Preparation and Investigation of the β-Nucleated Polypropylene/Polystyrene Blends

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ABSTRACT: In this work, β-polypropylene/polystyrene (β-PP/PS) blends were prepared with PP, PS, and a novel supported β-nucleating agent or β-nucleated PP and PS. The β-PP/PS blends were compatabilized by PP-g-MA, PP-g-GMA, POE-g-MA, and EVA-g-MA, respectively. For exploring the effect of PS amount and compatibilizers on the β-nucleation of PP, crystallization behavior and melting characteristics, the β-crystal content and crystal morphology of β-PP are characterized by differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD), and polarized light microscopy (POM). The results indicated that the PP with high content of β-crystal was obtained by addition of $CaCO_3$ supported β-nucleating agent (β-NA) into PP. The β-nucleation, crystallization behavior, and melting characteristics, and the β-crystal content of β-PP in these blends were not influenced by addition of PS and its amount. However, the increased content of PS decreased the size of β-spherulites of PP in these blends. The β-nucleation of PP in compatabilized blends slightly depended on the compatibilizers. β-PP/PS blends with high β-crystal content can easily be prepared. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Polypropylene (PP) blends with styrene polymers or copolymers attract much attention. To increase the rigidity of PP and improve toughness and solvent resistance of polystyrene (PS), the physical and mechanical properties,[1–7] morphologies[8–10] of PP/PS blends, compatibilized blends,[11–14] and filled blends[15–20] have been widely studied.

However, α-PP was generally formed in the PP blends. Although it was found that PS, as a special β-nucleating agent, could induce the formation of β-PP during PP crystallization,[2,3] the content of β-PP was very low in these blends. It was well known that β-PP possessed higher toughness and heat distortion temperature than those of α-PP.[21–27] If β-PP blends with other polymers could be prepared, they could be obtained with higher toughness and heat distortion temperature. Recently, the preparation of β-PP blends with other crystalline polymers by addition of β-nucleating agents and the effect of the second component on the β-nucleation of PP in these blends have been

reported.[21–40] It was found that addition of other crystalline polymers give different effects on the β-nucleation of PP in these blends. The β-nucleation of PP in these blends depended on the preparation methods and the crystallization temperature and α-nucleation of other crystalline polymers. If the crystallization temperature of other crystalline polymers was lower than that of PP or the α-nucleation of the second component was weak, the second component would not affect the β-nucleation of PP in these blends, e.g., LDPE.[24,25] On the contrary, if the crystallization temperature of other crystalline polymers was higher than that of PP, the α-nucleation of the second component could markedly decrease the β-nucleation of PP in these blends, and it was difficult to prepare β-PP blends with high content of β-crystal. However, PP blends with high content of β-crystal were obtained in compatibilized PP blends with polyamide 6, polyamide 66, and poly (ethylene terephthalate).[22–23,34–39]

Although β-PP blends with other crystalline and amorphous polymers have been investigated, there was no report on the β-PP blends with PS. In this work, β-PP blends with PS were

prepared by a novel CaCO$_3$ supported β-nucleating agent.[41–44] The influence of PS content, preparation methods, and different compatibilizers on β-nucleation, crystallization, and melting behavior, and β-crystal content of PP in these blends were investigated by differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WAXD). If β-PP blends with high β-crystal content could be obtained, it would provide an effective method for preparation of β-PP/PS blends with high toughness.

EXPERIMENTAL

Materials

A commercial grade of isotactic PP (N-T30S) used in the study was supplied by Sinopec Group, Maoming petroleum Chemical Industry Limited Company, China, and the MFI of PP was 3.2 g/10 min. PS (PG-33) was purchased from Chi Mei Industrial Factory, Taiwan, and the MFI of PS was 7.5–18.0 g/min. A CaCO$_3$ supported β-nucleating agent (β-NA) was prepared by mass ratio of nano-calcium carbonate/pimelic acid (100/1) in our laboratory.[41–44] Four kinds of compatibilizers, maleic anhydride-grafted PP (PP-g-MA), glycidyl methacrylate-grafted PP (PP-g-GMA), maleic anhydride-grafted ethylene-1-octene copolymer (POE-g-MA), and maleic anhydride-grafted ethylene-vinyl acetate copolymer (EVA-g-MA) were commercial products and supplied by Guangzhou Lushan Chemical Materials Co., China.

Specimen Preparation

Before blending, all the materials were adequately dried in a vacuum oven at appropriate temperatures for 12 h. β-PP/PS blends were prepared by two different methods. In Method one, all the components, PP, β-NA, and PS, were simultaneously added and mixed in an HL-200 internal mixer (Jinlin University Science and Education Instrument Factory, China) at temperature of 240°C, and 50 rpm for 5 min. The composition and the mark of β-PP/PS blends were listed in Table I. In Method two, β-PP was firstly prepared by a twin-screw extruder at temperature of 190°C. The extrudates were cooled in a water bath and cut into pellets by a pelletizer. Then they were mixed with PS pellets in the HL-200 internal mixer to prepare β-PP/PS blends. The obtained β-PP/PS blends were marked as β-PP-X, where X noted the PS content in β-PP/PS blends.

Apparatus and Characterization Procedures

DSC measurements were made on a Perkin-Elmer DSC-7 DSC, the temperature calibrated with indium in nitrogen atmosphere. About 5 mg sample was weighted. It was heated to 240°C at heating rate of 100°C/min, held there for 5 min, and then cooled to 50°C at cooling rate of 10°C/min. The sample was reheating to 200°C at heating rate of 10°C/min for melting characteristics study. Here, it should be pointed out: β-PP has a theoretical upper (T ($βα$) =140–141°C) and a lower limit temperature (T ($βα$) =105°C),[45] so the values of fusion enthalpy of the β-phase are lower than the real values because of β to α recrystallization. Therefore, the melting curves of recooled and reheated samples are not suitable for quantitative evaluation, and the values of the enthalpy of fusion were not listed.

WAXD experiment was conducted with a Rigaku Geigerflex Model D/Max-IIIA rotating anode X-ray diffractometer.

Table I. The Composition of β-PP/PS Blends Prepared by Different Methods

Sample		PP/wt %	β-NA/ wt %	PS/wt %
Method one	Method two			
PP	PP	100.00	0	0
β-PP	β-PP	95.00	5.00	0
PP-5	β-PP-5	90.25	4.75	5.00
PP-10	β-PP-10	85.50	4.50	10.00
PP-20	β-PP-20	76.00	4.00	20.00
PP-30	β-PP-30	66.50	3.50	30.00
PP-40	β-PP-40	57.00	3.00	40.00

Graphite monochromatic Cu-Ka radiation was used as a radiation source. The scanning range was 5–30° with the rate of 4°/min and a step length of 0.02. To keep the thermal history as same as the DSC measurements, the samples used in WAXD measures have been prepared in DSC by heating up to 240°C and held there for 5 min, then cooled to 50°C at scanning rate 10°C/min. The k value representing the content of β-PP in these blends was calculated from X-ray diffractograms according to Turner-Jones relation.[46]:

$$k_\beta = \frac{H_{\beta(300)}}{H_{\alpha(110)} + H_{\alpha(040)} + H_{\alpha(130)} + H_{\beta(300)}}, \qquad (1)$$

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

The observation of crystal morphology for samples was performed using a Leitz Orthoplan Pol microscope equipped with a Linkam THMS-600 hot stage. The thermal history of samples for crystal morphology investigation was the same as that of WAXD samples.

RESULTS AND DISCUSSION

β-Nucleation of β-PP/PS Blends Prepared by Method One

Figure 1 shows DSC crystallization (a) and melting (b) thermograms of β-PP/PS blends prepared by Method one, the corresponding data were listed in Table II. It could be seen that incorporation of nano-calcium carbonate supported β-nucleating agent markedly increases the peak temperature of the crystallization (T_{cp}) of PP. Moreover, addition of PS has little influence on the T_{cp} of PP in β-PP/PS blends. From DSC melting curves, it could be observed that pure PP presents only one melting peak at temperature of 162.8°C, attributed to the melting of α-crystal. β-PP and β-PP/PS blends show three melting peaks. One strong melting peak at temperature of 150°C is due to the melting of β-crystal. Double weak melting peaks at temperature of 162°C and 168°C are corresponded to the fusion of $α_1$- and $α_2$-crystal, respectively. Varga et al. suggested that the low temperature α-peak corresponds to the melting of the α-form formed during the primary crystallization, but the high temperature peak reflects to melting of the α-crystals formed as
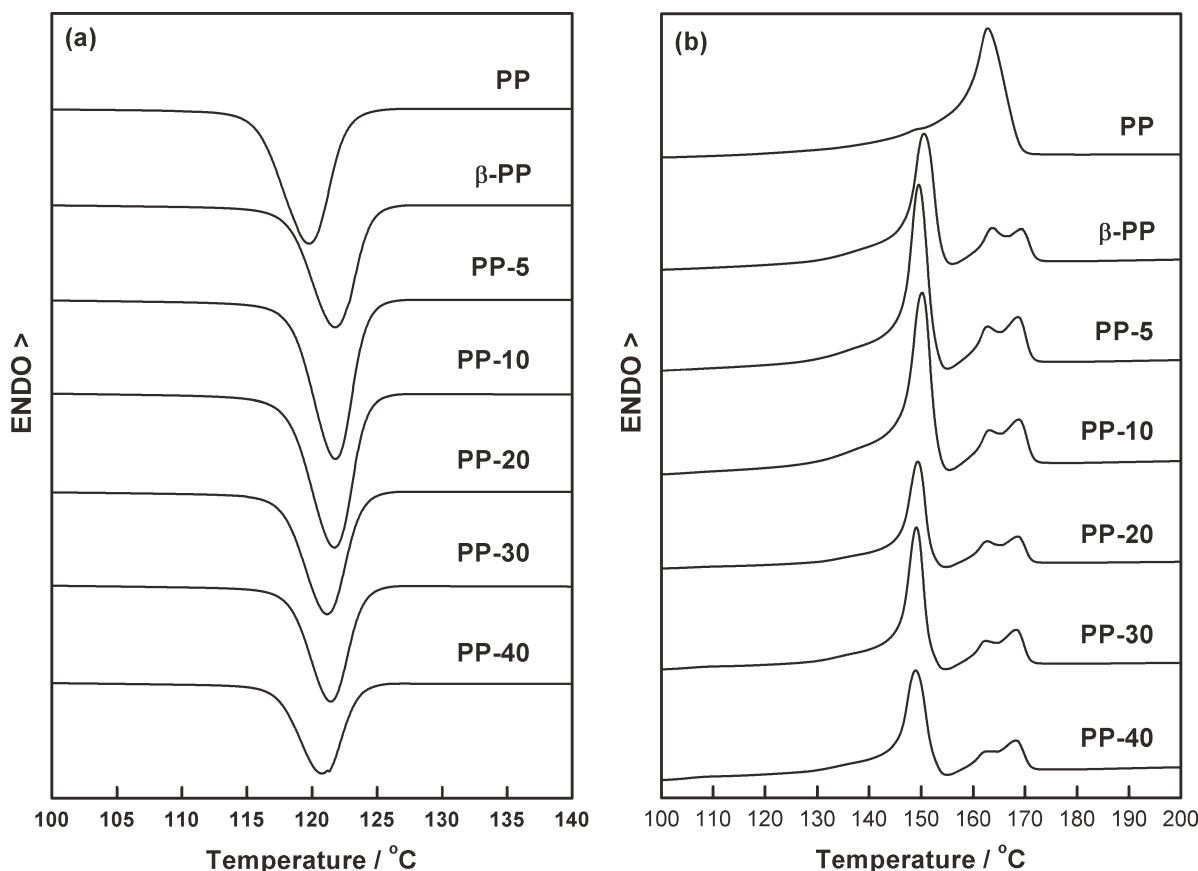
Figure 1. DSC crystallization (a) and melting (b) thermograms of β-PP/PS blends prepared by Method one.

a result of β to α recrystallization during the partial melting of the β-crystal.[21-27] Addition of PS slightly decreases the peak temperature of melting (T_{mp}) of β-crystal, α_1-crystal, and α_2-crystal of PP. However, the T_{mp} of PP has not been influenced with increasing the content of PS. Compared with β-PP, the intensity of α_1-crystal melting peak is lower than that of α_2-crystal for β-PP/PS blends, whereas the intensity of α_1-crystal melting peak is higher than that of α_2-crystal for β-PP. Furthermore, the content of PS had little effect on the relative intensity of α_1- and α_2-crystal melting peak of PP. The intensity of β-crystal melting peak in β-PP/PS blends is than that of α-crystal. It indicates that β-PP/PS blends prepared by Method one possesses strong β-nucleation and β-PP/PS blends with high β-crystal content can be easily obtained.

Figure 2 presents the X-ray diffraction diagrams of β-PP and β-PP/PS blends. It shows that β-PP and β-PP/PS blends mainly forms β-crystal, whereas PP only forms α-crystal. The β-crystal content (k_β) calculated from the eq. (1)[46] based on Figure 2, is listed in Table II. The results showed that the k value of the β-nucleated samples is of 0.99 in the case of PP filled by 5 wt % nano-calcium carbonate supported β-nucleating agent. Although the β-crystal content in β-PP/PS blends prepared by Method one is lower than that of β-PP, the k_β values are higher than 0.95. It is considered that the PS content has little influence on the β-crystal content in β-PP/PS blends. All the results above indicate that nano-calcium carbonate supported

β-nucleating agent prepared in our laboratory possesses high efficient β-nucleation for PP crystallization, induced PP to form almost pure β-PP. The addition of PS has little influence on the β-nucleation of β-PP, and β-PP/PS blends with the β-crystal content above 0.95 could be easily prepared by simultaneously mixing PP, β-nucleating agent, and PS.

β-Nucleation of β-PP/PS Blends Prepared by Method Two
Figure 3 presents DSC crystallization (a) and melting (b) thermograms of β-PP/PS blends prepared by Method two, the corresponding data were listed in Table III. It could be seen that the crystallization and melting behavior of β-PP/PS blends prepared by Method two is similar to those of β-PP/PS blends prepared by Method one. The melting thermograms of β-PP

Table II. DSC Data and β-Crystal Amount of β-PP/PS Blends Prepared by Method One

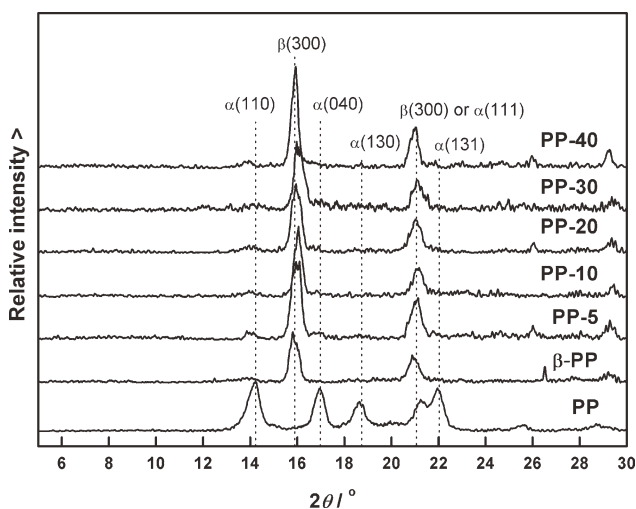| Sample	T_{cp} (°C)	T_{mp}^β (°C)	T_{mp}^α (°C)	k_β
PP	119.6	–	162.8	0
β-PP	121.8	150.6	163.8, 169.6	0.99
PP-5	121.8	149.6	162.5, 168.6	0.97
PP-10	121.7	150.2	162.8, 168.7	0.96
PP-20	121.2	149.4	162.4, 168.6	0.95
PP-30	121.4	149.1	162.0, 168.2	0.96
PP-40	120.8	149.0	162.1, 168.1	0.95

Figure 2. WAXD spectra of β-PP/PS blends prepared by Method one.

Table III. DSC Data and β-Crystal Amount of β-PP/PS Blends Prepared by Method Two

Sample	T_{cp} (°C)	T_{mp}^{β} (°C)	T_{mp}^{α} (°C)	k_{β}
PP	119.6	–	162.8	0
β-PP	121.8	150.6	163.8, 169.6	0.99
β-PP-5	121.6	149.5	162.5, 168.6	0.98
β-PP-10	121.1	149.0	162.4, 168.9	0.95
β-PP-20	120.3	149.6	163.1, 169.2	0.92
β-PP-30	120.6	148.3	161.8, 168.4	0.93
β-PP-40	120.2	148.2	161.6, 168.3	0.94

and β-PP/PS blends show a strong melting peak of β-crystal at around 150°C, and two weak melting peaks at about 162 and 168°C, corresponding to the fusion of β-, α₁- and α₂-crystal, respectively. Compared with β-PP/PS blends prepared by Method one, the intensity of α₁-crystal melting peak is higher than that of α₂-crystal for β-PP/PS blends prepared by Method two. The T_{cp} and T_{mp} of β-crystal and α-crystal slightly

decrease with increasing PS content. On the basis of eq. (1) and Figure 4, the β-crystal content is listed in Table III. Although the β-crystal content in β-PP/PS blends prepared by Method two is lower than that in Method one, the k_{β} values are higher than 0.90. The above results indicate that addition of PS has a little influence on the β-nucleation of PP in these blends prepared by Method two and PP in these blends mainly forms β-crystal. β-PP/PS blends with the β-crystal content above 90% could be obtained by mixing β-PP with PS.

β-Nucleation of Etched β-PP/PS Blends

To confirm the dispersion of β-nucleating agent, the blends were etched with sulfuric acid to remove PS phase. Figure 5 shows
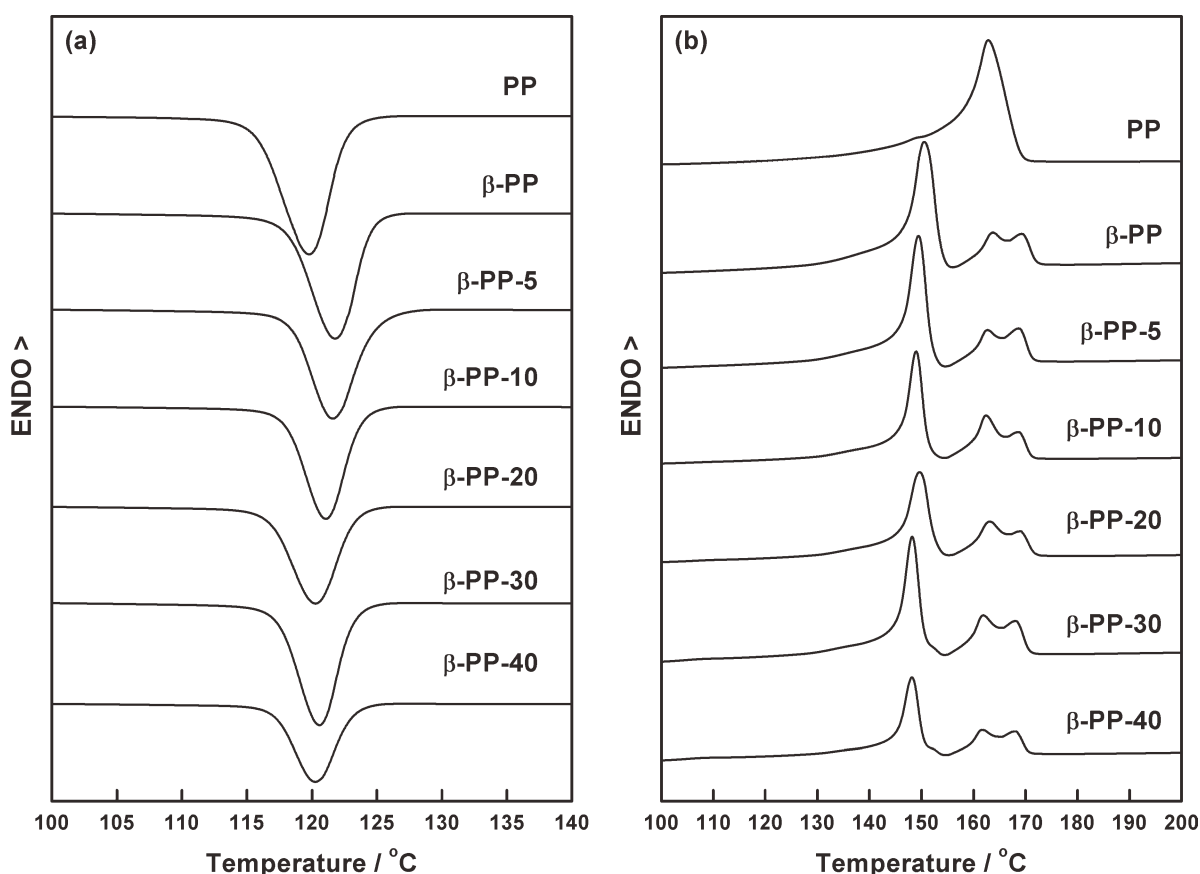

Figure 3. DSC crystallization (a) and melting (b) thermograms of β-PP/PS blends prepared by Method two.
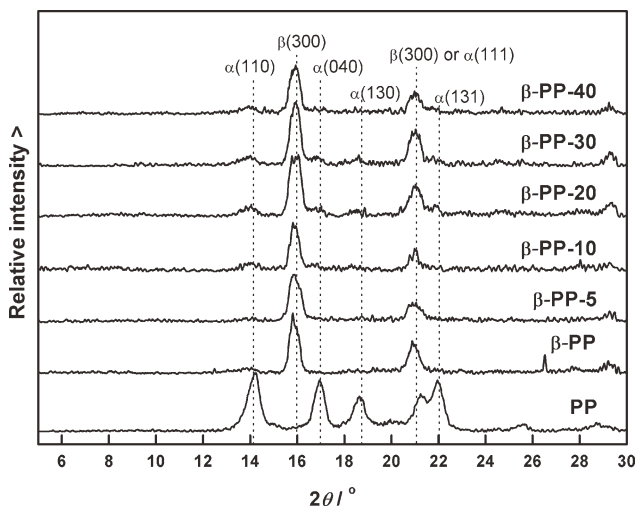
Figure 4. WAXD spectra of β-PP/PS blends prepared by Method two.

DSC crystallization (a) and melting (b) thermograms of β-PP/PS blends etched with sulfuric acid, the relative data were listed in Table IV. The β-PP/PS blends with 20 wt % PS (PP-20 and
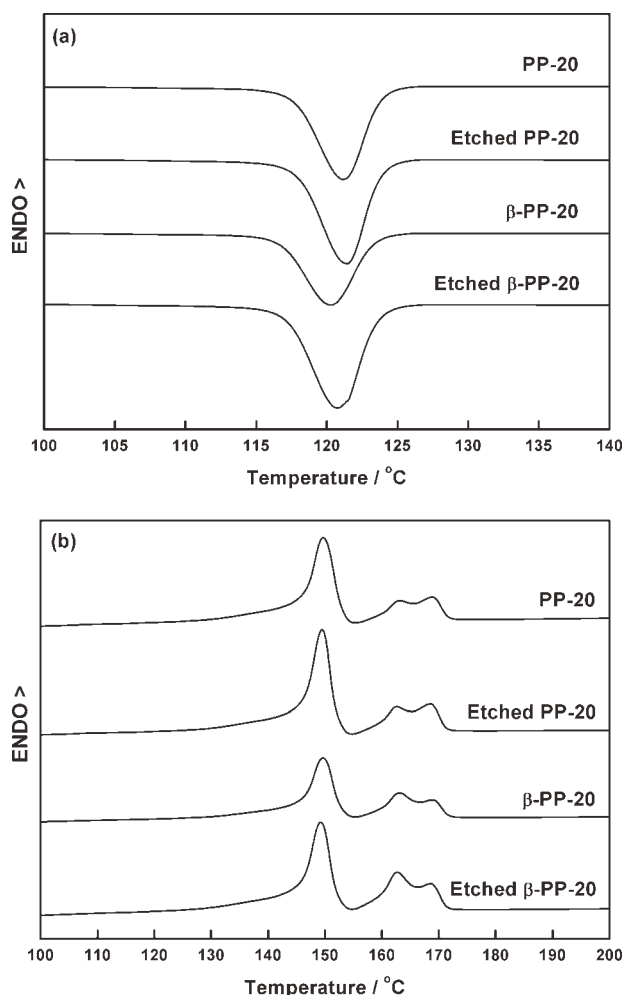

Figure 5. DSC crystallization (a) and melting (b) thermograms of β-PP/PS blends etched by sulfuric acid for 12 h.

Table IV. DSC Data and β-Crystal Amount of β-PP/PS Blends Etched by Sulfuric Acid for 12 h

Sample	T_{cp} (°C)	T_{mp}^{β} (°C)	T_{mp}^{α} (°C)	k_{β}
β-PP-20	120.3	149.6	163.1, 169.2	0.92
Etched β-PP-20	120.7	149.2	162.7, 168.9	0.89
PP-20	121.2	149.4	162.4, 168.6	0.95
Etched PP-20	120.7	149.2	162.7, 168.9	0.94

β-PP-20) were prepared by Methods one and two, respectively. It could be seen that the T_{cp}, T_{mp}, and the melting-peak intensity of β-PP/PS blends etched by sulfuric acid are similar to those of β-PP/PS blends with no treatment. The blends and etched blends present three melting peaks, and the melting-peak intensity of β-crystal in the blends is higher than that of α-crystal. It suggests that the blends mainly form β-crystal. The β-crystal content is calculated and listed in Table IV. By contrast with the blends without treatment, the β-crystal content of the etched blends decreases so small that sulfuric acid etching has little influence on the β-nucleation of β-PP/PS blends (Figure 6).

Crystal Morphology of β-PP/PS Blends
Figure 7 shows crystalline morphology of β-PP/PS blends. It could be observed that perfect β-spherulites are formed for PP filled by CaCO$_3$ supported β-nucleating agent. As the PS content below 10%, addition of PS has little influence on the β-spherulite morphology of PP. The PS phase disperses into β-spherulites of PP as small spherical particles. The size of dispersed PS phase enlarges with increasing the PS content. For β-PP blend containing 40% PS, the PS phase forms a larger irregular morphology dispersed in the PP matrix. The dispersed PS phase in β-PP matrix regards the growth of β-spherulites, resulting in the formation of small β-spherulites of PP in these blends.

Effect of Compatibilizers on β-Nucleation of β-PP/PS Blends
The compatibilizers, which have reactive anydride or epoxide groups, are generally used to improve dispersion of inorganic
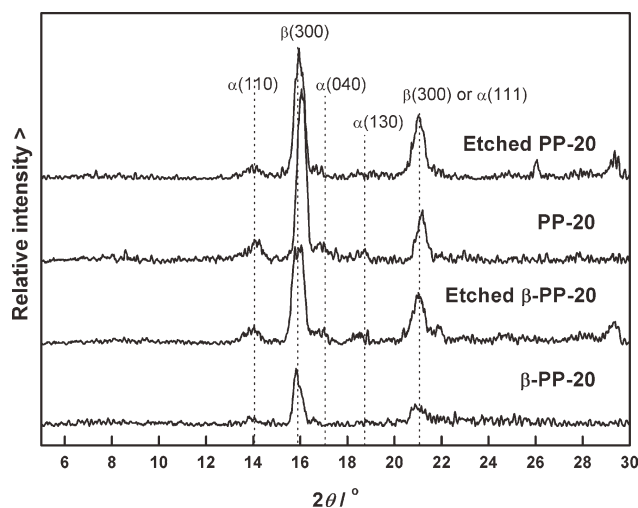

Figure 6. WAXD spectra of β-nucleated PP/PS etched by sulfuric acid for 12 h.
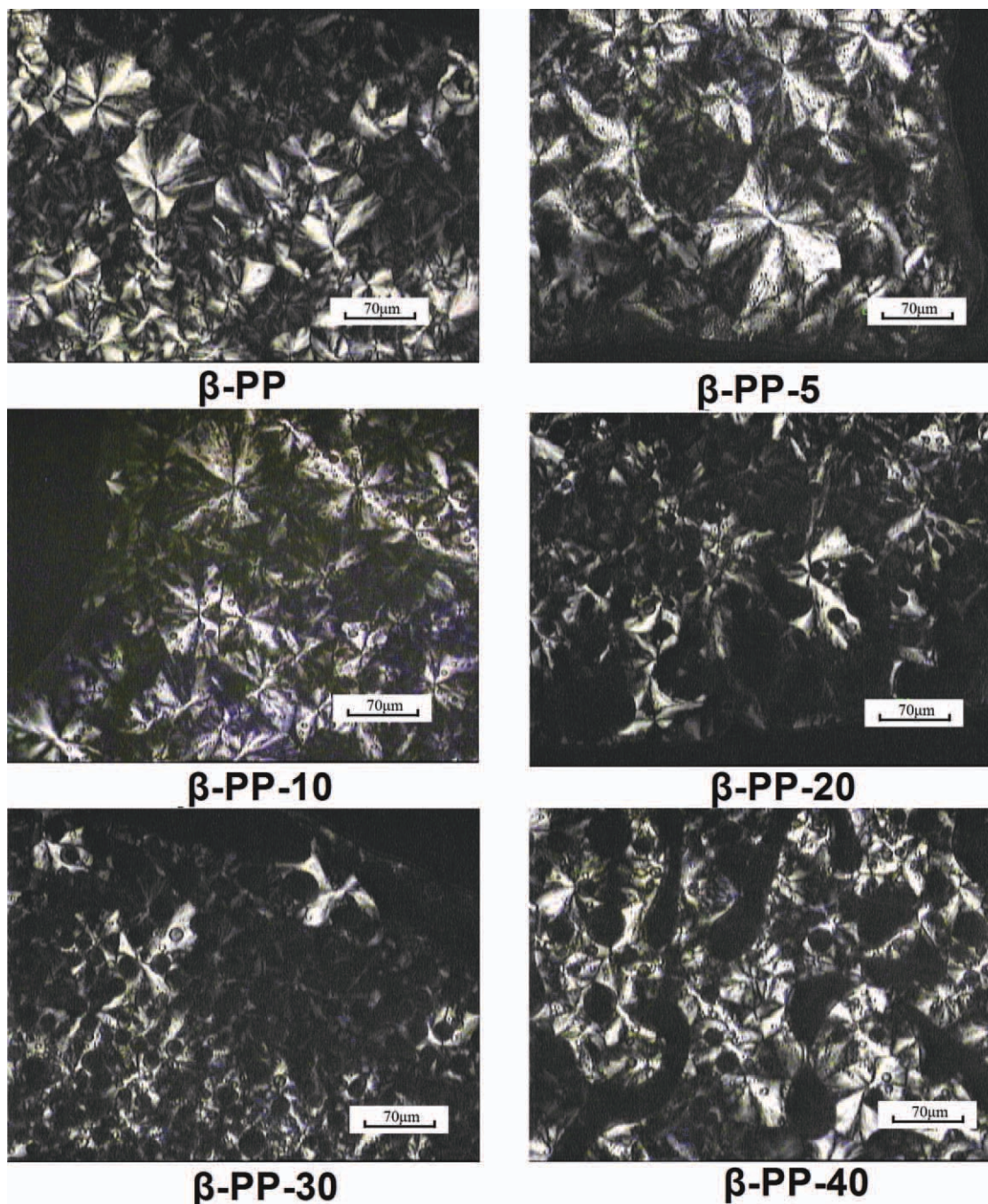
Figure 7. Polarized light microscopy (POM) of β-PP/PS blends prepared by Method two. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dispersed materials in the filled PP composites. To study the effect of compatibilizers and its reaction with the $CaCO_3$ supported β-nucleating agent on the β-nucleation, the compatibilize blends were prepared. Figure 8 shows DSC crystallization (a) and melting (b) thermograms of β-PP-20 and its compatibilized versions, the corresponding data were listed in Table V. It could be observed that the addition of PP-g-MA, PP-g-GMA, and POE-g-MA at the content of 8 phr slightly increases the T_{cp} of PP but has no influence on the crystallization behavior of PP.

However, the addition of EVA-g-MA decreases the T_{cp} of β-PP. The compatibilized PP/PS blends exhibit different melting characteristics. The PP/PS blends compatibilized by PP-g-MA, PP-g-GMA, and POE-g-MA present a strong melting peak of β-crystal at 149°C with a shoulder at high temperature and a melting peak of α_1-crystal at 162°C. Compared with the uncompatibilized PP/PS blend β-PP-20, the melting peak of β-crystal is transformed from a single melting peak to a strong melting peak with a shoulder melting peak in compatibilized PP/PS

blends. At the same time, the melting peak of α_2-crystal at high temperature disappears and the intensity of α_1-crystal melting peak significantly increases in compatibilized PP/PS blends. The difference of melting behavior between uncompatibilized and compatibilized blends suggests that the addition of compatibilizers slightly decreases the β-nucleation of PP and results in the formation of β-crystal with different morphology. However, PP-g-MA, PP-g-GMA, and POE-g-MA compatibilized PP/PS blends possesses strong β-nucleation, so they could be used to prepare compatibilized β-PP/PS blend with high content of β-crystal. In addition, the melting thermogram of the β-PP/PS blend compatibilized by EVA-g-MA shows only one typical melting peak of α-crystal without β-crystal. It is interesting that the EVA-g-MA is the only one exhibited no β-nucleation. Perhaps the compatibilizers could encapsulate or scavenge the nucleating agent. However, because of the polarity difference, EVA is immiscible whereas other compatibilizers are miscible with PP, so EVA-g-MA shows peculiar behavior. Different compatibilizers play various roles on the β-nucleation of β-PP/PS blends, but the relative mechanism need to be studied further.
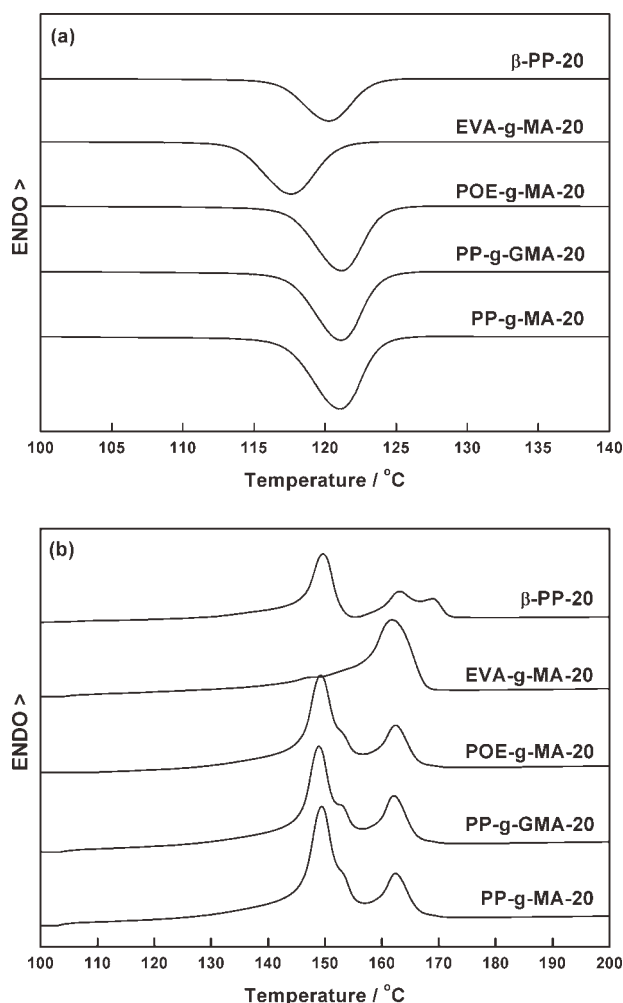
Table V. DSC Crystallization and Melting Data of Compatibilized β-PP/PS Blends

Sample	PP/PS/com[a]	T_{cp} (°C)	T^{β}_{mp} (°C)	T^{α}_{mp} (°C)
β-PP-20	80/20/0	120.3	149.6	163.1, 169.22
PP-g-MA-20	80/20/8	121.1	149.4	162.5
PP-g-GMA-20	80/20/8	121.1	148.9	162.2
EVA-g-MA-20	80/20/8	121.2	149.3	162.5
POE-g-MA-20	80/20/8	117.6	–	161.8

[a]Compatibilizer.

CONCLUSIONS

To improve the yield strength and elastic modulus of β-PP, β-PP/PS blends with high content of β-crystal were prepared by mixing PP, PS, and CaCO$_3$ supported β-nucleating agent or β-PP and PS. The PP with high content of β-crystal was obtained by addition of CaCO$_3$ supported β-nucleating agent (β-NA) into PP. The addition of PS and the increased content of PS have little influence on the β-nucleation, crystallization behavior and melting characteristics, and the β-crystal content of β-PP. The PS content has no influence on the β-spherulite morphology of PP in these blends. The presence of PS retards the growth of β-spherulites, which decreases the size of β-spherulites and reduces the integrity of β-spherulites with increasing the content of PS. The compatabilization of PP-g-MA, PP-g-GMA, and EVA-g-MA slightly decreases the β-nucleation of PP in these blends. The β-PP/PS blends and compatibilized β-PP/PS blends with high β-crystal content can be prepared by mixing PP, PS, and CaCO$_3$ supported β-nucleating agent or β-PP and PS in this article.

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Figure 8. Crystallization (a) and melting (b) thermograms of compatabilized β-PP/PS blends.

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