

# The $\beta$ -nucleation of polypropylene random copolymer filled by nano-CaCO<sub>3</sub> supported $\beta$ -nucleating agent

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**Abstract** In this article,  $\beta$ -nucleation of nano-CaCO<sub>3</sub> (CC) supported  $\beta$ -nucleating agent (Sup- $\beta$ -NA) for random polypropylene copolymer (PPC) crystallization was studied by differential scanning calorimetry (DSC) and wide-angle X-ray diffraction. The results showed that Sup- $\beta$ -NA not only increased the peak temperature of the crystallization of PPC but also induced PPC to form almost pure  $\beta$ -modification. It indicated that Sup- $\beta$ -NA possessed effective  $\beta$ -nucleation. The content of Sup- $\beta$ -NA had little influence on the crystallization behavior and melting characteristics together with the  $\beta$ -modification content of PPC, but those were affected by the mass ratio of CC/ $\beta$ -NA (calcium pimelate) in the Sup- $\beta$ -NA. The final temperature of the melt between 300 and 180 °C did not affect the  $\beta$ -nucleation of Sup- $\beta$ -NA, although the  $\beta$ -nucleation of Sup- $\beta$ -NA would be decreased with the final temperature of the melt lower than 170 °C. In addition, DSC multiple heating and cooling scanning had little influence on the thermal stability of  $\beta$ -nucleation of Sup- $\beta$ -NA.

**Keywords**  $\beta$ -Nucleation · Polypropylene copolymer · Supported  $\beta$ -nucleating agent · Crystallization

## Introduction

Polypropylene (PP) has low rigidity and slow crystallization rate, thus, there were a great number of reports on improving the rigidity and accelerating the crystallization rate of PP. Up to now, introduction of inorganic particle fillers [1–5] and nucleating agents [6–22] into PP is one of the most common and simple methods to improve the mechanical properties and accelerate the crystallization rate of PP, respectively.

In general, the nucleating agent of PP was divided into  $\alpha$ - and  $\beta$ -nucleating agent. PP nucleated by  $\alpha$ -nucleating agent formed  $\alpha$ -modification ( $\alpha$ -PP) [6–15] with good rigidity, while PP nucleated by  $\beta$ -nucleating agent might form  $\beta$ -modification ( $\beta$ -PP) with special properties [16–22], such as higher impact strength and heat distortion temperature than that of  $\alpha$ -modification.

Comparing with PP homopolymer (PPH), there was less investigation on random PP copolymer (PPC) nucleated by nucleating agent. Wang et al. [6] studied the effect of  $\alpha$ -nucleating agent (DBS) on the crystalline structure of an injection-molded bar of PPC. The results showed that pure PPC forms a simple skin–core crystalline structure. However, PPC/DBS formed an interesting and complicated hierarchy crystalline structure: there was a transition layer between the skin layer and the core zone. In that transition layer, the crystalline structure consists of some perfect spherulites and many tiny crystallites. Further research suggested that the formation of the hierarchy crystalline structure depended on the content of the nucleating agent in the PPC matrix and the mold temperature during the injection-molding processing.

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Zhu et al. [14] prepared PPC filled with or without a nucleating agent and/or nano-CaCO<sub>3</sub> particles by in situ reactor copolymerization and studied the crystallization properties of the samples. The results showed that the nucleating agent dramatically decreased the half-time of crystallization  $t_{1/2}$ , as well as increased the overall crystallization rate of PPC. Those effects were further promoted in the presence of the nano-CaCO<sub>3</sub> particles. The incorporation of the nucleating agent and nano-CaCO<sub>3</sub> particles into PPC remarkably improved its mechanical properties and heat distortion temperature.

Zhang et al. [15] studied the crystallization characteristics of PPH and PPC with and without nucleating agents talc (300 mesh). They introduced a new estimation method to determine the non-isothermal crystallization rate of those materials. The results indicated that nucleating agent was more efficient in PPC than that in PPH.

Polypropylene copolymer nucleated by  $\beta$ -nucleating agent has been reported. Varga et al. [16] found that the  $\beta$ -nucleating ability of the random copolymers was decreased with the decreasing of the chain regularity. Juhász et al. [17] indicated that adding  $\beta$ -nucleating agent into random copolymers did not suppress the formation of the  $\gamma$ -form. Varga et al. [18] also synthesized calcium salts of suberic and pimelic acid (PA) as an effective  $\beta$ -nucleating agent for PP crystallization. They found that the calcium suberate and calcium pimelate (CaPA) not only increased the peak temperature of the crystallization and the crystallinity of PPC, but also induced PPC to form almost pure  $\beta$ -modification in nucleated PPC. Their further investigation [19] indicated that propylene homo-, random-, and block-copolymers containing calcium suberate and CaPA crystallized principally in pure  $\beta$ -modification as demonstrated in isothermal and non-isothermal crystallization experiments.

Hao et al. [20] investigated the crystallization properties of PPC containing  $\beta$ -nucleating agent a blend of PA and calcium hydroxide, and found that high content of  $\beta$ -modification was obtained for PPC. The result showed that PPC also had a most favorable temperature near 132 °C for  $\beta$ -modification crystal growth. The crystallization rate of PPC containing  $\beta$ -nucleating agent was much higher than that of PPH containing  $\beta$ -nucleating agent. The observation of spherulite morphology of  $\beta$ -nucleated PPC and  $\beta$ -nucleated PPH showed that the spherulites of  $\beta$ -nucleated PPC were more imperfect than those of  $\beta$ -nucleated PPH.

Na et al. [21] found  $\beta$ -nucleating agent (aromatic amide derivative with trade name TMB-5) nucleated PPC could form  $\gamma$ -modification at slow cooling rates (e.g., 1 °C min<sup>-1</sup>), where the formation of  $\beta$ -modification was suppressed to a large extent. The detailed morphological observations indicated that the formation of  $\gamma$ -modification in the  $\beta$ -nucleated PPC at slow cooling rate was unambiguously attributed to the nucleating duality of the  $\beta$ -nucleating agent toward  $\alpha$ - and

$\beta$ -polymorphs. The  $\alpha$ -modification, induced by the  $\beta$ -nucleating agent, served as seeds for predominant growth of the  $\gamma$ -modification. Moreover, the presence of the  $\beta$ -nucleating agent, acting as heterogeneous nuclei, promoted the formation of  $\gamma$ -phase in the nucleated PPC, at least to some extent.

Izer et al. [22] used  $\beta$ -crystal forms of PPH and PPC nucleated by calcium suberate as matrix materials to prepare self-reinforced PP composites. Based on the results, the optimum processing temperature was determined and found by 20–25 °C above the related matrix melting temperature. It was established that the  $\beta$ -modified PPH based one-component self-reinforced PP composites possessed similar attractive mechanical properties as the intensively studied  $\alpha$ -PPC based two-component ones.

Although  $\beta$ -PP possess high impact strength, the yield strength and modulus of  $\beta$ -PP is lower than that of  $\alpha$ -PP. In order to improve the strength and rigidity of  $\beta$ -PP and prepare  $\beta$ -PP blends and composites with high toughness, the  $\beta$ -PP blends with other polymers and  $\beta$ -PP composites filled by inorganic fillers have been reported in recent years [23–31]. Unfortunately, the second components generally have  $\alpha$ -nucleation for PP crystallization, which restrains the  $\beta$ -nucleation of  $\beta$ -nucleating agent for PP crystallization and retards the growth of  $\beta$ -modification in multi-component system. Therefore, it is difficult to obtain  $\beta$ -PP blends and  $\beta$ -PP composites with high  $\beta$ -modification content. [26, 32] In order to decrease the effect of inorganic fillers with  $\alpha$ -nucleation on  $\beta$ -nucleation efficiency of  $\beta$ -nucleating agent, we found a novel supported  $\beta$ -nucleating agent (Sup- $\beta$ -NA) [33–36] using nano-CaCO<sub>3</sub> (CC) as support. The Sup- $\beta$ -NA was prepared through chemical reaction between CC and PA loaded on the surface of CC to form traditional  $\beta$ -nucleating agent CaPA supported on the surface of CC. In our lab, Sup- $\beta$ -NA was used as  $\beta$ -nucleating agent for PPC crystallization. It is expected that the  $\beta$ -nucleating agent supported on the surface of CC decreases the effect of CC with  $\alpha$ -nucleation on the  $\beta$ -nucleation efficiency of  $\beta$ -nucleating agent and improves the toughness and rigidity of PPC due to the formation of  $\beta$ -modification with high toughness and the reinforcement of CC as rigid filler. In this article, the PPC filled by different content of Sup- $\beta$ -NA was prepared and the influences of the Sup- $\beta$ -NA content and the mass ratio of CC/PA in prepared Sup- $\beta$ -NA on the crystallization behavior, melting characteristics of PPC, the  $\beta$ -modification content of PPC, and the thermal stability of  $\beta$ -nucleation for PPC crystallization was determined.

## Experiment

### Materials

A commercial grade random PPC with 8.1 wt% ethylene, PPC (EPC30R, containing antioxidants, MFR = 7.6 g

10 min<sup>-1</sup> at 230 °C) used in the study was supplied by Sinopec Group, Maoming Petroleum Chemical Industry Limited Company, China. A commercial grade nano-CaCO<sub>3</sub> with the particle diameter between 40 and 60 nm was obtained from Guangping Chemical Industry Limited Company, China.

### Sample preparation

Before samples preparation, all materials were adequately dried in a vacuum oven at appropriate temperatures. The CC supported  $\beta$ -nucleating agent (Sup- $\beta$ -NA $x$ ) with different mass ratio ( $x$ ) of CC/PA was prepared by impregnating CC into acetone solution of PA at room temperature and then vaporized the acetone for 6 h at room temperature [29–32]. PPC filled by CC, PPC nucleated by CaPA and PPC filled by Sup- $\beta$ -NA were homogenized at 190 °C, and 50 rpm for 8 min using a HL-200 internal mixer (Jinlin University Science and Education Instrument Factory, China).

### Characterizations

#### Differential scanning calorimetry

The crystallization behavior and melting characteristics of samples were carried on a TA DSC Q10 differential scanning calorimetry (DSC), the temperature and the enthalpy had been calibrated with indium at different rates in our experiments. All DSC curves in this article had been normalized. About 5 mg of sample was weighted very accurately. The samples were cooled to room temperature in this article. The detail was that the samples were heated up to the final temperature of the melt ( $T_{\text{melt}}$ ) and held there for 5 min in order to erase their thermal and mechanical history. After melting, the samples were cooled to 50 °C at the cooling rate of 10 °C min<sup>-1</sup> for investigation of the crystallization behavior, and then subsequently reheated to  $T_{\text{melt}}$  at the heating rate of 10 °C min<sup>-1</sup> investigation of the melting behavior and the determination of the polymorphic composition. Besides especially noting, the  $T_{\text{melt}}$  was 220 °C.

#### Wide-angle X-ray diffraction

Wide-angle X-ray diffraction (WAXD) experiment was conducted with a Rigaku Geigerflex Model D/Max-III A rotating anode X-ray diffractometer. Graphite monochromatic Cu-K $\alpha$  radiation was employed as a radiation source. The scanning range was 5°–40° with the rate of 4° min<sup>-1</sup> and a step length of 0.02. In order to remain the thermal history as same as the DSC measures, the samples used in WAXD measures had been prepared in DSC by heating up

to 220 °C and held there for 5 min, then cooled to 50 °C with the cooling rate of 10 °C min<sup>-1</sup>. The  $K$  value representing the  $\beta$ -modification content in PPC was calculated from X-ray diffractograms according to Turner-Jones et al. [37]:

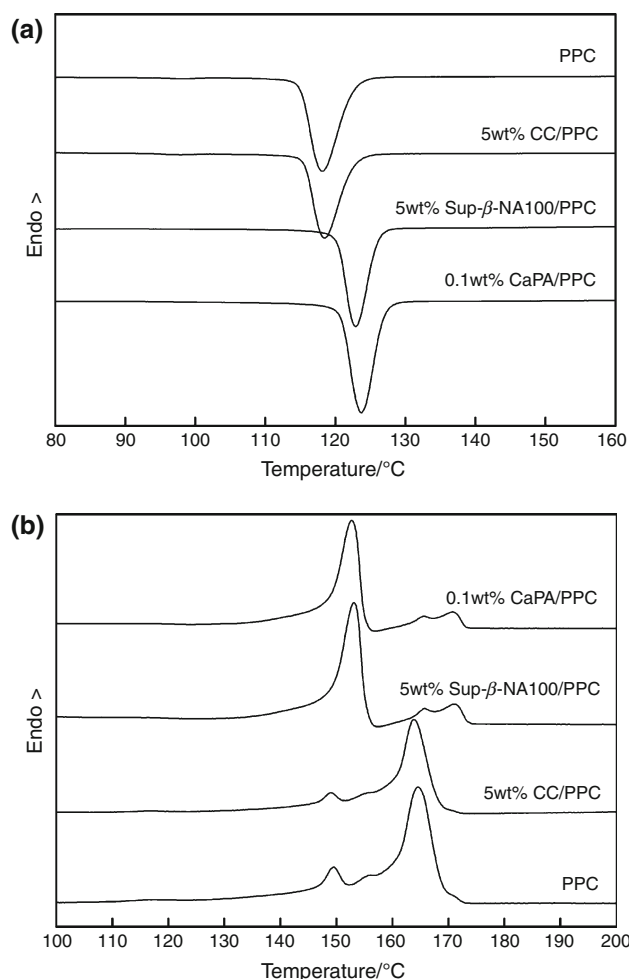
$$K_{\beta} = \frac{H_{\beta(300)}}{H_{\alpha(110)} + H_{\alpha(040)} + H_{\alpha(130)} + H_{\beta(300)}} \quad (1)$$

where  $H_{\alpha(110)}$ ,  $H_{\alpha(040)}$ , and  $H_{\alpha(130)}$  are the intensities of  $\alpha$ -diffraction peaks corresponding to angles  $2\theta$  equals 14.2°, 17.0°, and 18.8°, respectively, and  $H_{\beta}$  is the intensity of  $\beta$ -diffraction peak at  $2\theta$  equals 16.2°.

## Results and discussion

### The $\beta$ -nucleation of Sup- $\beta$ -NA for PPC crystallization

Figure 1 showed DSC crystallization and melting curves of PPC, CC-filled PPC, CaHA-nucleated PPC, and Sup- $\beta$ -



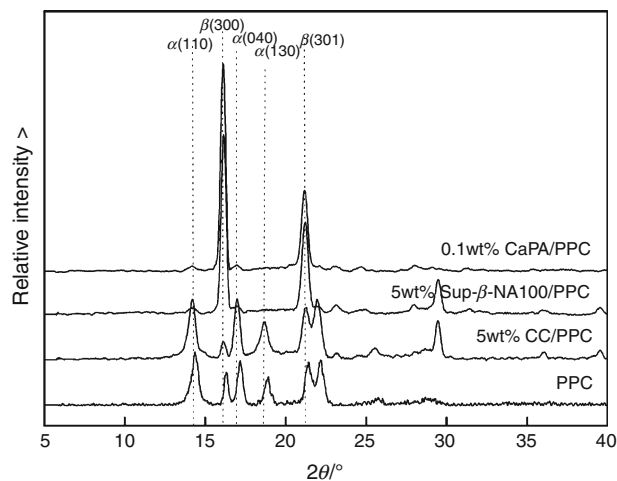
**Fig. 1** DSC crystallization (a) and melting (b) curves of PPC, CC-filled PPC, CaPA-nucleated PPC, and Sup- $\beta$ -NA100-filled PPC

NA100-filled PPC, the relative data was listed in Table 1. For the crystallization behavior, PPC crystallized at temperature of 118.2 °C. CC-filled PPC had almost the same crystallization behavior as that of PPC. However, addition of CaPA and Sup- $\beta$ -NA100 markedly increased the peak temperature of the crystallization ( $T_{cp}$ ) of PPC from 118.2 to 123.7 °C and 122.9 °C, respectively. For the melting characteristics, PPC and CC-filled PPC showed a strong melting peak at temperature of 164 °C due to the melting of  $\alpha$ -modification and a weak melting peak at temperature of 149 °C due to the melting of  $\beta$ -modification. However, the CaPA-nucleated PPC and Sup- $\beta$ -NA100-filled PPC presented a strong melting peak at temperature of 153 °C due to the melting of  $\beta$ -modification and a double weakened melting peaks at temperature around 165 °C. The above results indicated that the Sup- $\beta$ -NA100 possessed high effective  $\beta$ -nucleation for PPC crystallization similar to that of traditional  $\beta$ -nucleating agent CaPA. The melting characteristic of Sup- $\beta$ -NA100-filled PPC was different from that of CC-filled PPC. It was suggested that the nucleation mechanism of CC changed from  $\alpha$ -nucleation to  $\beta$ -nucleation by  $\beta$ -nucleating agent supported on the surface of CC.

Figure 2 presented X-ray diffraction diagrams of PPC, CC-filled PPC, CaHA-nucleated PPC and Sup- $\beta$ -NA100-filled PPC. Table 1 showed the  $K$  values of the samples calculated by Eq. 1. The  $K$  values of PPC and CC-filled PPC were 0.16 and 0.05, respectively. It was indicated that although CC had no influence on the crystallization behavior, addition of CC slightly restrained the formation of  $\beta$ -modification in PPC, resulting in the low  $K$  values. However, the introduction of CaPA and Sup- $\beta$ -NA100 remarkably increased the  $K$  values of PPC, and the  $\beta$ -modification content of PPC was above 0.90. The CaPA as  $\beta$ -nucleating agent possessed high efficient  $\beta$ -nucleation, which had been reported by Varga et al. [18, 19, 26]. It could be seen from Table 1 that the  $K$  value of Sup- $\beta$ -NA100-filled PPC was higher than that of CaHA-nucleated PPC. It was proved that the Sup- $\beta$ -NA not only change the nucleation mechanism of CC from  $\alpha$ -nucleation to  $\beta$ -nucleation by supported  $\beta$ -nucleating agent on the surface of CC but also has higher  $\beta$ -nucleation than that of CaHA for PPC crystallization.

**Table 1** Data of PPC, CC-filled PPC, CaHA-nucleated PPC, and Sup- $\beta$ -NA100-filled PPC

Samples	$T_c/^\circ\text{C}$	$\Delta H_c/\text{J g}^{-1}$	$T_m^\beta/^\circ\text{C}$	$T_m^\alpha/^\circ\text{C}$	$T_m^{22}/^\circ\text{C}$	$K_\beta$
PPC	118.2	82.3	148.7	164.7	–	0.16
5 wt% CC/PPC	118.5	77.7	149.4	163.8	–	0.05
0.1 wt% CaPA/PPC	123.7	76.5	152.8	165.6	170.8	0.94
5 wt% Sup- $\beta$ -NA100/PPC	122.9	73.2	153.2	165.7	171.0	0.99

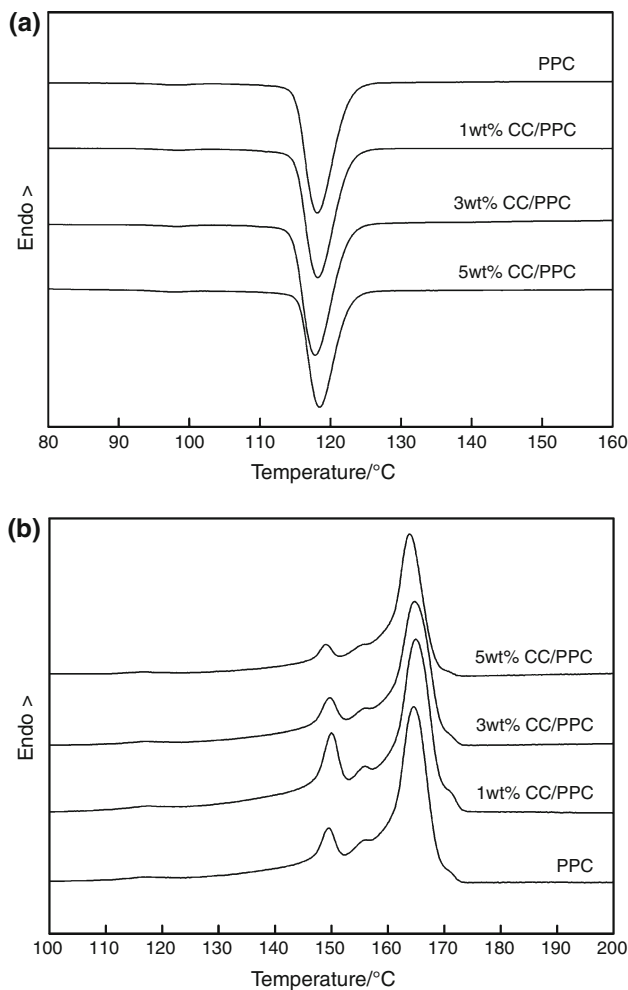


**Fig. 2** X-ray diffraction diagrams of PPC, CC-filled PPC, CaPA-nucleated PPC, and Sup- $\beta$ -NA100-filled PPC

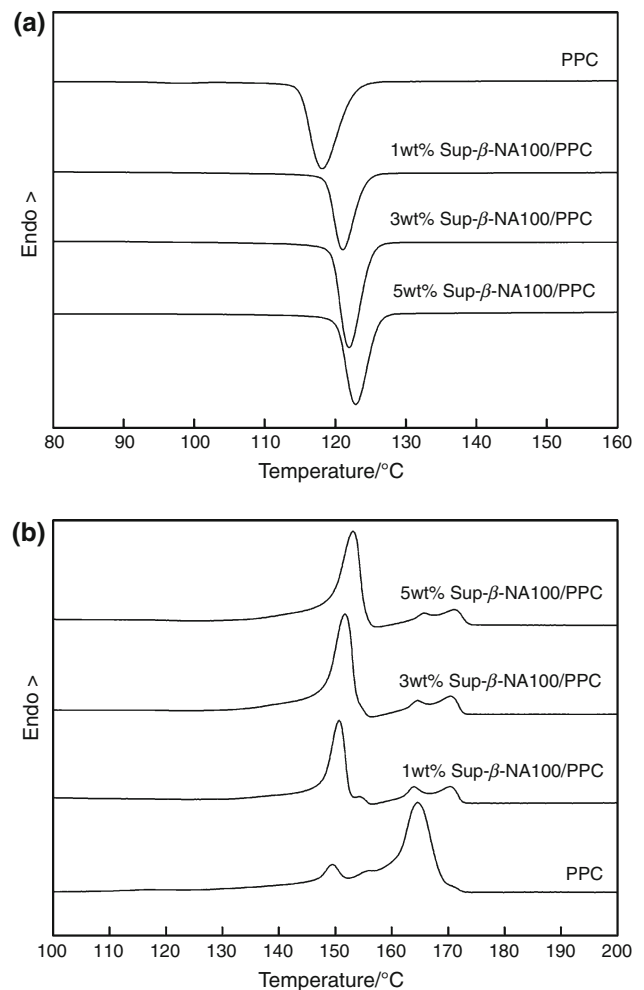
#### Effect of Sup- $\beta$ -NA content on $\beta$ -nucleation of PPC

In order to investigate the influence of Sup- $\beta$ -NA content on the  $\beta$ -nucleation of PPC, PPC filled by different content of CC and Sup- $\beta$ -NA100 were prepared. Figures 3 and 4 showed the DSC crystallization behavior and melting characteristics of CC and Sup- $\beta$ -NA100-filled PPC, respectively, and the related data were listed in Table 2. It could be observed that the CC content had no influence on the crystallization and melting behavior of PPC. Three melting peaks could be seen from Fig. 3, two melting peaks for  $\beta$ -modification and one strong melting peak for  $\alpha$ -modification. The intensity of melting peak for  $\beta$ -modification at low temperature of PPC decreased with increasing the content of CC. The results suggested that addition of Sup- $\beta$ -NA100 increased the  $T_{cp}$  of PPC. 1 wt% Sup- $\beta$ -NA100-filled PPC crystallized at temperature of 121.2 °C. It was different from that of CC-filled PPC, the  $T_{cp}$  of PPC slightly increased with increasing the content of Sup- $\beta$ -NA100. For the melting characteristics of PPC filled by Sup- $\beta$ -NA100, the melting characteristics of 1 wt% Sup- $\beta$ -NA100-filled PPC was slightly different from that of 3 and 5 wt% Sup- $\beta$ -NA100-filled PPC. 1 wt% Sup- $\beta$ -NA100-filled PPC exhibited four melting peaks. The intensity of  $\alpha$ -modification melting peak at low temperature had the same as that of  $\alpha$ -modification at high temperature. However, three melting peaks were observed for 3 and 5 wt% Sup- $\beta$ -NA100-filled PPC, and the intensity of  $\alpha$ -modification melting peak at low temperature was lower than that of  $\alpha$ -modification at high temperature. The melting temperatures of  $\beta$ - and  $\alpha$ -modification at low temperature slightly increased with increasing the content of Sup- $\beta$ -NA100 due to the high  $T_{cp}$ .

Figure 5 shows X-ray diffraction diagrams of CC and Sup- $\beta$ -NA100 CC-filled PPC. The  $K$  values were listed in



**Fig. 3** DSC crystallization (a) and melting (b) curves of CC-filled PPC



**Fig. 4** DSC crystallization (a) and melting (b) curves of Sup- $\beta$ -NA100 CC-filled PPC

Table 2. It could be observed that the increased content of CC slightly decreased the  $K$  value of PPC filled by CC. For PPC filled by Sup- $\beta$ -NA100, the content of  $\beta$ -modification was holding above 0.94 and the  $K$  value increased slightly with increasing the content of Sup- $\beta$ -NA100. The above results suggested that CC possessed  $\alpha$ -nucleating ability for PPC crystallization and the  $\beta$ -nucleating ability decreased with increasing the content of CC. Nevertheless, Sup- $\beta$ -NA100 possessed high efficient  $\beta$ -nucleation and the  $\beta$ -nucleating ability increased with increasing the content of Sup- $\beta$ -NA100.

Effect of mass ratio of CC/PA in prepared Sup- $\beta$ -NA on  $\beta$ -nucleation of PPC

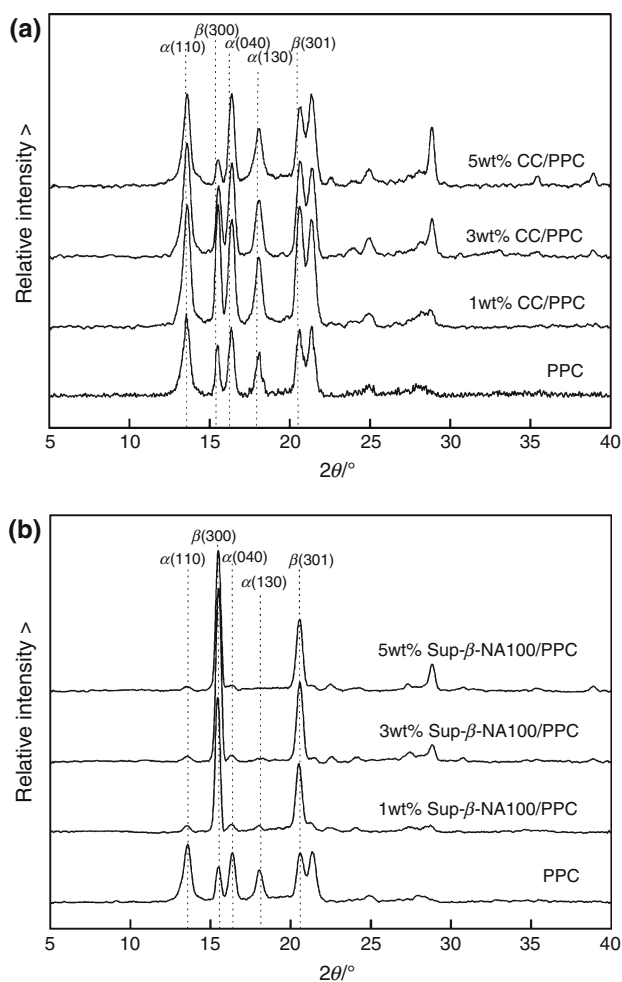
Because the Sup- $\beta$ -NA was prepared by CC supported different content of PA, Sup- $\beta$ -NA $_x$  prepared by different mass ratio ( $x$ ) of CC/PA contained different content of CaPA  $\beta$ -nucleating agent. In order to investigate the effect

**Table 2** Data of CC-filled PPC and Sup- $\beta$ -NA-filled PPC

Samples	$T_c/^\circ\text{C}$	$\Delta H_c/\text{J g}^{-1}$	$T_m^\beta/^\circ\text{C}$	$T_m^{21}/^\circ\text{C}$	$T_m^{22}/^\circ\text{C}$	$K_\beta$
Neat PPC	118.2	82.3	148.7	164.7	–	0.16
1 wt% CC/PPC	118.2	81.7	149.9	165.0	–	0.25
3 wt% CC/PPC	117.9	79.3	149.5	164.7	–	0.18
5 wt% CC/PPC	118.5	77.7	149.4	163.8	–	0.05
1 wt% Sup- $\beta$ -NA100/PPC	121.1	74.3	150.7	164.0	170.5	0.94
3 wt% Sup- $\beta$ -NA100/PPC	122.0	75.6	151.7	164.7	170.4	0.98
5 wt% Sup- $\beta$ -NA100/PPC	122.9	73.2	153.2	165.6	171.0	0.99

of mass ratio of CC/PA on  $\beta$ -nucleation of Sup- $\beta$ -NA, PPC filled by Sup- $\beta$ -NA containing different mass ratio of CC/PA was prepared and the  $\beta$ -nucleation of Sup- $\beta$ -NA was studied. Figure 6 showed the DSC crystallization and



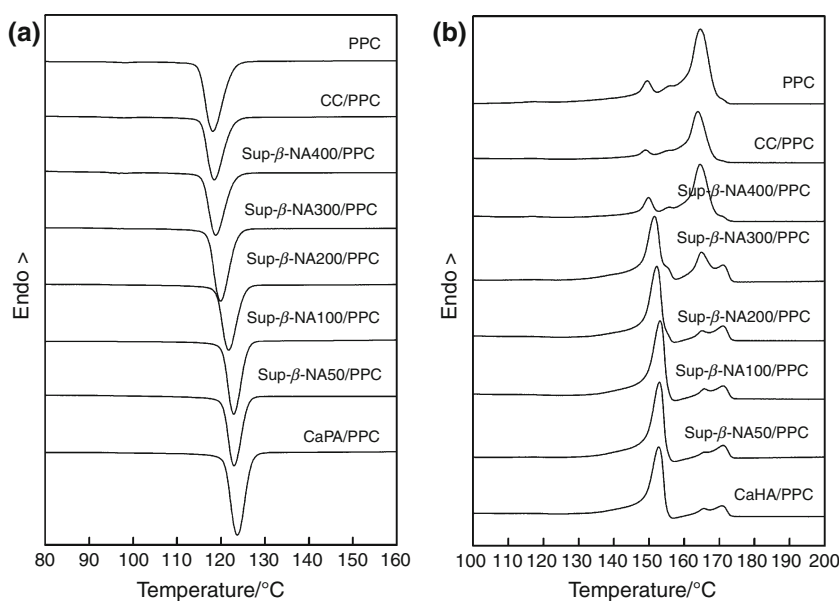


**Fig. 5** X-ray diffraction diagrams of CC-filled PPC (a) and Sup- $\beta$ -NA-filled PPC (b)

melting curves of PPC filled by Sup- $\beta$ -NA prepared with different mass ratio of CC/PA and the relative data was listed in Table 3. It could be seen that the  $T_{cp}$  of Sup- $\beta$ -NA-filled PPC decreased with increasing the mass ratio of CC/PA. The  $T_{cp}$  of PPC filled by Sup- $\beta$ -NA50 increased to 123.0 °C, as same as that of PPC nucleated by CaPA. However, the  $T_{cp}$  of PPC filled by Sup- $\beta$ -NA400 decreased to 118.8 °C, nearing to those of PPC and CC-filled PPC.

The melting behavior of PPC and  $\beta$ -nucleation of Sup- $\beta$ -NA for PPC crystallization depended on the mass ratio of CC/PA in the preparation of Sup- $\beta$ -NA. The melting behavior and  $\beta$ -nucleation of PPC filled by Sup- $\beta$ -NA50 was similar to that of PPC nucleated by CaPA. However, the intensity of  $\alpha_1$ -modification melting peak of PPC filled by Sup- $\beta$ -NA50 was lower than that of PPC nucleated by CaPA. As the mass ratio of CC/PA was increased to 100, the melting behavior and  $\beta$ -nucleation of PPC filled by Sup- $\beta$ -NA100 was same as that of PPC nucleated by CaPA. The intensity of  $\alpha$ -modification melting peak at low temperature was lower than that of  $\alpha$ -modification at high temperature. As the mass ratio of CC/PA was higher than 100, the increased intensity of  $\alpha$ -modification at low temperature and the decreased intensity of  $\beta$ -modification melting peak at low temperature of Sup- $\beta$ -NA-filled PPC were observed with increasing the mass ratio of CC/PA. PPC filled by Sup- $\beta$ -NA300 showed a strong melting peak around 150 °C and a double melting peaks around 165 °C, in which the intensity of  $\alpha$ -modification melting peak at low temperature was higher than that of  $\alpha$ -modification at high temperature. The melting behavior of PPC filled by Sup- $\beta$ -NA400 was similar to that of PPC, showed a strong melting peak around 164 °C and a weak melting peak around 150 °C.

**Fig. 6** Crystallization (a) and melting (b) curves of PPC filled by Sup- $\beta$ -NA $x$



**Table 3** Data of PPC filled by Sup- $\beta$ -NA $x$ 

Samples	$T_c/^\circ\text{C}$	$\Delta H_c/\text{J g}^{-1}$	$T_m^\beta/^\circ\text{C}$	$T_m^{\alpha_1}/^\circ\text{C}$	$T_m^{\alpha_2}/^\circ\text{C}$	$K_\beta$
PPC	118.2	82.3	148.7	164.7	–	0.16
CaPA/PPC	123.7	76.5	152.8	165.6	170.8	0.94
CC/PPC	118.5	77.7	149.4	163.8	–	0.05
Sup- $\beta$ -NA400/PPC	118.8	78.1	149.8	164.5	–	0.21
Sup- $\beta$ -NA300/PPC	119.9	74.3	151.6	165.0	171.2	0.93
Sup- $\beta$ -NA200/PPC	121.7	74.1	152.2	165.1	171.0	0.91
Sup- $\beta$ -NA100/PPC	122.9	73.2	153.2	165.7	171.0	0.99
Sup- $\beta$ -NA50/PPC	123.0	74.3	153.0	166.9	171.0	0.99

The content of CC and Sup- $\beta$ -NA in PPC is 5 wt% and CaPA is 0.1 wt%

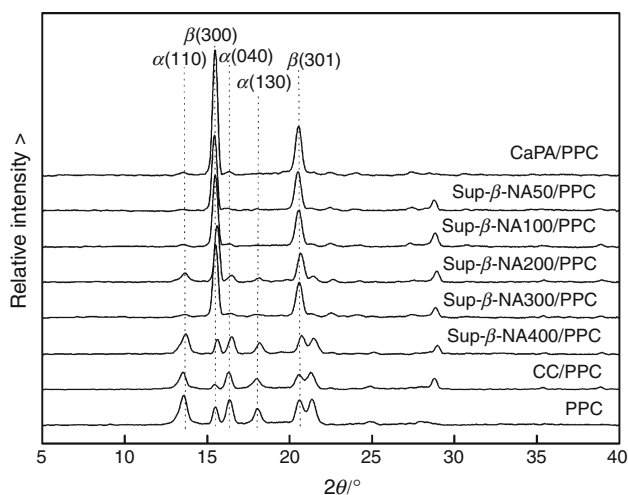
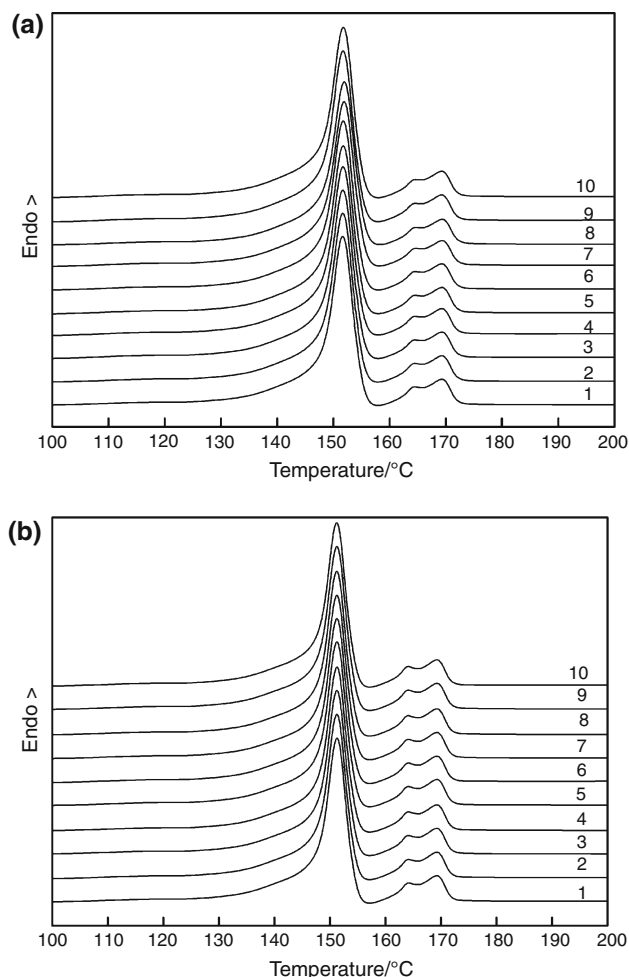
**Fig. 7** X-ray diffraction diagrams of PPC filled by Sup- $\beta$ -NA $x$ 

Figure 7 showed X-ray diffraction diagrams of PPC filled by Sup- $\beta$ -NA $x$  and the  $K$  values of  $\beta$ -modification were listed in Table 3. It could be seen that the  $K$  values were above 0.90 for PPC filled by Sup- $\beta$ -NA $x$  with the mass ratios of CC/PA between 50 and 300. When the mass ratios of CC/PA was higher than 300, the  $K$  values significantly decreased. The above results indicated that the  $K$  values of  $\beta$ -modification and  $\beta$ -nucleation depended on the mass ratio of CC/PA in preparation of Sup- $\beta$ -NA. The mass ratio of CC/PA between 200 and 300 was critical value for preparation of Sup- $\beta$ -NA with the high  $\beta$ -nucleation and low cost.

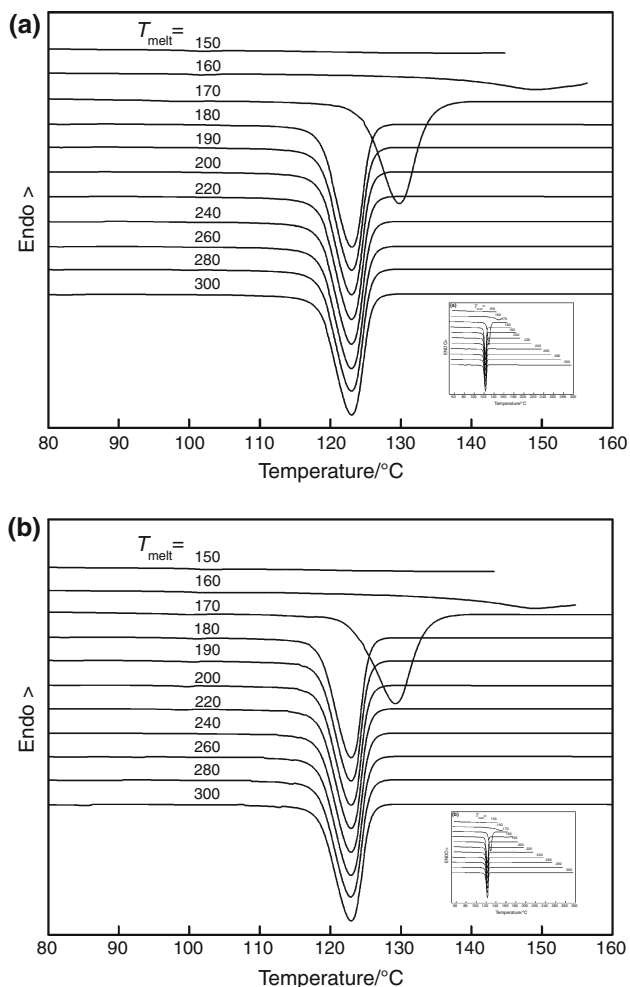
#### The thermal stability of supported $\beta$ nucleating system

Figure 8 presented the DSC melting curves of PPC nucleated by CaPA and PPC filled by Sup- $\beta$ -NA100 during

**Fig. 8** DSC multiple melting curves of CaPA-nucleated PPC (a) and Sup- $\beta$ -NA100-filled PPC (b)

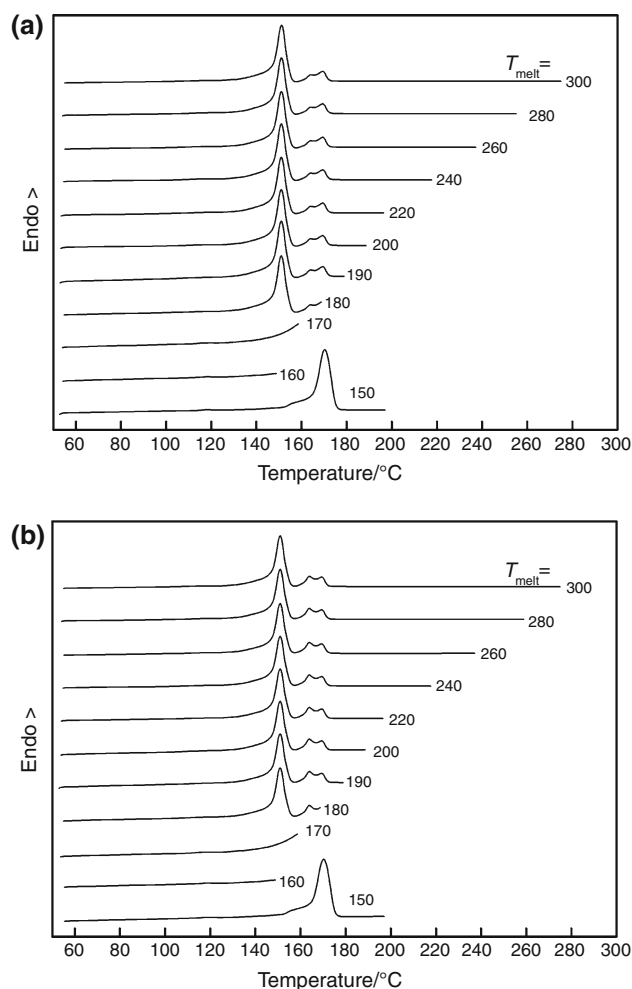
multiple heating and cooling scanning. It could be observed that the DSC melting curves were almost overlapping together. The results suggested that Sup- $\beta$ -NA with high thermal stability of  $\beta$ -nucleation. It could induce the formation of  $\beta$ -modification during multiple heating and cooling scanning, which was benefit for preparation of  $\beta$ -PPC from recycling of PPC filled by Sup- $\beta$ -NA.

Figures 9 and 10 showed the DSC crystallization and melting curves of CaPA-nucleated PPC and Sup- $\beta$ -NA100-filled PPC under multiple scans with different final temperature of the melt ( $T_{\text{melt}}$ ). The PPC was heated to  $T_{\text{melt}}$  (300  $^\circ\text{C}$ ) and held there for 5 min. After melting, the samples were cooled to 50  $^\circ\text{C}$  at the cooling rate of 10  $^\circ\text{C min}^{-1}$  for investigation of the crystallization behavior, and then subsequently reheated to the next lower  $T_{\text{melt}}$  (280  $^\circ\text{C}$ ) at the heating rate of 10  $^\circ\text{C min}^{-1}$  investigation of the melting behavior and the determination of the polymorphic composition. The  $T_{\text{melt}}$  was decreased to 150  $^\circ\text{C}$  in repeating scanning. It could be observed that the  $T_{\text{melt}}$



**Fig. 9** Crystallization curves of CaPA-nucleated PPC (a) and Sup- $\beta$ -NA100-filled PPC (b) with different melting temperatures

between 180 and 300 °C had no influence on crystallization behavior and melting characteristics of CaPA-nucleated PPC and Sup- $\beta$ -NA100-filled PPC. The melting curves showed a strong melting peak of  $\beta$ -modification and two weak melting peaks of  $\alpha_1$ - and  $\alpha_2$ -modification, respectively. It indicated that CaPA and Sup- $\beta$ -NA100 possesses high effective  $\beta$ -nucleation for PPC crystallization with the  $T_{melt}$  higher than 180 °C. When the  $T_{melt}$  was decreased to 170 °C, the  $T_{cp}$  of CaPA-nucleated PPC and Sup- $\beta$ -NA100-filled PPC markedly increased, but the enthalpy of the crystallization decreased. However, no integrated melting peak could be seen for CaPA-nucleated PPC and Sup- $\beta$ -NA100-filled PPC crystallized from the melting temperature of 170 °C. Because the melting peak of  $\beta$ -modification was lower than 160 °C, the results indicated that no  $\beta$ -modification formed in the nucleated PPC and Sup- $\beta$ -NA100-filled PPC when the  $T_{melt}$  decreased to 170 °C. It was suggested that PPC had not melted completely at



**Fig. 10** Melting curves of CaPA-nucleated PPC (a) and Sup- $\beta$ -NA100-filled PPC (b) with different melting temperatures

170 °C for 5 min. The non-melted crystal acted as  $\alpha$ -crystal nucleus for PPC crystallization, resulted in the formation of  $\alpha$ -modification during the cooling progress. It was indicated that the  $\alpha$ -nucleated ability of non-melted crystal was higher than the  $\beta$ -nucleation of CaPA and Sup- $\beta$ -NA. When the  $T_{melt}$  decreased to 160 °C, the  $T_{cp}$  of PPC continued to increase. Meanwhile, there was no melting peak could be seen. When the  $T_{melt}$  was decreased to 150 °C, it showed no crystallization peak and only  $\alpha$ -melting peak of CaPA-nucleated PPC and Sup- $\beta$ -NA100-filled PPC during heating process. The above observations were in good agreements with the conclusion of Varga et al. [38]. All the results above indicated that the  $T_{melt}$  between 300 and 180 °C had no influence on the  $\beta$ -nucleating efficiency of CaPA-nucleated PPC and Sup- $\beta$ -NA100-filled PPC. Sup- $\beta$ -NA with high  $\beta$ -nucleated efficiency and thermal stability could be used to prepare  $\beta$ -PP alloy with engineering plastic and  $\beta$ -PP composites in a wide range of temperatures.



## Conclusions

Addition of nano-CaCO<sub>3</sub> supported CaPA  $\beta$ -nucleating agent (Sup- $\beta$ -NA) into PPCs PPC was an effective method for preparation of filled PPC with high  $\beta$ -modification content. The CC possessed weak  $\beta$ -nucleating ability for PPC crystallization and the  $\beta$ -modification content in CC-filled PPC decreased with increasing the content of CC. The addition of Sup- $\beta$ -NA prepared through chemical reaction between CC and PA coated on the surface of CC increased the  $T_{cp}$  of PPC. The Sup- $\beta$ -NA had more effective  $\beta$ -nucleation than CaPA  $\beta$ -nucleating agent for PPC crystallization and the content  $\beta$ -modification of PPC increased with increasing the content of Sup- $\beta$ -NA. The  $\beta$ -modification content and  $\beta$ -nucleation of PPC increased with decrease in the CC/PA mass ratio in preparation of Sup- $\beta$ -NA. The CC/PA mass ratio between 200 and 300 was critical value for preparation of Sup- $\beta$ -NA with the high  $\beta$ -nucleation and low cost. CC supported  $\beta$ -nucleating agent resulted in the nucleation mechanism of CC changed from  $\alpha$ -nucleation to  $\beta$ -nucleation. The  $\beta$ -nucleating agent used had high thermal stability and had little been influenced by multiple heating and cooling cycles and by end temperature of the melt.

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## References

- Nurdina AK, Mariatti M, Samayamutthirian P. Effect of filler surface treatment on mechanical properties and thermal properties of single and hybrid filler-filled PP composites. *J Appl Polym Sci.* 2011;120(2):857–65.
- Ghugare SV, Govindaiah P, Avadhani CV. Polypropylene–organoclay nanocomposites containing nucleating agents. *Polym Bull.* 2009;63(6):897–909.
- Preschilla N, Sivalingham G, Abdul Rasheed AS, Tyagi S, Biswas A, Bellare JR. Quantification of organoclay dispersion and lamellar morphology in poly(propylene)-clay nanocomposites with small angle X-ray scattering. *Polymer.* 2008;49(19):4285–97.
- Huang H, Han B, Wang L, Miao N, Mo H, Zhou N, Ma Z, Zhang J, Shen J. Crystallization kinetics of polypropylene composites filled with nano calcium carbonate modified with maleic anhydride. *J Appl Polym Sci.* 2011;119(3):1516–27.
- Xu Y, Yang W, Xie B, Liu Z, Yang M. Effect of injection parameters and addition of nanoscale materials on the shrinkage of polypropylene copolymer. *J Macromol Sci B.* 2009;48(3):573–86.
- Wang Y, Gao Y, Shi J. Hierarchy crystallization structure of a polypropylene random copolymer injection-molded bar induced by a nucleating agent. *J Appl Polym Sci.* 2008;107(1):309–18.
- Varga J, Menyhárd A. Effect of solubility and nucleating duality of *N,N'*-dicyclohexyl-2,6-naphthalene-dicarboxamide on the supermolecular structure of isotactic polypropylene. *Macromolecules.* 2007;40(7):2422–31.
- Tu Z, Mai K, Wu Z. Study of nucleation activity and application of a nucleating agent to copolypropylene. *J Appl Polym Sci.* 2006;101(6):3915–9.
- Libster D, Aserin A, Garti N. A novel dispersion method comprising a nucleating agent solubilized in a microemulsion, in polymeric matrix. I. Dispersion method and polymer characterization. *J Colloid Interface Sci.* 2006;299(1):172–81.
- Zhang Y, Li X, Wei X. Non-isothermal crystallization kinetics of isotactic polypropylene nucleated with 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol. *J Therm Anal Calorim.* 2010;100(2):661–5.
- Zhang G, Xin Z, Yu J, Gui Q, Wang S. Nucleating efficiency of organic phosphates in polypropylene. *J Macromol Sci B.* 2003;42B(3–4):467–78.
- Nogales A, Mitchell GR, Vaughan AS. Anisotropic crystallization in polypropylene induced by deformation of a nucleating agent network. *Macromolecules.* 2003;36(13):4898–906.
- Ou C. The crystallization characteristics of polypropylene and low ethylene content polypropylene copolymer with copolyesters. *Eur Polym J.* 2002;38(3):467–73.
- Zhu W, Zhang G, Yu J, Dai G. Crystallization behavior and mechanical properties of polypropylene copolymer by in situ copolymerization with a nucleating agent and/or nano-calcium carbonate. *J Appl Polym Sci.* 2004;91(1):431–8.
- Zhang R, Zheng H, Lou X, Ma D. Crystallization characteristics of polypropylene and low ethylene content polypropylene copolymer with and without nucleating agents. *J Appl Polym Sci.* 1994;51(1):51–6.
- Varga J, Schulek-Tóth F. Crystallization, melting and spherulitic structure of a  $\beta$ -nucleated polypropylene random copolymer. *J Thermal Anal Calorim.* 1996;47(4):941–55.
- Juhász P, Varga J, Belina K, Belina G. Efficiency of  $\beta$ -nucleating agents in propylene/alpha-olefin copolymers. *J Macromol Sci B.* 2002;41(4–6):1173–89.
- Varga J, Mudra I, Ehrenstein GW. Highly active thermally stable  $\beta$ -nucleating agents for isotactic polypropylene. *J Appl Polym Sci.* 1999;74(10):2357–68.
- Varga J, Mudra I, Ehrenstein GW. Crystallization and melting of  $\beta$ -nucleated isotactic polypropylene. *J Therm Anal Calorim.* 1999;56(3):1047–57.
- Hao W, He Y, Luo X, Ma D. Crystallization characteristics of  $\beta$ -phase crystals in copolymers of polypropylene with low ethylene content. *Chin J Polym Sci.* 2001;19(3):317–22.
- Na B, Lv R, Xu W, Chen R, Zhao Z, Yi Y. Effect of nucleating duality on the formation of  $\gamma$ -phase in a  $\beta$ -nucleated isotactic polypropylene copolymer. *Polym Int.* 2008;57(10):1128–33.
- Izer A, Bárány T, Varga J. Development of woven fabric reinforced all-polypropylene composites with beta nucleated homo- and copolymer matrices. *Compos Sci Technol.* 2009;69(13):2185–92.
- Varga J. Modification of polypropylene and its two-component systems. *J Thermal Anal.* 1989;35(6):1891–912.
- Varga J, Schulek Tóth F. Filled compounds of the  $\beta$ -modification of polypropylene. *Angew Makromol Chem.* 1991;188(1):11–25.
- Zhang X, Xie F, Pen Z, Zhang Y, Zhang Y, Zhou W. Effect of nucleating agent on the structure and properties of polypropylene/poly(ethylene-octene) blends. *Eur Polym J.* 2002;38(1):1–6.
- Menyhárd A, Varga J, Liber A, Belina G. Polymer blends based on the  $\beta$ -modification of polypropylene. *Eur Polym J.* 2005;41(4):669–77.
- Yang Z, Zhang Z, Tao Y, Mai K. Preparation, crystallization behavior and melting characteristic of  $\beta$ -nucleated isotactic polypropylene blends with polyamide 6. *J Appl Polym Sci.* 2009;112(1):1–8.

28. Yang Z, Zhang Z, Tao Y, Mai K. Effects of polyamide 6 on the crystallization behavior and melting characteristic of  $\beta$ -nucleated polypropylene. *Eur Polym J.* 2008;44(11):3754–63.
29. Cao Y, Feng J, Wu P. Simultaneously improving the toughness, flexural modulus and thermal performance of isotactic polypropylene by  $\alpha$ - $\beta$  crystalline transition and inorganic whisker reinforcement. *Polym Eng Sci.* 2010;50(2):222–31.
30. Kotek J, Kelnar I, Baldrian J, Raab M. Tensile behaviour of isotactic polypropylene modified by specific nucleation and active fillers. *Eur Polym J.* 2004;40:679–84.
31. Labour T, Gauthier C, Séguéla R, Vigier G, Bomal Y, Orange G. Influence of the  $\beta$  crystalline phase on the mechanical properties of unfilled and  $\text{CaCO}_3$ -filled polypropylene. I. Structural and mechanical characterisation. *Polymer.* 2001;42:7127–35.
32. Grein C. Toughness of neat, rubber modified and filled  $\beta$ -nucleated polypropylene: from fundamentals to applications. *Adv Polym Sci.* 2005;188:1104–43.
33. Zhang Z, Chen C, Wang C, Guo J, Mai K. Nonisothermal crystallization kinetics of isotactic polypropylene nucleated with a novel supported  $\beta$ -nucleating agent. *J Therm Anal Calorim.* 2011;130(1):311–8.
34. Zhang Z, Chen C, Wang C, Zhang J, Mai K. A novel highly efficient  $\beta$ -nucleating agent for polypropylene using nano- $\text{CaCO}_3$  as support. *Polym Int.* 2010;59:1199–204.
35. Zhang Z, Wang C, Yang Z, Mai K. Crystallization behaviors and melting characteristics of PP nucleated by a novel supported  $\beta$ -nucleating agent. *Polymer.* 2008;49:5137–45.
36. Zhang Z, Tao Y, Yang Z, Mai K. Preparation and characteristics of nano- $\text{CaCO}_3$  supported  $\beta$ -nucleating agent of polypropylene. *Eur Polym J.* 2008;44:1955–61.
37. Turner-Jones A, Aizlewood J, Beckett D. Crystalline forms of isotactic polypropylene. *Makromol Chem.* 1964;75(1):134–58.
38. Varga J, Garzó G, Ille A. Effect of fusion conditions of  $\beta$ -polypropylene on the new crystallization. *Colloid Polym Sci.* 1991;269(7):655–64.