSTRACT: To investigate the interfacial interaction of AI(OH)$_3$/polypropylene (PP) composites modified by *in situ*-functionalized polypropylene (FPP), AI(OH)$_3$/polypropylene (PP) composites containing a low AI(OH)$_3$ content, modified by *in situ*-grafted acrylic acid, were prepared by a one-step melt-extrusion process. The effect of *in situ* FPP on the crystallization and melting behavior, crystalline morphology of the composites, and interfacial interaction between the filler and PP was investigated. The crystallization and melting behavior and crystalline morphology of PP in the composites depended upon the interfacial physical [heterogeneous nucleation of AI(OH)$_3$; cocrystallization and compabilitization of PP with *in situ* FPP] and the interfacial chemical interaction between both the components in the composites. FTIR results indicated that there exists a chemical reaction between AI(OH)$_3$ and *in situ* FPP. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 110–120, 2002; DOI 10.1002/app.10270

Key words: functionalized polypropylene; Al(OH)$_3$; interfacial interaction

INTRODUCTION

Studies have shown that the addition of a functionalized polymer is an effective method for the modification of the compatibility of immiscible polymer blends and interfacial adhesion in polymeric composites.[1–32] In our laboratory,[33–36]

polypropylene functionalized with acrylic acid, PP-*g*-AA [functionalized polypropylene (FPP)], was prepared by the melt-extrusion process and the effect of FPP on the structure and physical and mechanical properties of PP and PP composites filled with different Al(OH)$_3$ contents were investigated. The experimental results indicated that the addition of FPP resulted in an increase in the melt-flow index, flame retardance, and mechanical properties of the composites. The crystallization and melting behavior of neat PP and PP in the composites was affected by the addition of FPP. Incorporation of FPP improved the thermal stability of the PP composites. It was found that improvement in the physical and mechanical properties of Al(OH)$_3$/PP composites modified by *in situ* FPP was higher than that of Al(OH)$_3$/PP

composites modified by the addition of FPP. It is suggested that there exists interfacial interaction between the two components, resulting in an improvement in interfacial adhesion and an increase in the physical and mechanical properties of the composites. However, it is difficult to study the interfacial interaction between two phases due to the higher filler content. In this article, Al(OH)$_3$/PP composites containing a lower filler content, modified by *in situ* FPP, were prepared by a one-step melt-extrusion process. The crystallization and melting behavior, crystalline morphology of PP in the composites, and interfacial physical and chemical interaction of the Al(OH)$_3$/PP composites containing different the Al(OH)$_3$ contents were studied.

EXPERIMENTAL

Materials

PP, powdered F401, was a commercial product of the Guangzhou Petrochemical Co. (Guangzhou, China). Chemical-grade AA was purchased from the Fushan Chemical Factory (Guangdong, 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 the Shanghai Chemical Reagent Factory (Shanghai, China). Al(OH)$_3$ was obtained from the Shandong Aluminum Co. (Shandong, China). The solvent, acetone, was obtained from the Guangzhou Chemical Reagent Factory (Guangzhou, China).

Preparation of Samples

DCP and AA were dissolved in acetone, then blended with powdered PP and Al(OH)$_3$. After the solvent, acetone, had completely evaporated, the mixture of AA, DCP, powdered PP, and Al(OH)$_3$ was extruded by an XJ-01 single-screw extruder at a temperature of 190°C, with the screw speed set at 60 rpm.

Characterization of Structure and Properties

Melting and crystallization of the samples were studied by differential scanning calorimetry (DSC) using a Perkin–Elmer DSC-7 in a nitrogen atmosphere with 10°C/min heating and cooling. The samples were heated from 30 to 220°C and held at that temperature for 3 min. The nonisothermal crystallization process was recorded from 220 to 50°C, followed by heating from 50 to 210°C for the second heating run. The crystallization and melting parameters were obtained from the cooling and reheating scans. The transition temperature and heat of crystallization and fusion were calibrated using an indium standard.

Some compositions were characterized on a Nicolet 205 FTIR spectrophotometer. The sample was dissolved for 7 h by the refluxing of xylene, followed by cooling, and then precipitated by acetone three times. The extracted sample was vacuum-dried for 19 h at 70°C and then diluted with KBr powder.

The microscopical observations were performed with a Olympus BH-2 polarized light microscope. The samples were prepared by crystallization for 3 h at 130°C after melting at 210°C for 3 min.

RESULTS AND DISCUSSION

Interfacial Nucleation Interaction of Al(OH)$_3$/PP Composites Modified by *In Situ* FPP

The compositions and DSC results of Al(OH)$_3$/PP and Al(OH)$_3$/PP composites modified by *in situ* FPP are given in Table I. The DSC cooling and heating curves of PP and the Al(OH)$_3$/PP composites are shown in Figure 1. It was found that the addition of Al(OH)$_3$ and increase of the filler content resulted in an increase in the crystallization temperature of PP. Al(OH)$_3$ acted as nucleating agent, leading to an enhanced nucleating ability of PP. Some fillers have been found to act as nucleating agents of PP, for example, talc, where loading as low as 0.5% by weight had an effect.[37,38] However, Al(OH)$_3$ is a weak nucleating agent and only produces a significant effect at high loadings.[39,40] The crystallization temperature of PP increased with an increasing filler content.[34] Such a concentration-dependent nucleation is considered to arise when only a small fraction of the filler particles have the required surface feature and/or when the melt-stress concentration occurs at the filler surface.[39,40] Similarly to the results of PP by the addition of DCP, double melting peaks were observed for the Al(OH)$_3$/PP composites by addition of DCP (Fig. 1), attributed to the degradation of PP induced by DCP. Because of the lower filler content, the filler content had little influence on the melting temperature and degree of crystallization of PP.

Table I Composition and DSC Results of Al(OH)$_3$/PP Composites Modified by *In Situ* FPP

	PP	AA (phr)	DCP (phr)	Al(OH)$_3$ (phr)	T_c (°C)	T_{c0} (°C)	T_{m1} (°C)	T_{m2} (°C)	T_{m0} (°C)	X_c (%)
1	100	4	0.5	2	119.9	123.6	159.3	—	154.1	39.9
2	100	4	0.5	5	117.4	121.1	158.0	—	153.5	42.6
3	100	4	0.5	10	117.2	120.7	156.7	161.9	153.0	41.1
4	100	2	0.5	2	115.1	119.2	156.1	162.5	152.8	42.9
5	100	2	0.5	5	117.6	122.4	158.1	163.0	152.8	41.6
6	100	2	0.5	10	118.7	124.7	156.3	162.7	152.6	40.8
7	100	—	0.5	2	113.7	117.9	154.1	161.3	150.6	43.2
8	100	—	0.5	5	114.3	118.7	155.7	162.5	152.6	42.0
9	100	—	0.5	10	115.7	119.5	154.0	160.0	153.4	41.5
11	100	2	0.5	—	115.6	119.0	155.4	161.9	152.4	39.4
12	100		0.5	—	113.7	115.9	156.7	163.2	151.1	40.6

$\Delta H_f = 207.15$ J/g.[41]

For the modified composites containing different Al(OH)$_3$ contents, the AA content influenced the crystallization and melting behavior of PP in the composites. Figure 2 shows the DSC cooling and heating curves of PP in the composites containing a filler content of 2 phr. Increasing the content of AA resulted in an increased crystallization temperature of PP in the composites. Double melting peaks were observed for the AA content of 2 phr. When the AA content was increased to 4 phr, the lower-temperature melting peak shifted to a higher temperature and became a single melting peak. For the modified composites containing a filler content of 5 phr (Fig. 3), the addition of AA further increased the crystallization temperature of PP in the composites, but the content of AA did not influence the crystallization temperature. However, the melting behavior was more significantly affected by the content of AA. The addition of an AA content of 2 phr led to shift the lower-temperature melting peak to a higher temperature and combine with the higher-temperature melting peak to become a higher-temperature melting peak with a shoulder peak in the high-temperature region. This effect was more significant for a higher content of AA.

Double melting peaks were observed for an AA content of 2 phr. When the AA content was increased to 4 phr, the lower-temperature melting peak shifted to a higher temperature and became a single melting peak. For the composites containing a filler content of 10 phr (Fig. 4), the addition of an AA content of 2 phr also resulted in an increased crystallization temperature. However, the crystallization temperature decreased as the AA content was increased to 4 phr, but was higher than that

for the Al(OH)$_3$/PP composites. It was consistent with the results of composites containing a higher Al(OH)$_3$ content. In the composites containing a filler content above 20% by weight, it was found that the crystallization temperature of PP in the composites decreased with an increasing AA content.[36] It is suggested that both PP-*g*-AA and the AA homopolymer (PAA) can be formed during the preparation process of the composites modified by *in situ* FPP.

The formation of *in situ* FPP and PAA depend upon the AA and filler content. For the lower filler content, the formation of FPP was dominant with an increasing AA content due to the large interfacial area between PP and AA, but for the higher filler content, the increase in the AA content resulted in the formation of *in situ* FPP with a higher grafting rate and the formation of PAA with a low molecular weight due to an increase in the interfacial area between AA and Al(OH)$_3$. The increase in the number of grafting sites and the length of the grafting chain of FPP restricted the nucleation and crystallization of PP. The PAA formed during the grafting reaction reacted with the surface of Al(OH)$_3$ and decreased the effect of the heterogeneous nucleation of Al(OH)$_3$ on PP. This action is more significant in the composites containing the higher content, modified by *in situ* FPP. It was found that the surface treatment of Al(OH)$_3$ by fatty acid led to a decrease in the heterogeneous nucleation of Al(OH)$_3$ in Al(OH)$_3$/PP composites.[39,40]

The increase in the crystallization temperature of PP in the composites containing the lower filler content indicated enhanced heterogeneous nucleation of PP by *in situ* formation of FPP. Enhanced
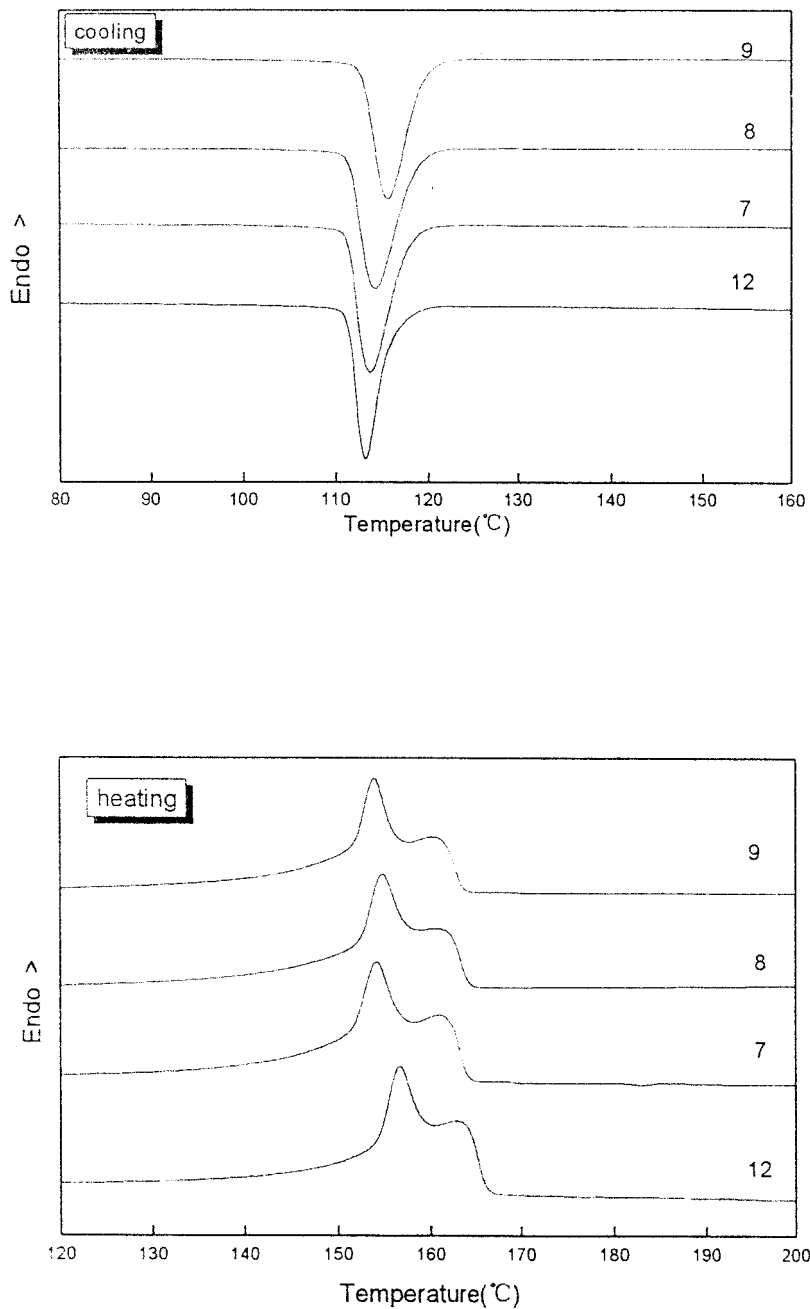
Figure 1   DSC cooling and heating curves of PP and Al(OH)$_3$/PP composites with different Al(OH)$_3$ contents.

heterogeneous nucleation resulted in an increase in the density of nucleation and the formation of small spherulites of PP. Figure 5 shows the crystalline morphology of PP, OPP (prepared from the mixture of PP and DCP without AA), and FPP crystallized at 130°C for 3 h. The spherulitic morphology of PP was affected by the addition of DCP into the PP. The grafting of AA onto PP, the formation of FPP, led to the formation of smaller spherulites of PP, indicating an enhanced nucleating ability of PP. The crystalline morphologies of the Al(OH)$_3$/PP composites depend on the content of Al(OH)$_3$ and AA. For the lower Al(OH)$_3$ content (Fig. 6), the addition of AA and the increase of the AA content resulted in the formation of smaller spherulites of PP, indicating an in-
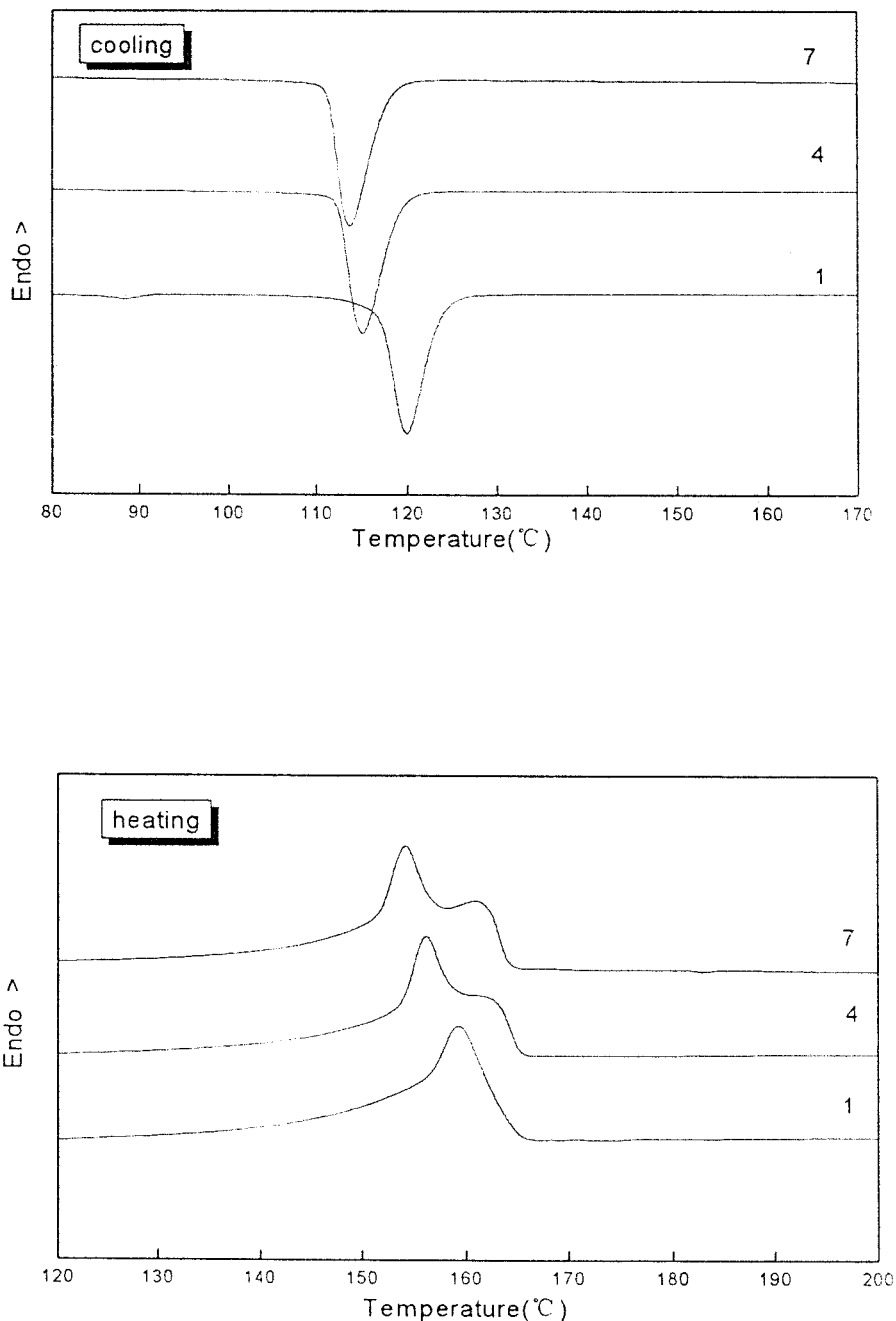
Figure 2   DSC cooling and heating curves of Al(OH)$_3$/PP composites modified by AA; Al(OH)$_3$ = 2 phr.

creased density of nucleation with an increasing AA content. For the Al(OH)$_3$ content of 5 phr, the size of the PP spherulites decreased more significantly by the addition of AA, but the AA content had little influence on the crystalline morphology of PP (Fig. 7). When the Al(OH)$_3$ content was increased to 10 phr, the addition of 2 phr of AA resulted in an increased nucleation density and the formation of smaller spherulites of PP, but increasing the AA content led to a decreased heterogeneous nucleating ability and nucleation density (Fig. 8). This is consistent with the results of the crystallization temperature and was attributed to the formation of PAA in a higher Al(OH)$_3$ content to reduce the heterogeneous nucleating ability of Al(OH)$_3$.
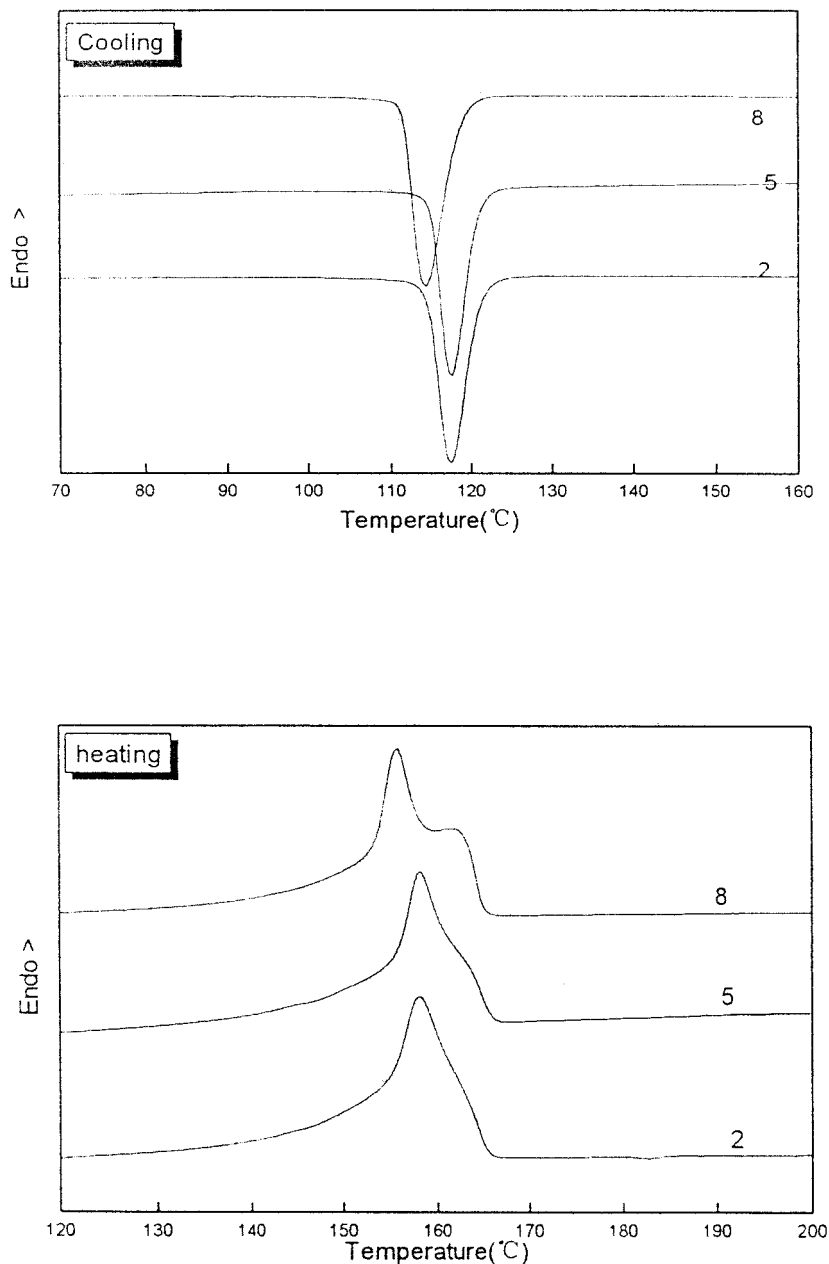
Figure 3 DSC cooling and heating curves of Al(OH)$_3$/PP composites modified by AA; Al(OH)$_3$ = 5 phr.

Interfacial Chemical and Physical Interaction of Al(OH)$_3$/PP Composites Modified by *In Situ* FPP

FTIR spectra of the Al(OH)$_3$/PP and Al(OH)$_3$/PP composites modified by *in situ* FPP are shown in Figure 9. In comparing spectra for the unmodified and modified composites, a large absorption can be seen at 1714 cm^{-1} for the modified composites, which is attributed to carboxylic acid. It is apparent that, in addition to the carboxylic acid absorption at 1714 cm^{-1}, there are peaks evident at 1598 cm^{-1}, associated with carboxylic acid salt formation, and at 3400 cm^{-1}, which is characteristic of hydrogen bonding between hydroxyl groups. During the preparation of the Al(OH)$_3$/PP composites modified by *in situ* FPP, *in situ* FPP molecules are chemically bonded on the filler surface by an acid–base interaction between carboxyl groups grafted onto FPP and hydroxyl groups from the filler surface. This provides evidence of an acid–base interaction between the
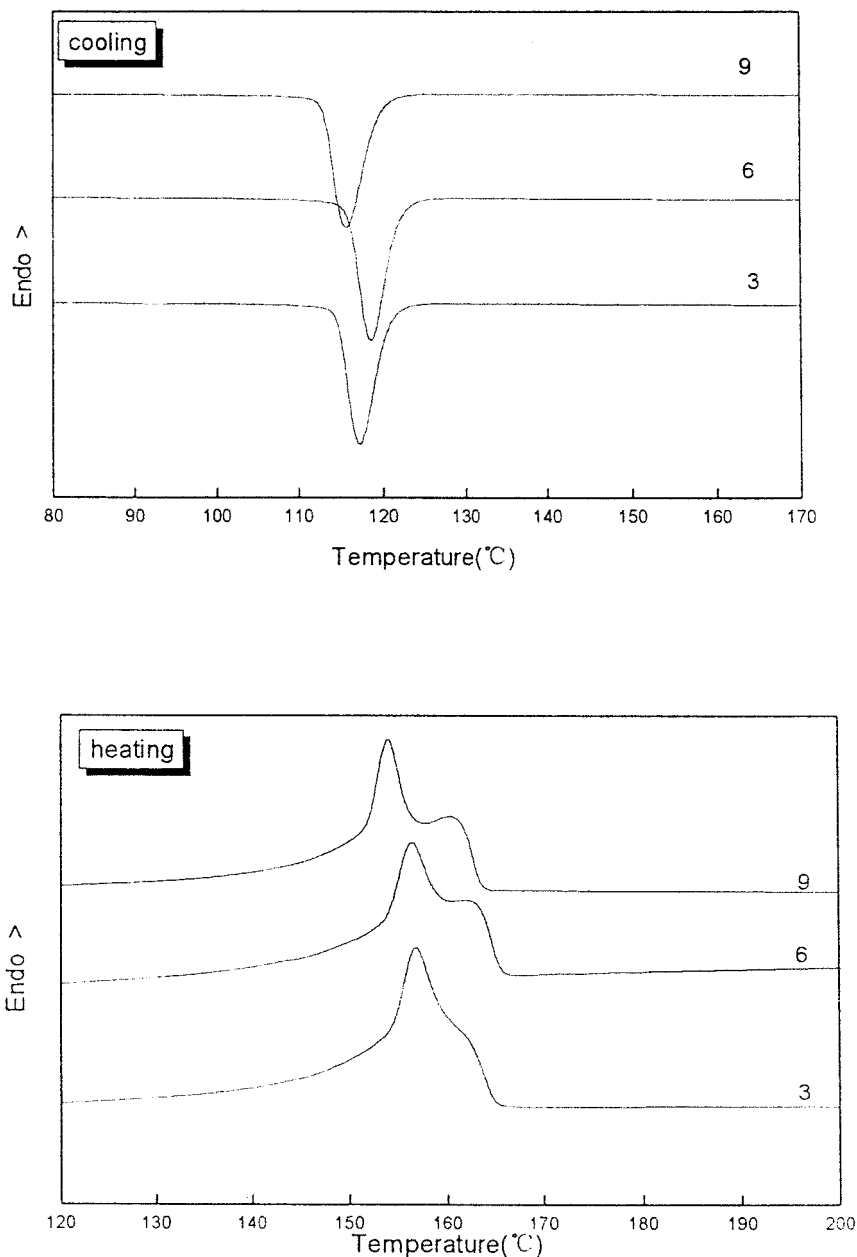
Figure 4 DSC cooling and heating curves of Al(OH)$_3$/PP composites modified by AA; Al(OH)$_3$ = 10 phr.

Al(OH)$_3$ surface and the carboxylic acid functionality. Hence, it is suggested that there exists a chemical reaction between Al(OH)$_3$ and FPP in composites modified by *in situ* FPP.

On the other hand, an interfacial physical interaction between two components also influenced the interfacial adhesion and physical and mechanical properties of the composites. Compared to aliphatic chains of low molecular weight organic modifiers, *in situ* FPP molecules are suf-

ficiently long to create physical entanglements with PP molecules from the matrix bulk and *in situ* FPP activates nucleation centers on the filler surface. PP chains in the *in situ* FPP can cocrystallize and compatibilize with the PP matrix. The change in the matrix crystallinity and crystalline morphology in the interface between the filler and the PP matrix also affects the interfacial properties. Hence, the interfacial adhesion between two components in the Al(OH)$_3$/PP composites modi-
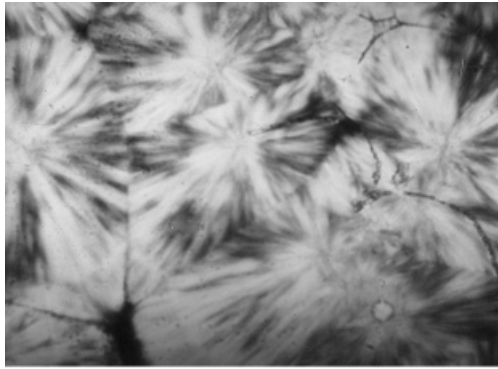
PP
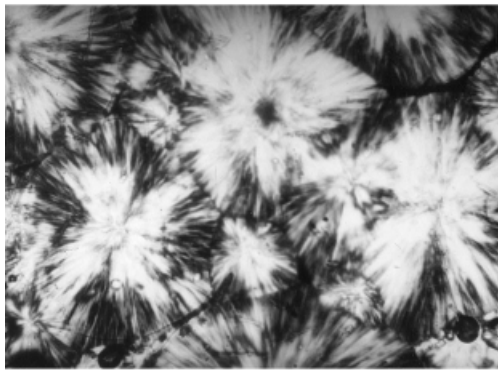
OPP
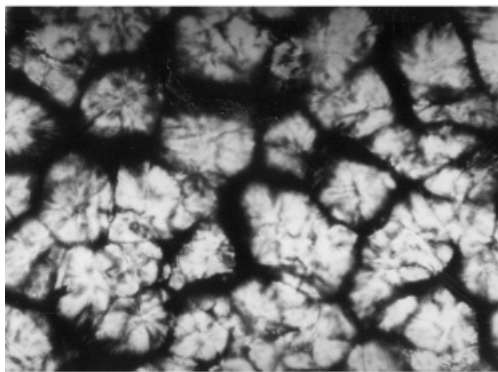
FPP

Figure 5 Optical micrographs of PP, OPP, and PP.

fied by *in situ* FPP and the physical and mechanical properties of the composites depend upon the chemical and physical (heterogeneous nucleation, cocrystallization, and compatibilization) interaction among the filler, FPP, and PP matrix.

CONCLUSIONS

To investigate the interfacial interaction of the Al(OH)$_3$/PP composites modified by FPP, the

Al(OH)$_3$/PP composite containing a low Al(OH)$_3$ content, modified by *in situ*-grafted AA, were prepared by a one-step melt-extrusion process. The addition of Al(OH)$_3$ and an increase of the filler content resulted in an increase in the crystallization of PP due to the heterogeneous nucleation of Al(OH)$_3$. However, the filler of low content had little influence on the melting temperature and
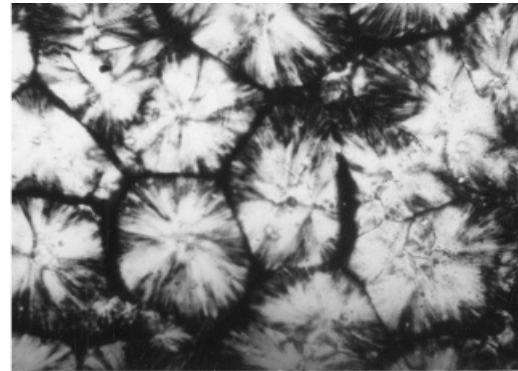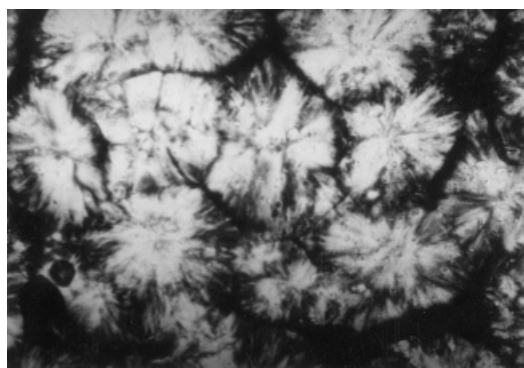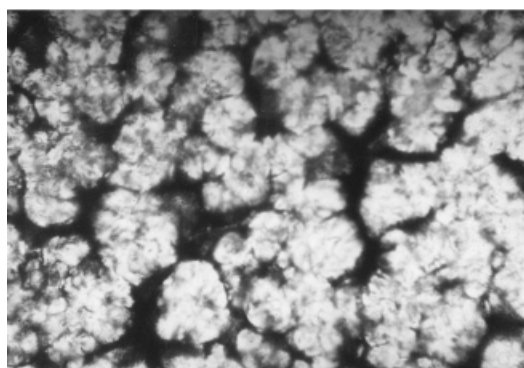

(a)
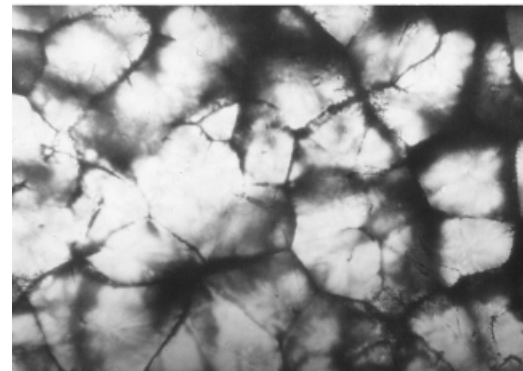
(b)
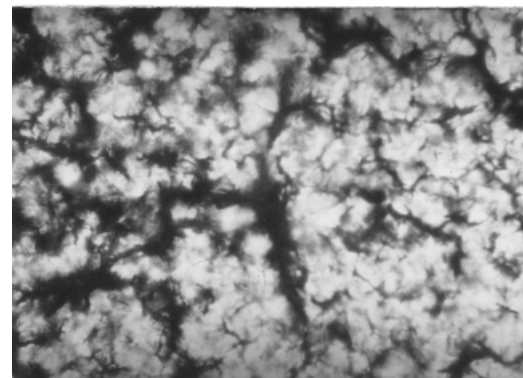
(c)

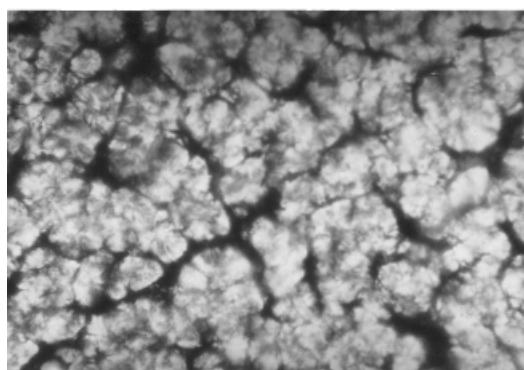**Figure 6** Optical micrographs of Al(OH)$_3$/*in situ* FPP/PP composites. Al(OH)$_3$: 2 phr; AA (phr): (a) 0; (b) 2; (c) 4.

(a)

(b)

(c)

Figure 7 Optical micrographs of Al(OH)$_3$/*in situ* FPP/PP composites. Al(OH)$_3$: 5 phr; AA (phr): (a) 0; (b) 2; (c) 4.

degree of crystallization of PP. For the modified composites, the addition of AA and the increase in the AA content resulted in an increased crystallization temperature of PP in the composites and the formation of smaller spherulites of PP. It is suggested that the formation of *in situ* FPP activates the heterogeneous nucleation centers on the filler surface and enhanced the heterogeneous nucleation of PP in the composites modified by *in*

situ formation of FPP. In the modified composites, there exists a chemical interaction between Al(OH)$_3$ and *in situ* FPP due to the acid–base interaction between carboxyl groups grafted onto FPP and hydroxyl groups from the filler surface. The *in situ* FPP can cocrystallize and compatibilize with the PP matrix. The interfacial adhesion and physical and mechanical properties of the
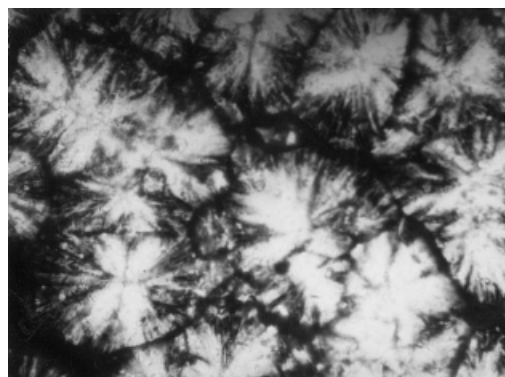
(a)
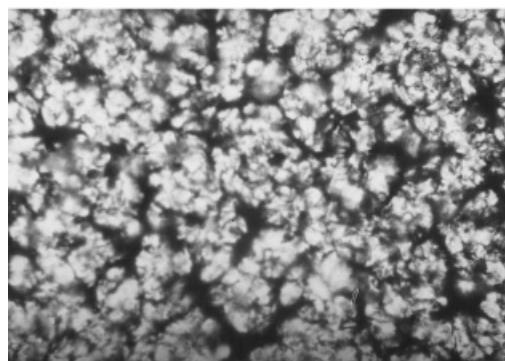
(b)
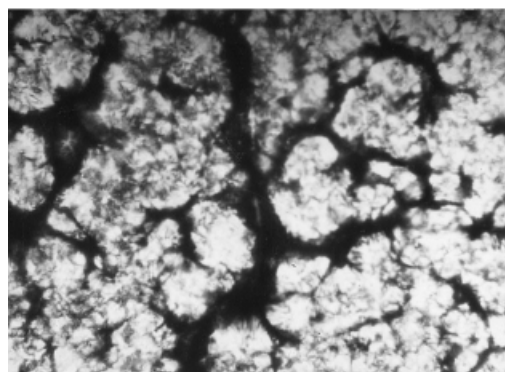
(c)

Figure 8 Optical micrographs of Al(OH)$_3$/*in situ* FPP/PP composites. Al(OH)$_3$: 10 phr; AA (phr): (a) 0; (b) 2; (c) 4.
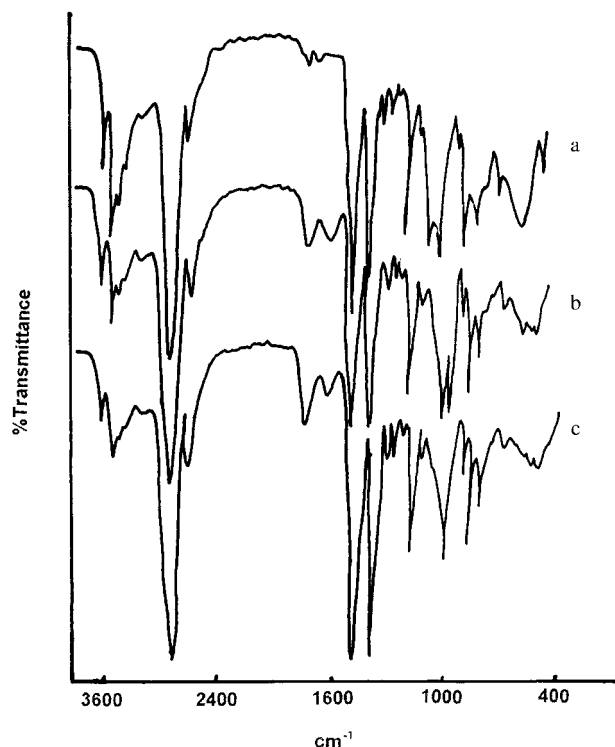
Figure 9 FTIR spectra of Al(OH)$_3$/PP composites modified by AA. AA(phr): (a) 0; (b) 2; (c) 4; Al(OH)$_3$ = 10.

Al(OH)$_3$/PP composites modified by *in situ* FPP depend upon the chemical and physical interaction (heterogeneous nucleation, cocrystallization, and compatibilization) among the filler, FPP, and PP.

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