

# Non-isothermal crystallization behavior of PP/Mg(OH)<sub>2</sub> composites modified by different compatibilizers

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## Abstract

Polypropylene (PP) blends with three kinds of grafted macromolecules, PP/Mg(OH)<sub>2</sub> composites and its composites modified by different compatibilizers were prepared by melt extrusion in a twin screw extruder. The crystallization and melting behaviors of PP blends and PP/Mg(OH)<sub>2</sub> composites were investigated with differential scanning calorimeter (DSC). The results indicated that addition of PP-g-MA has no influence on the crystallization temperature of PP, but POE-g-MA and EVA-g-MA decrease the crystallization temperature of PP. For PP/Mg(OH)<sub>2</sub> composites, addition of Mg(OH)<sub>2</sub> increases the crystallization temperature of PP and induces the formation of β-crystal in PP matrix. For PP/Mg(OH)<sub>2</sub> composites modified by different compatibilizers, the synergism effect of heterogeneous nucleation of Mg(OH)<sub>2</sub> and PP-g-MA or POE-g-MA further increases the crystallization temperatures. For PP/Mg(OH)<sub>2</sub> composites modified by EVA-g-MA, the addition of EVA-g-MA to PP/Mg(OH)<sub>2</sub> composite has little effect on the crystallization and melting behavior of PP. It is suggested the synergism effect of heterogeneous nucleation of Mg(OH)<sub>2</sub> and compatibilizer depends upon the compatibilization between PP and compatibilizer. The increase in crystallization temperatures of PP in PP/Mg(OH)<sub>2</sub>/compatibilizer facilitates the formation of α-PP, but weakens the formation of β-PP.

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**Keywords:** Polypropylene; Mg(OH)<sub>2</sub>; Compatibilizer; Crystallization and melting behaviors

## 1. Introduction

Polypropylene (PP) is a most common commodity plastic, which is of practical use in many areas, such as home appliances, automotive, construction, and other industrial applications. However, the poor flame resistance hinders its practical application in some fields. Compounding PP with flame retardants, such as magnesium hydroxide (Mg(OH)<sub>2</sub>), has been of wide interest and it has been an effect way to improve the flame resistance of PP. But the unfortunate consequence is a reduction in mechanical properties [1–5].

Interfacial adhesion is regarded as the most important factor responsible for deterioration in the mechanical properties of polymer composites. Mg(OH)<sub>2</sub> has highly polar hydrophilic surfaces, whereas the polymers (e.g., PP) are often non-polar and hydrophobic. When they compound each other, interfacial

adhesion between the filler surface and the matrix is poor. Many studies [6,7] have been focused on the modification of the filler surface through coating. Hornsby and Watson [7] studied the mechanical behavior of PP composites containing Mg(OH)<sub>2</sub>. They found that very significant improvements in toughness were obtained when high levels of magnesium stearate were used to ensure complete coverage of the Mg(OH)<sub>2</sub> surface. Modification of the filler surface through coating alters the properties of the surface, and the degree of interfacial adhesion may thereby be improved.

The interfacial adhesion can also influence the crystalline of PP in mineral-filled PP composites. Generally, mineral fillers can influence the crystallization process of the PP matrix by acting as heterogeneous nuclei. The heterogeneous nucleation leads to the increase in nucleation and crystallization rate. The improvement of the interfacial adhesion between polymer and filler can reduce the free energy of a nucleation process, which is favorable to the nucleation process at the phase boundary [8]. Lin et al. [9] studied the crystallization and melting behavior of PP/Mg(OH)<sub>2</sub> composites modified by acrylic acid grafting

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PP (PP-g-AA). Addition of PP-g-AA into PP/Mg(OH)<sub>2</sub> composites further enhanced the crystallization temperatures of PP. They suggested that there is an activation of PP-g-AA to the heterogeneous nucleation effect of Mg(OH)<sub>2</sub> surface. At the same time, there are many experiments that showed that the filler's nucleation action was reduced after surface modification, especially when modified by a coupling agent having a long fatty chain [10]. Velasco et al. [11] reported that the nucleation activity of Mg(OH)<sub>2</sub> particles on PP was reduced in coated grades of Mg(OH)<sub>2</sub>. The employed coatings worked isolating and preserving particles surface from direct interaction with polymer chains.

Above investigations indicated that the crystallization behavior of PP in PP/Mg(OH)<sub>2</sub> composite depends upon the interfacial interaction between Mg(OH)<sub>2</sub> and PP. In order to investigate the interfacial interaction between Mg(OH)<sub>2</sub> and PP, and between PP and modifier, on crystallization behavior of PP, a series of the compatibilizer/PP blends, PP/Mg(OH)<sub>2</sub> composites and modified PP/Mg(OH)<sub>2</sub> composites were prepared. The compatibilizers, including PP-g-MA, POE-g-MA and EVA-g-MA, have the same polar groups but different backbones. The same polar groups will result in the same interfacial interaction between Mg(OH)<sub>2</sub> and compatibilizer. Different compatibilizers with different backbones will result in different compatibility with PP and interfacial interaction between Mg(OH)<sub>2</sub> and PP. The different interfacial interaction among the PP, Mg(OH)<sub>2</sub> and compatibilizer will result in a change in the crystallization behavior of PP in PP/Mg(OH)<sub>2</sub> composite. In this paper, DSC and WAXD were used to investigate the structure and crystallization and melting behaviors of PP blends with different compatibilizers and PP/Mg(OH)<sub>2</sub> composites modified by different compatibilizers.

## 2. Experimental

### 2.1. Materials

Polypropylene was EPS.30R, supplied by Dushanzi Pcg (Xinjiang, China). This is a blend of isotactic polypropylene and propylene–ethylene rubber. Magnesium hydroxide, employed as filler, was a high purity untreated grade (1.8–2.4 μm) supplied by Foshan Jinge Firefighting materials Co. (Foshan, China). PP-g-

MA, POE-g-MA and EVA-g-MA were supplied by Guangzhou Lushan Chemical Materials Co. (Guangzhou, China). Characteristics of PP and compatibilizers are given in Table 1.

### 2.2. Sample preparation

All materials were dried in an oven at 60 °C for 12 h before melting extrusion. In the experiment, PP/Mg(OH)<sub>2</sub>/compatibilizer composites were prepared by melt-mixing all the components in a one-step procedure using a Berstoff ZE25A corotating twin-screw extruder ( $L/D=40$ ,  $D=35.5$  mm) at a rotating speed of 250 rpm. The blending temperature profile is 200/190/200/200/220/210/200 °C. A summary of the compositions for the different PP/Mg(OH)<sub>2</sub>/compatibilizers composites used in this study is given in Table 2.

### 2.3. DSC measurements

DSC measurements were made on a Perkin-Elmer DSC-7 thermal system (Perkin-Elmer Cetus Instruments, Norwalk, CT) in nitrogen atmosphere with 10 °C/min heating and cooling rate. Calibration was performed using pure indium at the same heating rate. Each sample weighed about 4–6 mg. The samples were heated from 50 to 220 °C, melted at 220 °C 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.

The percentage of (β-phase,  $\Phi_\beta$ , can be obtained from the crystallinities of the α-phase and β-phase according to Ref. [12]

$$\Phi_\beta (\%) = \frac{X_\beta}{X_\alpha + X_\beta} \times 100 \quad (1)$$

$$X_i (\%) = \frac{\Delta H_i}{\Delta H_i^\theta} \times 100 \quad (2)$$

where  $X_\alpha$  and  $X_\beta$  are the crystallinities of the α- and β-phase, respectively, which can be calculated separately according to Eq. (2), where  $\Delta H_i$  is the calibrated specific fusion heat of either the α- or the β-form,  $\Delta H_i^\theta$  is the standard fusion heat of the α- and the β-crystals of iPP, being 178 J/g and 170 J/g, respectively [13]. Because the DSC curves of some samples exhibited both α- and β-fusion peaks, the specific fusion heats for α- and β-phase were determined according to the following calibration

Table 1  
Characteristics of PP and compatibilizers

Materials	Mark	Properties
Polypropylene (EPS.30R)	PP	ethylene content 2.87%, $M_n=52,000$ , $M_w/M_n=9.2$ , $MFI=0.88$ g/10 min <sup>a</sup> , and $T_c^P=114.5$ °C <sup>b</sup>
Isotactic polypropylene grafted with maleic anhydride	PP-g-MA	MA Grafting ratio 1.0%, $T_c^P=110.6$ °C <sup>b</sup> $MFI>15$ g/10 min <sup>a</sup>
Ethylene-octene copolymer grafted with maleic anhydride	POE-g-MA	MA Grafting ratio 1.1%, octene content 24–26% $T_g=-54.6$ °C <sup>c</sup> , and $MFI=0.72$ g/10 min <sup>a</sup>
Ethylene-vinyl acetate copolymer grafted with maleic anhydride	EVA-g-MA	MA grafting ratio 1.0%, VA content 28%, $T_g=-28.8$ °C <sup>c</sup> , $T_c^P=52.2$ °C <sup>b</sup> , $MFI=2.46$ g/10 min <sup>a</sup>

<sup>a</sup> 190 °C, 2.160 kgf.

<sup>b</sup> Cooling from 220 °C to room temperature (–10 °C/min).

<sup>c</sup> Melting from –90 to 220 °C.

Table 2

DSC data of PP/compatibilizer blends and PP/Mg(OH)<sub>2</sub> composites modified by different compatibilizers

Compatibilizers	PP/Mg(OH) <sub>2</sub> /compatibilizers	$T_c^P$ (°C)	$T_c^{on}$ (°C)	$\Delta Hc^a$ (J/g)	$T_m$ (°C)	$T_m^{on}$ (°C)	$\Phi_\beta$ (%)
	100/0/0	114.5	118.9	-79.7	163.9	158.3	-
	95/5/0	117.4	121.8	-81.0	164.6	159.4	16.7
	90/10/0	118.3	122.5	-81.5	165.0	160.2	23.2
	80/20/0	119.7	123.3	-80.2	164.6	160.6	22.4
	70/30/0	120.3	124.1	-85.3	164.9	160.7	18.7
	60/40/0	121.1	125.1	-82.0	165.9	160.8	17.2
PP-g-MA	95/0/5	114.8	119.0	-70.2	162.5	158.2	-
	55/40/5	132.4	136.7	-84.9	165.9	152.5	-
	50/40/10	130.9	135.5	-96.6	166.3	153.7	-
POE-g-MA	95/0/5	111.7	116.1	-82.8	162.1	157.4	-
	55/40/5	128.1	132.4	-82.1	166.0	158.4	-
	50/40/10	126.0	129.9	-88.9	165.7	159.8	-
EVA-g-MA	95/0/5	110.8	113.8	-79.8	161.3	165.4	-
	55/40/5	121.6	125.9	-80.3	166.1	161.0	15.9
	50/40/10	121.2	125.3	-79.4	165.3	160.6	16.7

<sup>a</sup>  $\Delta Hc = \Delta Hc^* \times m_c/m_p$ , where  $\Delta Hc^*$  is the original crystallization enthalpy measured in cooling experiment,  $m_c$  the mass of sample, and  $m_p$  is the mass of PP in the sample.

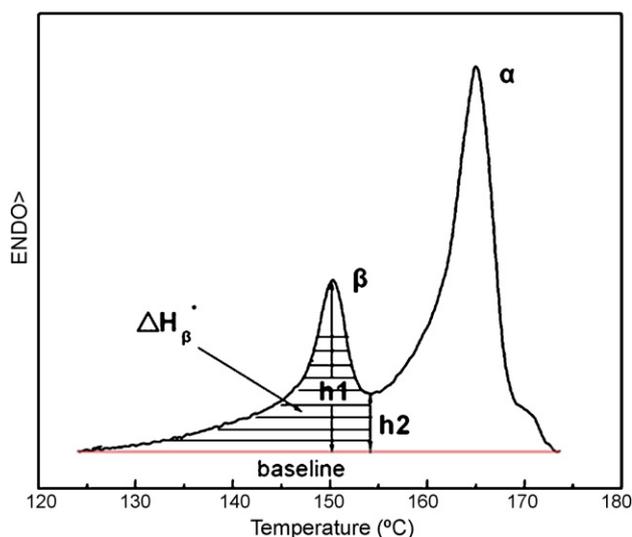
method [14]. A vertical line was drawn through the minimum between the  $\alpha$ - and  $\beta$ -fusion peaks and the total fusion heat was divided into  $\beta$ -component,  $\Delta H_\beta^*$ , and  $\alpha$ -component,  $\Delta H_\alpha^*$ . Since the less-perfect  $\alpha$ -crystals melt before the maximum point during heating and contributed to the  $\Delta H_\beta^*$ , the true value of  $\beta$ -fusion heat,  $\Delta H_\beta$ , has been approximated by a production of multiplying  $\Delta H_\beta^*$  with a calibration factor  $A$ .

$$\Delta H_\beta = A \times \Delta H_\beta^* \quad (3)$$

$$A = \left[ 1 - \frac{h_2}{h_1} \right]^{0.6} \quad (4)$$

$$\Delta H_\alpha = \Delta H - \Delta H_\beta \quad (5)$$

$h_1$  and  $h_2$  are the heights from the base line to the  $\beta$ -fusion peak and minimum point, respectively (Fig. 1).

Fig. 1. DSC melting curves of PP containing  $\beta$ -crystal.

#### 2.4. Wide angle X-ray diffraction

Wide angle X-ray diffraction (WAXD) patterns were obtained using a Rigaku D/max-2200 VPC with the Cu K $\alpha$  radiation at room temperature. The samples were prepared on Perkin-Elmer DSC-7 thermal system under primary experimental condition. The operating condition of the X-ray source was set at a voltage of 40 kV and a current of 30 mA in a range of  $2\theta = 5-40^\circ$ .

### 3. Results and discussion

#### 3.1. Crystallization and melting behavior of PP/compatibilizer blends

Fig. 2 shows DSC cooling and heating curves of PP and PP/compatibilizer blends, the crystallization and melting parameters are listed in Table 2. It can be observed from Table 2 that addition of PP-g-MA has little influence on the crystallization behavior of PP, while POE-g-MA and EVA-g-MA decrease the peak temperature ( $T_c^P$ ) and onset temperature of crystallization ( $T_c^{on}$ ) of PP. As we know, the compatibilities between compatibilizers and PP are different. PP-g-MA can be completely miscible with pure PP. PP and POE can be miscible for the blends having up to 10 wt% POE, and they are partial miscible [15]. The backbone of EVA-g-MA containing the polar acetate group, is different from that of PP and considered immiscible with PP [16]. Therefore, the order of compatibility from high to low between different compatibilizers and PP is PP/PP-g-MA > PP/POE-g-MA > PP/EVA-g-MA, which is in accordance with the  $T_c^P$  and  $T_c^{on}$  of PP. It is suggested that PP-g-MA contains heterogeneous nuclei, which is crystallizable at 110 °C, but the other two compatibilizers do not (seeing Table 1). In PP/POE-g-MA and PP/EVA-g-MA blends, heterogeneous nuclei present in PP diffuse in the other (less compatible) phase so that the starting of crystallization of PP is delayed.

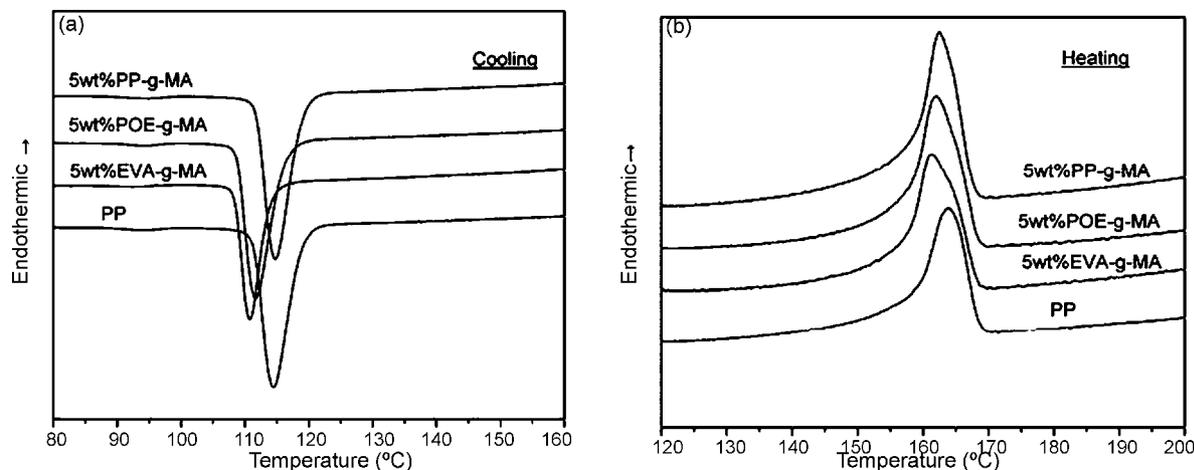


Fig. 2. DSC crystallization (a) and melting (b) curves of PP/compatibilizer blends.

From Fig. 2(b) and Table 2, it can be seen that all the blends exhibit lower melting temperatures. An obvious shoulder-peak in high temperature side of the melting peak appears in the heating curves of PP/POE-g-MA and PP/EVA-g-MA blends, which always happen in lower crystallization temperature of PP. Addition of compatibilizers decreases the perfection of PP crystals, resulting in low melting temperature.

### 3.2. Crystallization and melting behavior of PP/Mg(OH)<sub>2</sub> composites

Fig. 3 shows DSC cooling and heating curves of PP/Mg(OH)<sub>2</sub> composites, the crystallization and melting parameters are listed in Table 2. It can be observed from Fig. 3(a) and Table 2 that the  $T_c^{on}$  and  $T_c^P$  of PP/Mg(OH)<sub>2</sub> (95/5) were 121.8 °C and 117.4 °C, both of which were higher than those of pure PP. As has been shown, Mg(OH)<sub>2</sub> surface can act as nucleating centers. However, the crystallization parameters of PP changed slightly with increasing Mg(OH)<sub>2</sub> content. It possibly attributed to the fact that there would be a critical surface area for the heterogeneous nucleation effect of the Mg(OH)<sub>2</sub> surface for the crystallization of PP in PP/Mg(OH)<sub>2</sub> composites [9].

It is well known that PP mainly has three crystalline forms: monoclinic  $\alpha$ , hexagonal  $\beta$  and orthorhombic  $\gamma$ . Addition of  $\beta$ -nucleating agents is an efficient way to obtain  $\beta$ -PP. From Fig. 3(b), it can be seen that addition of Mg(OH)<sub>2</sub> not only increased the peak temperature of melting ( $T_m^P$ ), but also induced the formation of  $\beta$ -crystal in PP matrix. There is an obvious  $\beta$ -crystal melting peak near 150 °C in all PP/Mg(OH)<sub>2</sub> composites.

The relationship of the percentage of  $\beta$ -phase ( $\Phi_\beta$ ) in PP matrix, calculated according to Eqs (1)–(5), and Mg(OH)<sub>2</sub> content was shown in Fig. 4. It can be observed from Fig. 4 that the  $\Phi_\beta$  increased with increasing Mg(OH)<sub>2</sub> content and achieves maximum value when the Mg(OH)<sub>2</sub> content is up to 10 wt%, then the  $\Phi_\beta$  decreased with increasing Mg(OH)<sub>2</sub> content.

The addition of Mg(OH)<sub>2</sub> results in the formation of  $\beta$ -crystal. A possible reason for this phenomenon would be connected to the similar Bravais lattice of  $\beta$ -PP and Mg(OH)<sub>2</sub>, both hexagonal [11]. And the ionic spacing of the filler crystal lattice is close to the crystallographic dimensions of the polymer crystal, which can support epitaxial polymer crystallization on filler surfaces [17].

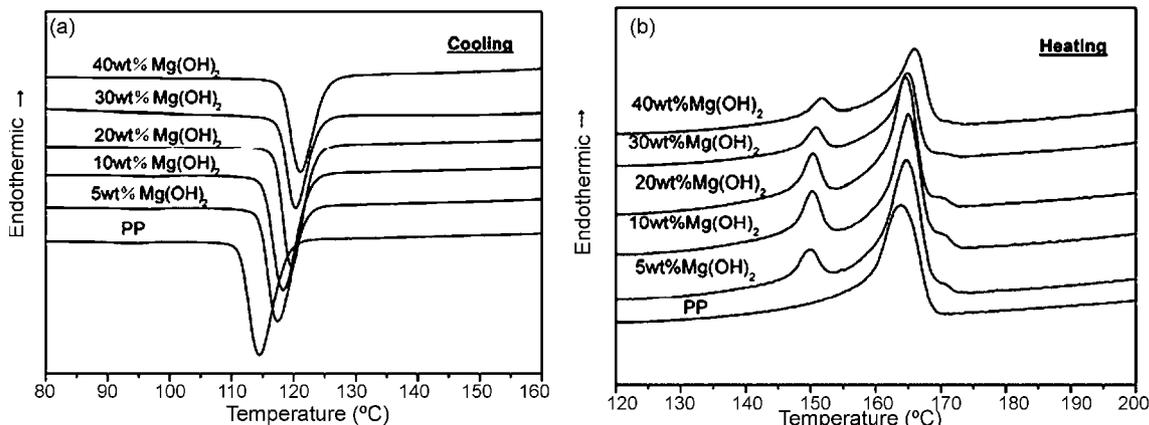


Fig. 3. DSC crystallization (a) and melting (b) curves of PP/Mg(OH)<sub>2</sub> composites.

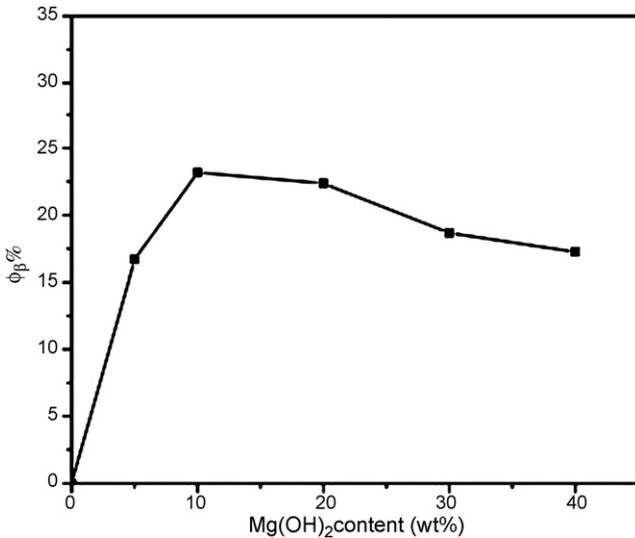


Fig. 4.  $\beta$ -form index ( $\phi_{\beta}$ ) of PP/Mg(OH)<sub>2</sub> composites.

### 3.3. Crystallization and melting behavior of PP/Mg(OH)<sub>2</sub> composites modified by compatibilizers

As we know [18], using maleated elastomer in PP/elastomer/filler systems results in encapsulation structure, where the elastomer encapsulates the filler particles. In our study, it is difficult to form a completely encapsulated core-shell particle structure between compatibilizers and Mg(OH)<sub>2</sub> due to the lower content of compatibilizer comparing with Mg(OH)<sub>2</sub>. So the non-encapsulated Mg(OH)<sub>2</sub> surface can still act as heterogeneous nucleation agent in some instances, which can induce the formation of  $\beta$ -crystal in PP matrix.

When PP-g-MA was used as compatibilizer, the crystallization and melting behavior of PP changed obviously (Fig. 5). The  $T_c^{on}$  and  $T_c^P$  of PP in PP/Mg(OH)<sub>2</sub>/PP-g-MA(55/40/5) composites reached to 136.7 °C and 132.4 °C, respectively, higher than those of PP-g-MA/PP(5/95) blend and PP/Mg(OH)<sub>2</sub>(60/40) composite. But no more  $\beta$ -crystal melting peak near 150 °C was

observed in PP/Mg(OH)<sub>2</sub>/PP-g-MA(55/40/5) composites. With increasing PP-g-MA content to 10 wt%, the peak of crystallization shifted to lower temperatures while the melting behavior of PP changed slightly. This is suggested that there exist a synergism of heterogeneous nucleation of PP-g-MA and Mg(OH)<sub>2</sub> for PP crystallization. In the PP/Mg(OH)<sub>2</sub>/PP-g-MA composites, the compatibility between Mg(OH)<sub>2</sub> and PP has been enhanced due to the strong interaction between PP-g-MA and Mg(OH)<sub>2</sub> and the compatibility between PP and PP backbone in PP-g-MA. The strong interaction between PP-g-MA and Mg(OH)<sub>2</sub> may activates the nucleation points on the surface of Mg(OH)<sub>2</sub> and results in position synergism of heterogeneous nucleation of PP, and increases the crystallization temperatures of PP [9]. However, the Mg(OH)<sub>2</sub> surface was encapsulated by PP-g-MA in PP/Mg(OH)<sub>2</sub> composite modified by the PP-g-MA content to 10 wt% and resulted in the decrease in the heterogeneous nucleation of Mg(OH)<sub>2</sub>. No more  $\beta$ -crystal melting peak near 150 °C was observed in PP/Mg(OH)<sub>2</sub>/PP-g-MA(50/40/10) composites too.

The application of POE-g-MA as compatibilizer also shifted the crystallization peaks of PP to higher temperature (Fig. 6). The  $T_c^P$  of PP in PP/Mg(OH)<sub>2</sub>/POE-g-MA (55/40/5) composite was 128.1 °C, higher than that of PP/POE-g-MA(95/5) blend and PP/Mg(OH)<sub>2</sub>(60/40) composite. Obviously, the heterogeneous nucleation effect of Mg(OH)<sub>2</sub> with POE-g-MA is weaker than that with PP-g-MA. An explanation for this is that POE in POE-g-MA and PP are partial miscible. With increasing POE-g-MA content to 10 wt%, the peak of crystallization curve shifted to lower temperatures, and a small  $\beta$ -crystal melting peak was observed in the melting curve due to low heterogeneous nucleation of POE-g-MA.

Fig. 7 shows DSC cooling and heating curves of PP/Mg(OH)<sub>2</sub> composites modified by EVA-g-MA, and the crystallization and melting parameters are listed in Table 2. It can be observed that the crystallization and melting behavior is different from that of PP/Mg(OH)<sub>2</sub>/PP-g-MA and PP/Mg(OH)<sub>2</sub>/POE-g-MA composites. Addition of the different EVA-g-MA content slightly influences the crystallization and melting temperatures, also the

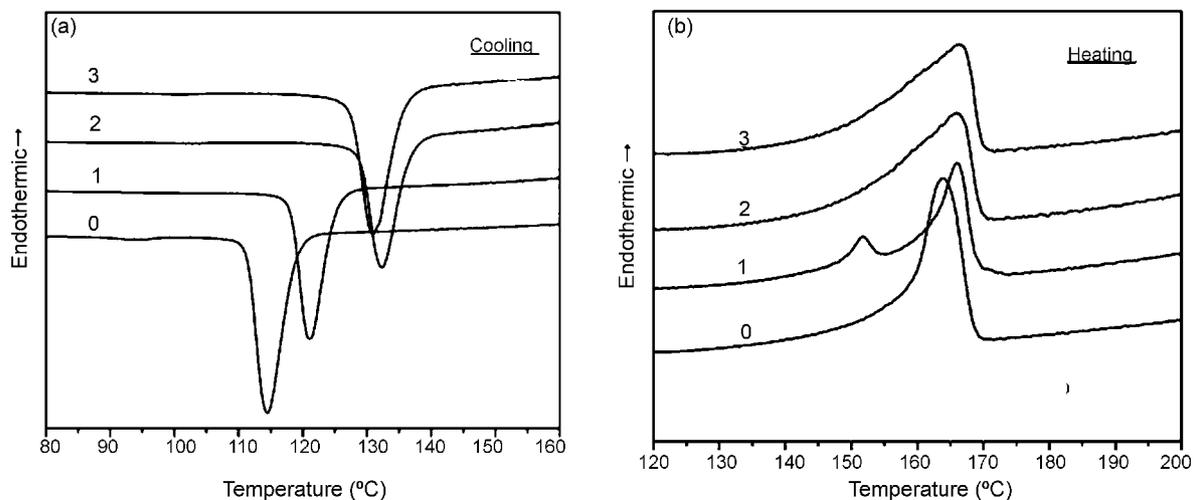


Fig. 5. DSC crystallization (a) and melting (b) curves of PP/Mg(OH)<sub>2</sub> composites modified by PP-g-MA (0) PP; (1) PP/Mg(OH)<sub>2</sub>(60/40); (2) PP/Mg(OH)<sub>2</sub>/PP-g-MA (55/40/5); (3) PP/Mg(OH)<sub>2</sub>/PP-g-MA (50/40/10).

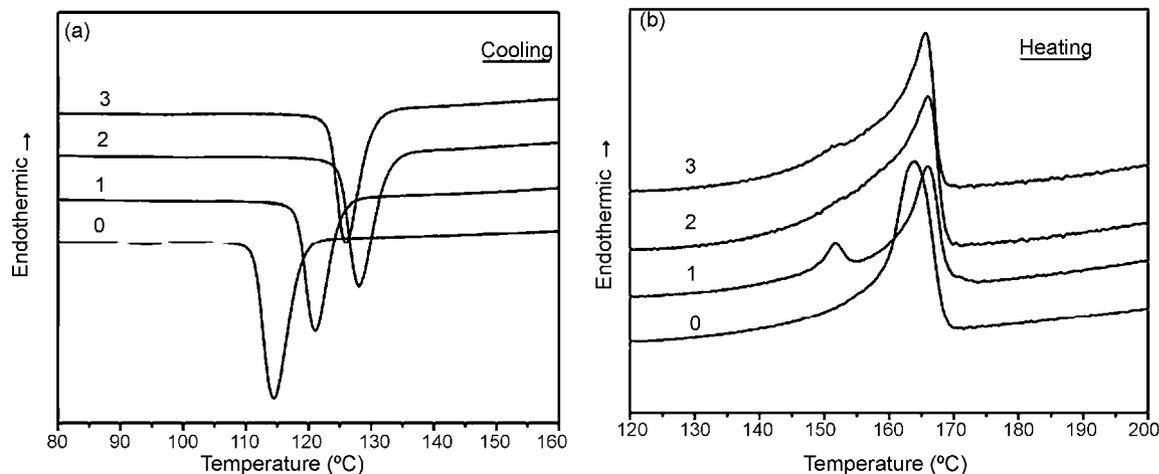


Fig. 6. DSC crystallization (a) and melting (b) curves of PP/Mg(OH)<sub>2</sub> composites modified by POE-g-MA (0) PP; (1) PP/Mg(OH)<sub>2</sub>(60/40); (2) PP/Mg(OH)<sub>2</sub>/POE-g-MA (5/40/55); (3) PP/Mg(OH)<sub>2</sub>/POE-g-MA (50/40/10).

shape of melting peaks of PP in PP/Mg(OH)<sub>2</sub> composites. In Fig. 7(b), a significant  $\beta$ -crystal melting peak was observed in the melting curves of PP/Mg(OH)<sub>2</sub>/EVA-g-MA composites. But the percentage of  $\beta$ -phase ( $\Phi_{\beta}$ ) in these composites decreased slightly, comparing with PP/Mg(OH)<sub>2</sub>(60/40).

Fig. 8 shows the WAXD spectra of the specimens after crystallized at cooling rate of 10 °C/min from 220 °C to 50 °C. It can be seen that the WAXD reflection of PP shows typical  $\alpha$ -monoclinic structures. For the PP/Mg(OH)<sub>2</sub>(60/40), the most intense (130) diffraction of PP overlaps with the (001) reflection of Mg(OH)<sub>2</sub>, and there exists an extra reflection at  $2\theta$  of 16.0°, which can be accounted for the (300) lattice planes of hexagonal  $\beta$ -PP. The same phenomena appears in the X-ray diffractions of PP/Mg(OH)<sub>2</sub>/EVA-g-MA. These are in good accordance with DSC results. However, there are no obvious reflections at  $2\theta$  of 16.0° in the X-ray diffractions of PP/Mg(OH)<sub>2</sub>/PP-g-MA and PP/Mg(OH)<sub>2</sub>/POE-g-MA. It is worth noting that the DSC result indicates the existence

of  $\beta$ -PP in the PP/Mg(OH)<sub>2</sub>/POE-g-MA(50/40/10) composite. However, it has not been identified in the WAXD experiments. This may be understandable that the WAXD reflects the overall crystalline structure of the sample. As a result, some crystalline structure of the minority crystalline phase could be covered up by the majority phase [19].

#### 3.4. Interfacial interaction in PP/Mg(OH)<sub>2</sub> composites modified by different compatibilizers

The above experimental results indicated that Mg(OH)<sub>2</sub> acts as heterogeneous nucleation agent increasing the crystallization temperature of PP in the PP/Mg(OH)<sub>2</sub> composites and inducing the formation of  $\beta$ -crystal in PP matrix due to PP directly contacts with Mg(OH)<sub>2</sub> surface.

In the PP/Mg(OH)<sub>2</sub> composites modified by different compatibilizers, the crystallization temperatures of PP depend on the compatibility between compatibilizer and PP. The interfacial

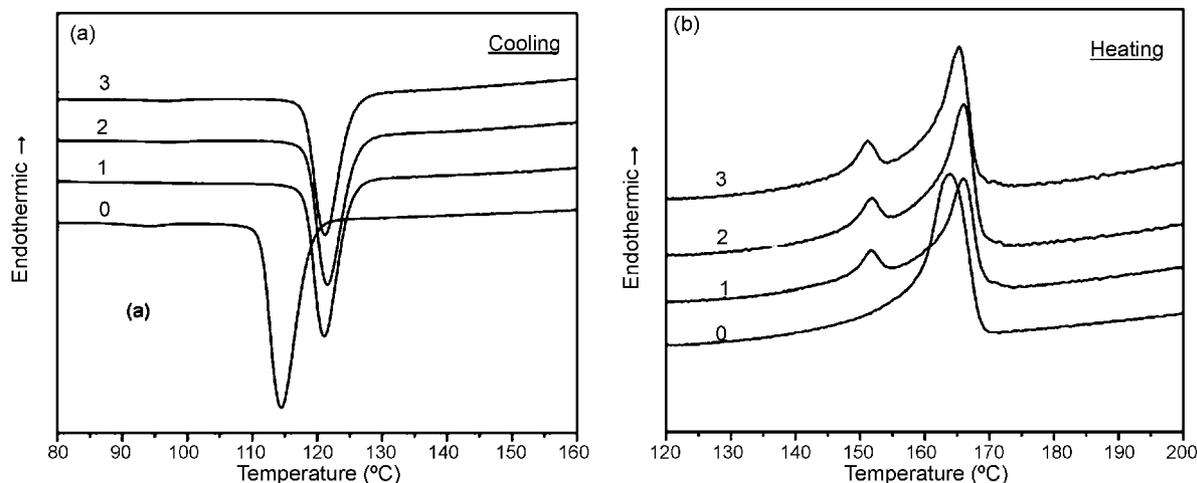


Fig. 7. DSC crystallization (a) and melting (b) curves of PP/Mg(OH)<sub>2</sub> composites modified by EVA-g-MA (0) PP; (1) PP/Mg(OH)<sub>2</sub>(40/60); (2) PP/Mg(OH)<sub>2</sub>/EVA-g-MA (55/40/5); (3) PP/Mg(OH)<sub>2</sub>/EVA-g-MA (50/40/10).

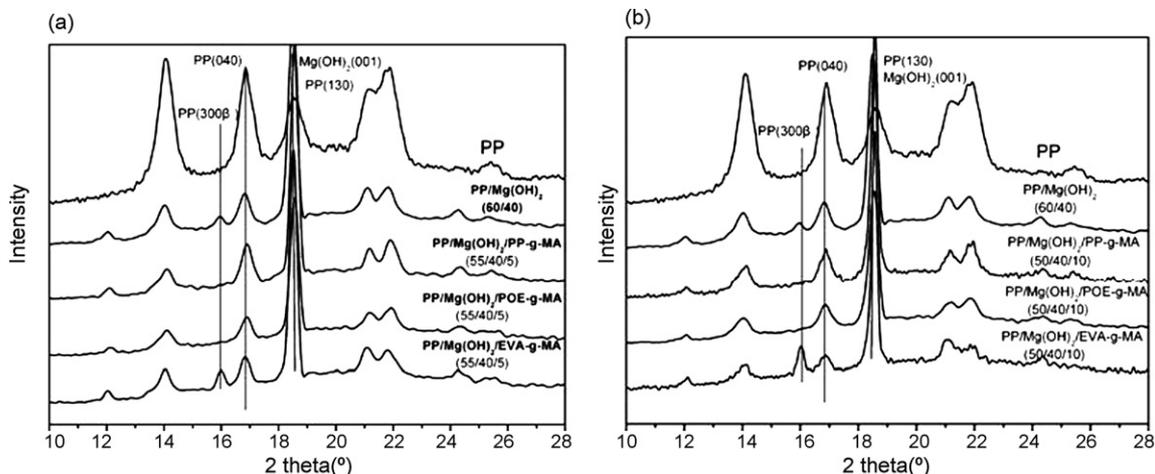


Fig. 8. X-ray diffractions of neat PP and PP/Mg(OH)<sub>2</sub> composites modified by different compatibilizers (a) 5 wt% compatibilizer and (b) 10 wt% compatibilizer.

interaction between compatibilizer and Mg(OH)<sub>2</sub> are the same due to the same polar groups (maleic anhydride) in compatibilizers. But the interfacial interactions between compatibilizers and PP are different, which depend on compatibility between PP and the long hydrocarbon chain in compatibilizer through physical entanglements and van der Waals interactions. For the PP/Mg(OH)<sub>2</sub> composites modified by PP-g-MA, PP and PP chain in PP-g-MA is completely miscible due to the same molecular chain. The interfacial interaction between PP-g-MA and Mg(OH)<sub>2</sub> results in the synergism of heterogeneous nucleation of PP, which can increase the crystallization temperatures of PP through the completely miscible interface phase. For the PP/Mg(OH)<sub>2</sub> composites modified by POE-g-MA, PP and POE in POE-g-MA is partial miscible. The partial miscible interface between PP and POE decreases the synergism of heterogeneous nucleation of POE-g-MA and Mg(OH)<sub>2</sub>. Therefore, the crystallization temperatures of PP in PP/Mg(OH)<sub>2</sub> composites modified by POE-g-MA is lower than that of PP/Mg(OH)<sub>2</sub> composites modified by PP-g-MA. For the PP/Mg(OH)<sub>2</sub> composites modified by EVA-g-MA, the compatibility between PP and EVA in EVA-g-MA is lower than that between PP and PP-g-MA or between PP and POE-g-MA. The immiscible interface between PP and EVA retards the synergism of heterogeneous nucleation of EVA-g-MA and Mg(OH)<sub>2</sub>. The main nucleation mechanisms in these composites is still heterogeneous nucleation of non-encapsulated Mg(OH)<sub>2</sub> surface, so the crystallization and melting behavior of PP changes slightly.

Whether the β-crystal formation or not depends on the crystallization temperature of PP in these composites. The increase in crystallization temperatures of PP facilitates the formation of α-PP, but weakens the formation of β-PP. There exists a critical temperature (almost 130 °C) for the formation of β-PP. When the crystallization starts at  $T_c^{on}$  above 130 °C (as in the case of PP/Mg(OH)<sub>2</sub>/PP-g-MA and PP/Mg(OH)<sub>2</sub>/POE-g-MA55/40/5 composites), it completes just when the crystallization of β-form could start, but it does not because no more crystallizable material is available as it is completely already crystallized in α-form. When the crystallization starts at  $T_c^{on}$  lower than 130 °C

(as in the case of PP/Mg(OH)<sub>2</sub>/POE-g-MA50/40/10 blends) it completes also at lower  $T$  where, now, the nuclei for the β-form have some melting material available to crystallize. For PP/Mg(OH)<sub>2</sub> composites modified by EVA-g-MA, the crystallization temperature of PP in modified PP/Mg(OH)<sub>2</sub> composite is the same as PP/Mg(OH)<sub>2</sub> composite. The β-crystal in PP matrix is formed for PP/Mg(OH)<sub>2</sub> composites modified by EVA-g-MA.

#### 4. Conclusions

The investigation results on the crystallization and melting behaviors of PP blends, PP/Mg(OH)<sub>2</sub> composites and its composites modified by different compatibilizers indicated that crystallization behavior of PP depends upon the compatibility between PP and compatibilizer. Addition of PP-g-MA has no influence on the crystallization temperature of PP, but addition of POE-g-MA and EVA-g-MA decrease the crystallization temperature of PP. Addition of Mg(OH)<sub>2</sub> increases the crystallization temperature of PP and induces the formation of β-crystal in PP matrix due to heterogeneous nucleation of Mg(OH)<sub>2</sub>. The crystallization temperatures of PP in modified PP/Mg(OH)<sub>2</sub> depend also upon compatibility between PP and compatibilizer. There is a synergistic heterogeneous nucleation effect between PP-g-MA and Mg(OH)<sub>2</sub> on the crystallization behavior of PP because the crystallization temperature of PP in PP/Mg(OH)<sub>2</sub>/PP-g-MA is higher than that in PP/Mg(OH)<sub>2</sub>. The synergism of heterogeneous nucleation of Mg(OH)<sub>2</sub> and POE-g-MA is observed due to a further increase in the crystallization temperatures of PP. The increase in crystallization temperatures of PP facilitates the formation of α-PP, but weakens the formation of β-PP. For PP/Mg(OH)<sub>2</sub> composites modified by EVA-g-MA, the addition of EVA-g-MA to PP/Mg(OH)<sub>2</sub> composite has little effect on the crystallization and melting behavior of PP, and Mg(OH)<sub>2</sub> in the composite still acts as a nucleation agent to facilitate the formation of PP β-crystal. Therefore, it is suggested the synergism of heterogeneous nucleation of Mg(OH)<sub>2</sub> and compatibilizer depends upon the compatibility between PP and compatibilizer.

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