



## Influence of Blending Mode on Crystalline Morphology, Structure and Mechanical Behaviors of Isotactic Polypropylene/Poly(*cis*-butadiene) Rubber Blends

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Isotactic polypropylene/poly(*cis*-butadiene) rubber (iPP/PcBR) blends with various blend ratio were prepared by two blending modes, the internal mixer and single screw extrusion, respectively. The single screw extrusion blending mode caused a more imperfect crystalline morphology and smaller spherulites. The increase of poly(*cis*-butadiene) rubber content and various blending modes did not affect the interplanar distance of the blends. The blends prepared by single screw extrusion had smaller crystal dimensions, higher the normalized relative degree of crystallinity and the polypropylene- $\beta$  crystal content. The blends prepared by single screw extrusion had higher toughness and strength compare to those blended by the internal mixer

**Keywords:** Isotactic polypropylene, Poly(*cis*-butadiene) rubber, Blending mode, Crystalline, Mechanical behaviors.

### INTRODUCTION

Toughness for blends of polyolefin materials and rubbers are of considerable importance, since the toughness of polymeric materials is an important selection criterion for many applications. Toughness generally reflects the degree of energy absorption from the beginning of the mechanical load to the final fracture. However, toughness is one of the most complex properties and difficult to control, because it is greatly influenced by many morphological and structural parameters. Therefore, it is of fundamental importance to understand the relationship among the morphology, structure and the mechanical properties of polymers for the development of polymer systems with improved toughness.

Isotactic polypropylene (iPP) is one of the most important crystalline polyolefin plastic from a sales tonnage standpoint. Since isotactic polypropylene can be synthesized from low-cost petrochemical raw materials, its one of the lowest in cost among commodity thermoplastics. The future consumption trend of isotactic polypropylene and its composites shows a raise in demand market. Although isotactic polypropylene is extensively used in many fields of applications, its utilization has been limited because of its poor toughness caused its relatively high isotacticity. One of the conventional methods for overcoming this drawback is blending with other polymers, especially with elastomers such as ethylene-propylenediene rubber (EPDM)<sup>1-4</sup> and ethylene-propylene rubber (EPR)<sup>5-6</sup>. In

our research, an addition to the family of the thermoplastic elastomer is the poly(*cis*-butadiene) rubber (PcBR), which is easily available, nonpolar and has excellent elasticity compared to other elastomers.

In our previous research, the toughening modification of isotactic polypropylene with poly(*cis*-butadiene) rubber has been researched for several years. Isotactic polypropylene/poly(*cis*-butadiene) rubber (iPP/PcBR) blends were prepared by melt blending with the internal mixer under lower rotation speed. Under this blending mode, the development of crystalline morphology, structure and impact properties during blending of iPP/PcBR blends was studied<sup>7</sup>. The partial miscibility between isotactic polypropylene and poly(*cis*-butadiene) rubber had been confirmed because the miscibility between components is an important factor in tailoring the properties of polymer blends<sup>8</sup>. For binary polymer blend with a crystalline phase, like iPP/PcBR, it is important to study the crystallization kinetics for optimizing industrial processes and establishing the structure-property correlations. So, isothermal and non-isothermal crystallization kinetics of iPP/PcBR had been studied. A heterogeneous nucleation effect of poly(*cis*-butadiene) rubber upon crystallization of isotactic polypropylene was ascertained. In addition, an attempt was made to use some classical kinetics model to describe the crystallization kinetics process of isotactic polypropylene and our blends<sup>9-10</sup>. Other researchers have also investigated iPP/PcBR blends. Sheng *et al.*<sup>11</sup> and Ma *et al.*<sup>12,13</sup> studied the phase structure and

morphology of PP/PcBR with different compositions by various techniques and obtained some quantitative parameters for the study of the average particle diameter of the dispersed phase and the domain size. Ma and coworkers also examined the miscibility of the two components by IR spectra and SAXS and draw opposite conclusion to our results.

Our previous study paid more attention to the effect of the poly(*cis*-butadiene) rubber content on the structure and properties of the blends since the toughness of blends are influenced by the properties of the matrix material and the structure of the blend. However, the morphology, structure and mechanical properties of blend materials are closely influenced by the blending mode. The purpose of this research was to precisely investigate the influence of the blending mode on crystalline morphology, structure and mechanical behaviors of iPP/PcBR blend with various blending ratio. Our blends were prepared by melt blending by use of the internal mixer and single screw extruder, respectively. The crystalline morphology and structure of the blends were investigated by SALS and WAXD, some quantitative analysis was achieved by our software. Finally, the mechanical behaviors of the blends were tested. The results permit addressing some relationship between blending mode, structure and mechanical behaviors of this blend.

## EXPERIMENTAL

Isotactic polypropylene having a melt index of 8 g/10 min and density of 0.91 g/cm<sup>3</sup>, was provided by Tianjin Petrochemical Co. (China). Poly(*cis*-butadiene) rubber, having a Mooney viscosity of 46 and density of 1.05 g/cm<sup>3</sup>, was supplied by Beijing Yanshan Petrochemical Co. (China).

**Preparation of blends:** iPP/PcBR blends with various poly(*cis*-butadiene) rubber content were prepared by melt blending on a internal mixer (XXS-30 mixer, Shanghai Changjiang Instrument Co., China) at a temperature of 200 °C and a rotation speed of 80 rpm and then they were took out from this mixer after having been mixed for 10 min and cooled at room temperature. In this paper, blends with 10, 20 and 30 vol % poly(*cis*-butadiene) rubber content are represented by PP90, PP80 and PP70, respectively.

Moreover, the blends with 10-30 vol % poly(*cis*-butadiene) rubber content were mixed by the single screw extrusion (PLD-651, D19 and L/D25, Brabender Co., Germany) under the identical blending temperature, speed and time with those of the internal mixer blending, followed by the pelletizing step. These blends are marked by PP90ex, PP80ex and PP70ex, respectively, in order to distinguish from those prepared by the internal mixer.

**Small angle light scattering (SALS):** The crystalline morphology and spherulitic size of neat isotactic polypropylene and iPP/PcBR blends prepared by two blending modes were studied by a SALS apparatus made by our laboratory. The apparatus was attached to a He-Ne source; its wavelength ( $\lambda$ ) was 6328. Thin films of samples less than 100  $\mu$ m thickness were sandwiched between microscope cover glasses by melt-pressing at 200 °C for 5 min and then cooled at room temperature. The  $H_v$  patterns of the samples were treated using our software.

**Wide angle X-ray diffraction (WAXD):** The crystalline structure of neat isotactic polypropylene and blends were

analyzed using a Rigaku D/MAX X-ray diffract meter, using CuK $\alpha$  larger radiation in the 2 $\theta$  range of 8-30° with the scanning velocity of 4°/min for WAXD and in the 2 $\theta$  range of 0.1-3° with steps of 0.01° for SAXS. The accelerating voltage was 40 kV and the tube current was 150 mA. All measurements were performed at room temperature.

**Impact properties:** The notched Izod impact strength measurements were carried out with a UT10/40 602106 testing machine, purchased from Chengde Precision Tester Ltd. (China), at ambient temperature. The rectangular bars of 4 mm thickness were smoothly cut from the slabs and a notch of about 1.3 mm depth was made on the bars for impact testing. At least five samples were tested for each material and the average values were reported.

**Tensile properties:** The tensile properties of neat isotactic polypropylene and blends were measured by a M350-20KN universal testing machine, purchased from Testometric Co. (United Kingdom), at room temperature according to GB1040-74. Dumbbell samples were compressed at 200 °C for 5 min and cooled to the room temperature. All the tests were conducted at a constant crosshead speed of 50 mm/min. Five samples were tested and the average values were presented.

## RESULTS AND DISCUSSION

Fig. 1 shows small angle light scattering ( $H_v$ ) patterns of neat isotactic polypropylene and iPP/PcBR blends with various blend ratio prepared by use of the internal mixer and single screw extrusion blending modes, respectively. The  $H_v$  patterns of neat isotactic polypropylene and all of our blends showed the usual four lobes type of pattern that corresponds to light scattering  $H_v$  patterns of spherulites. Compared to the  $H_v$  patterns of those blends prepared by use of the internal mixer, the four lobes of the samples prepared by single screw extrusion became more diffuse and vague, indicating the perfection of spherulites is less under the extrusion blending mode. From the angular position of the scattering maximum in the  $H_v$  pattern,  $\theta_{\max}$ , the average radius of the spherulites ( $R_s$ ) can be calculated by the following formula<sup>14</sup>:

$$R_s = \frac{4.1}{\frac{4\lambda}{\pi} \sin\left(\frac{\theta_{\max}}{2}\right)} \quad (1)$$

The  $R_s$  values of neat isotactic polypropylene and the blends are plotted in Fig. 2 as a function of the poly(*cis*-butadiene) rubber content under two blending modes. It was seen that the  $R_s$  value of our neat isotactic polypropylene is 75.2 nm. The  $R_s$  values of blends respectively decreased to 28 nm for the internal mixer blending and to 13.8 nm for single screw extrusion blending with the addition of 30 wet % poly(*cis*-butadiene) rubber content. Obviously, the  $R_s$  values of the blends prepared by single screw extrusion were smaller compared to the internal mixer blending mode, implying that the extrusion blending mode is beneficial for comminution of poly(*cis*-butadiene) rubber phase for isotactic polypropylene spherulites and limitation to growth of crystal, which quantitatively confirms the results from  $H_v$  pattern of SALS.

Fig. 3 shows wide angle X-ray diffraction curves of neat isotactic polypropylene and iPP/PcBR blends with various

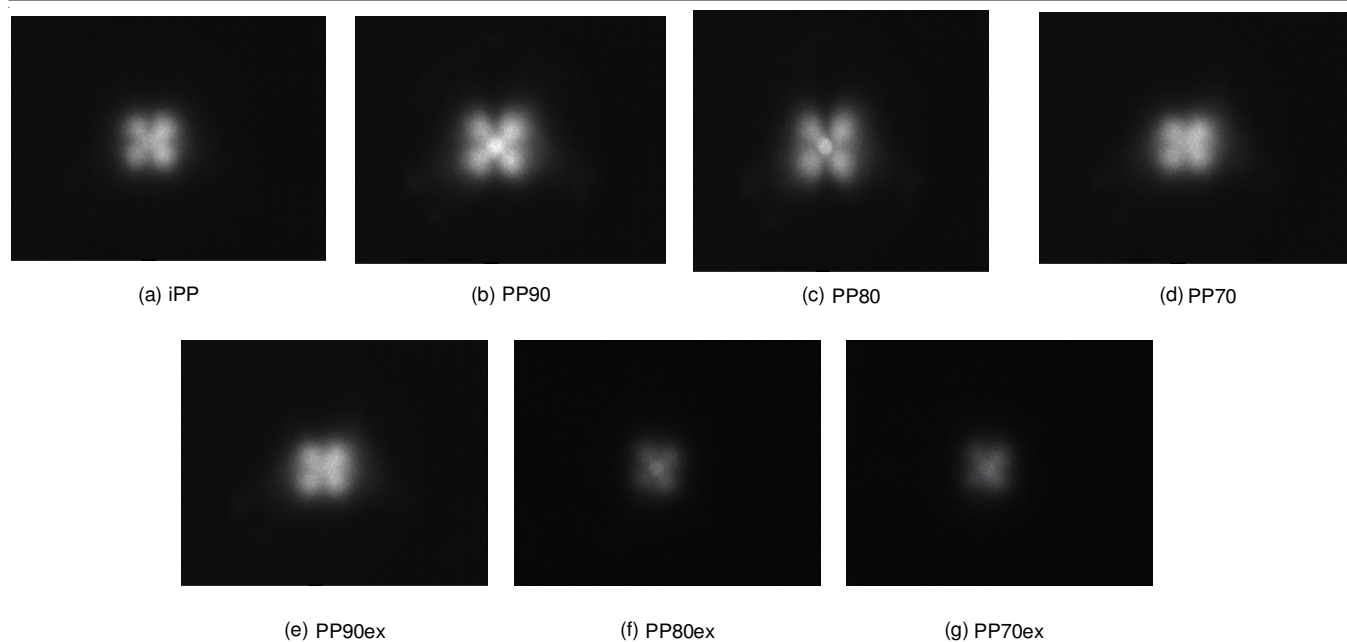


Fig. 1. Small angle light scattering ( $H_v$ ) patterns of neat iPP and iPP/PcBR blends with blend ratio prepared by two blending modes

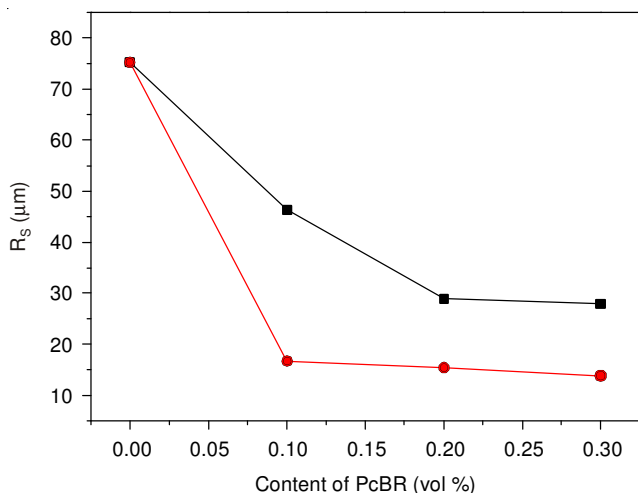


Fig. 2. Average spherulites radius of isotactic polypropylene and iPP/PcBR blends with various blend ratio prepared by two blending modes ■ the blends prepared by the internal mixer ● the blends prepared by the single screw extrusion

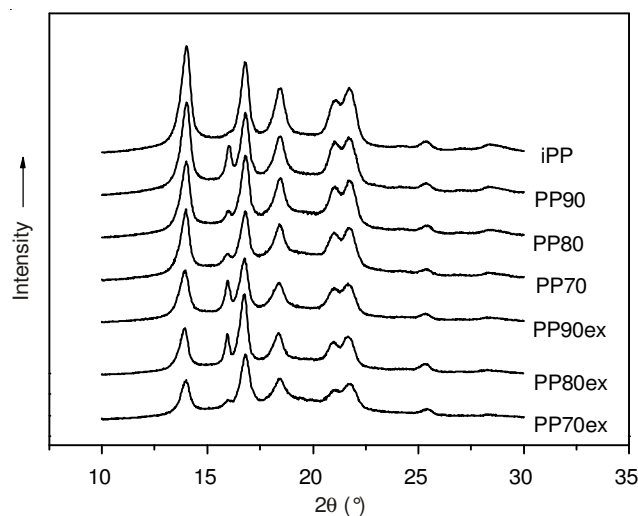


Fig. 3. WAXD curves of neat isotactic polypropylene and iPP/PcBR blends with various blend ratio prepared by two blending modes

blend ratio prepared by two blending modes. The wide angle X-ray diffraction curves showed the presence of the predominant  $\alpha$  form in neat isotactic polypropylene. There is a peak at  $2\theta = 16.0^\circ$ , corresponding to the (300) crystal plane of  $\beta$ -form, on every curve of the blends under two blending modes, in addition to the five distinct crystalline peaks of  $\alpha$ -form of isotactic polypropylene. Isotactic polypropylene is known to display at least three different crystalline forms, namely the monoclinic  $\alpha$ -form, the hexagonal  $\beta$ -form and the triclinic  $\gamma$ -form. In melt crystallized polypropylene, normally the  $\alpha$ -form is produced. The  $\beta$ -form occurs only occasionally, the  $\beta$ -spherulites developing sporadically in the melt at high undercooling. Under special crystallization conditions or when selective  $\beta$ -nucleators are used, higher levels of  $\beta$ -form can be produced<sup>15</sup>. High purity  $\beta$ -form polypropylene exhibits lower values of elastic modulus and yield stress. It was found that regardless of the blending modes, the incorporation of 10-30 vol % poly(*cis*-butadiene) rubber induced the formation of PP- $\beta$  crystal, favoring the improvement of toughness of isotactic polypropylene according to the  $\beta$ -spherulites structure characteristic.

Furthermore, WAXD curves of isotactic polypropylene and the blends prepared under two blending modes are analyzed quantitatively and the results are listed in Table-1. The interplanar distance of isotactic polypropylene and the blends ( $d$  value) was not affected by the addition of poly(*cis*-butadiene) rubber and the two blending mode. Correspond to our previous research, the addition of poly(*cis*-butadiene) rubber caused to a decrease in the crystal dimensions ( $L_{hkl}$ ) of the blends, calculated by the Scherrer equation. However, the difference of the blending mode also led to the change of the crystal dimensions ( $L_{hkl}$ ) of the blends with the same blend ratio. It was seen that the crystal dimensions ( $L_{hkl}$ ) of the blends prepared by the single screw extrusion became smaller than those blends prepared by the internal mixer. It is suggested that the stronger shear force from the extrusion blending mode could increase the blending uniformity of our blends and

TABLE-1  
CRYSTALLINE PARAMETERS OF NEAT iPP AND iPP/PcBR (VOL % 80/20) BLENDS PREPARED BY TWO BLENDING MODES

Sample	$d_{hkl}$ (nm)			$L_{hkl}$ (nm)			$X_c$	$K_\beta$
	110	040	130	110	040	130		
iPP	6.31	5.27	4.80	18.4	23.2	15.4	0.588	0
PP90	6.31	5.25	4.80	17.6	23.1	14.3	0.541	0.113
PP80	6.32	5.25	4.80	17.4	21.7	14.3	0.497	0.086
PP70	6.33	5.23	4.81	16.7	21.4	14.2	0.419	0.079
PP90ex	6.34	5.28	4.81	14.5	18.4	14.1	0.540	0.213
PP80ex	6.35	5.29	4.81	14.0	18.0	13.5	0.529	0.197
PP70ex	6.34	5.27	4.82	13.8	16.7	12.3	0.448	0.112

decrease the crystal dimensions. On the other hand, like the poly(*cis*-butadiene) rubber content, the various blending mode could also influence the normalized relative degree of crystallinity of the blends ( $X_c$ ). Table-1 showed that the  $X_c$  values of neat isotactic polypropylene were 0.588. The  $X_c$  values of the blends decreased as the poly(*cis*-butadiene) rubber content increased. Under the same blend ratio, the blends with 20-30 vol % poly(*cis*-butadiene) rubber prepared by the single screw extrusion had the higher  $X_c$  value than those blends prepared by the internal mixer. Generally, the polymer materials with higher  $X_c$  value mean the improvement of rigidity and strength.

Moreover, the content of PP- $\beta$  crystal ( $K_\beta$ ) of our blends under two blending modes can be calculated by means of the following Turner Jones relationship<sup>16</sup>

$$K_\beta = \frac{I_{300}}{I_{300} + I_{110} + I_{040} + I_{130}} \quad (2)$$

where  $I_{300}$ ,  $I_{110}$ ,  $I_{040}$ , and  $I_{130}$  are, respectively, the integrated intensities of different crystal planes (300, 110, 040 and 130) of isotactic polypropylene crystal. The  $K_\beta$  values are listed in Table-1. It was found that the  $K_\beta$  values of blends decreased with the increase of the poly(*cis*-butadiene) rubber content. The  $K_\beta$  values of the blends prepared by the single screw extrusion were higher compared to those prepared by the internal mixer. It seems that the powerful shear force of the extrusion could favor the formation of PP- $\beta$  crystal in blending process.

**Impact properties:** The notched Izod impact strength of neat isotactic polypropylene and iPP/PcBR blends prepared by two blending modes is shown in Fig. 4. In our testing, the notched impact strength of neat isotactic polypropylene was 2.42 kJ/m<sup>2</sup>. The notched impact strength values of the blends increased as the content of poly(*cis*-butadiene) rubber increased from 10 to 30 vol % under two blending modes. The increase in impact strength of blends is attributed to the addition of rubber. The rubber particles in isotactic polypropylene matrix initiate and blunt crazes; the more crazes the more impact energy absorbed. Moreover, all of the notched Izod impact strength of the blends prepared by single screw extrusion exceeded those blends prepared by the internal mixer. The reason is that poly(*cis*-butadiene) rubber particles were equally dispersed by stronger shear force of extrusion in the smaller and more domains form, which contributes to blunting crazes and suppressing matrix deformation.

**Tensile properties:** Figs. 5 and 6 shows the trends of Young's modulus and tensile strength vs. poly(*cis*-butadiene) rubber content in our blends prepared by two blending modes. The Young's modulus of neat isotactic polypropylene was

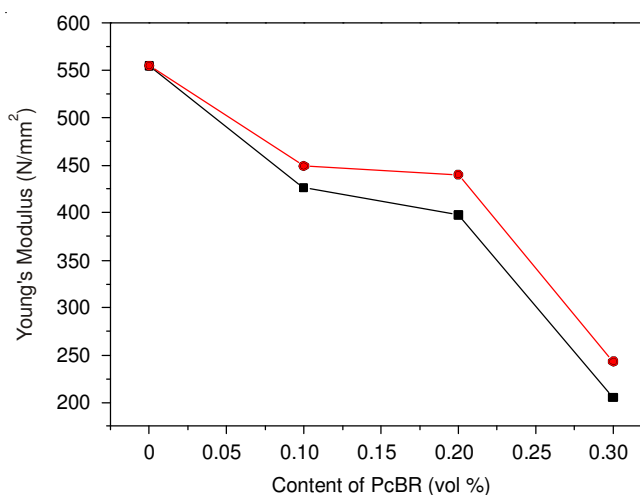


Fig. 4. Curves of Young's Modulus vs. poly(*cis*-butadiene) rubber content in iPP/PcBR blends prepared by two blending modes. ■ the blends prepared by the internal mixer ● the blends prepared by the single screw extrusion

555.02 N/mm<sup>2</sup> and its tensile strength was 34.2 N/mm<sup>2</sup>. Regardless of the blending modes, as the concentration of the soft rubbery component poly(*cis*-butadiene) rubber increases in the blend, the hardness of the material decreases and the Young's modulus and tensile strength decrease. The observed behavior can be analyzed as a combined effect of both components of the blend. The decrease in Young's modulus and tensile strength with increasing poly(*cis*-butadiene) rubber content in the blends indicates a reduction in the rigidity and an increase in the elastomeric nature of the blend. An elastomeric nature improves the toughness of the blends systems. For the blends with the same blend ratio, the Young's modulus and tensile strength of the blends prepared by single screw extrusion were more than those prepared by the internal mixer. It is explained that stronger shear force from the single screw extrusion in blending process led to the increase in  $X_c$  values of the blends and the reduction in domain size which means an increase in number of domains. In blending process, although the incorporation of rubber could present the excellent toughness effect, the rigidity and strength of blends added could show a negative deviation from the additivity. It is critical to find out an optimal blending mode in order to prepare the blends having the desired toughness and strength. As a result, the single screw extrusion blending mode favor the toughness improvement of our blends under less strength loss compared to the internal mixer blending mode.



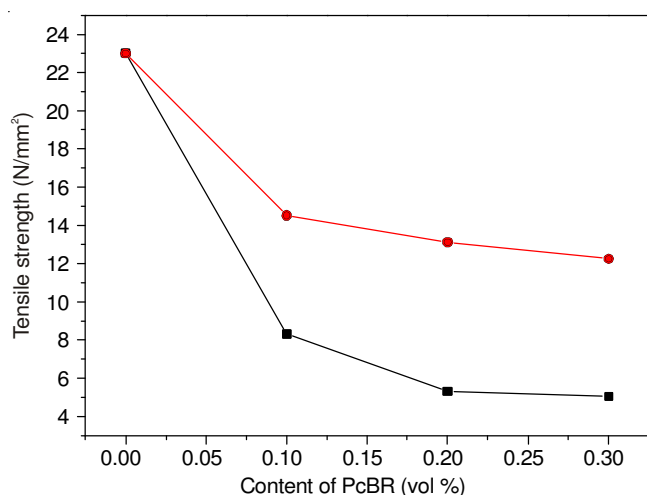


Fig. 5. Curves of Tensile strength vs. poly(*cis*-butadiene) rubber content in iPP/PcBR blends prepared by two blending modes. ■ the blends prepared by the internal mixer ● the blends prepared by the single screw extrusion

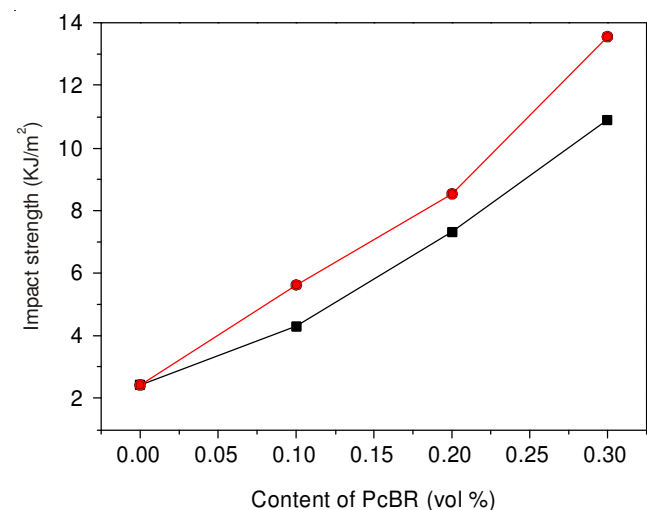


Fig. 6. Curves of impact strengths vs. poly(*cis*-butadiene) rubber content in iPP/PcBR blends prepared by two blending modes. ■ the blends prepared by the internal mixer ● the blends prepared by the single screw extrusion

## Conclusion

Isotactic polypropylene/poly(*cis*-butadiene) rubber blends with various blend ratio were prepared by two melt blending modes, the internal mixer and single screw extrusion, respectively. The effect of two blending mode on crystalline morphology, structure and mechanical behaviors of blends was studied. Crystalline morphology of neat isotactic polypropylene and the blends was observed by small angle light scattering (SALS) and the average radius of the spherulites of samples were calculated by our software according to  $H_v$  patterns of small angle light scattering. The increasing of poly(*cis*-butadiene) rubber content and the single screw extrusion blending mode led to a more imperfect crystalline morphology and smaller spherulites size. Crystalline structure of the blends was measured by wide angle X-ray diffraction (WAXD) and some quantitative para-

eters were analyzed. The addition of 10-30 vol % poly(*cis*-butadiene) rubber induced the formation of PP- $\beta$  crystals. The increase of poly(*cis*-butadiene) rubber content and two blending modes used in this paper did not affect the interplanar distance of our blends. However, the crystal dimensions, the normalized relative degree of crystallinity of the blends and the PP- $\beta$  crystal content decreased as the poly(*cis*-butadiene) rubber content increased. The blends prepared by single screw extrusion had smaller crystal dimensions and higher the PP- $\beta$  crystal content. Compared to the internal mixer blending mode, the extrusion blending mode enhanced the normalized relative degree of crystallinity of the blends with 20-30 vol % poly(*cis*-butadiene) rubber. In mechanical behaviors measurement, the notched Izod impact strength of blends increased while the Young's modulus and tensile strength decreased as the content of poly(*cis*-butadiene) rubber increased. Compared to those blended by the internal mixer, the blends prepared by extrusion blending mode had higher the notched Izod impact strength, the Young's modulus and tensile strength, meaning that the extrusion blending mode favored the enhancement of toughness and strength of our blends compared to the internal mixer blending mode.

## ACKNOWLEDGEMENTS

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