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Structure and properties of polypropylene/poly(ethylene-*co*-propylene) in-situ blends synthesized by spherical Ziegler–Natta catalyst

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Abstract

A polypropylene/poly(ethylene-*co*-propylene) (iPP/EPR) in-situ blend synthesized by spherical Ziegler–Natta catalyst was fractionated by temperature-gradient extraction fractionation. The fractions were characterized using FTIR, ^{13}C NMR, DSC and WAXD. The in-situ blend was found to contain mainly three portions: an ethylene–propylene random copolymer, a series of segmented copolymer with PE and PP segments of different length, and propylene homopolymer. The impact strength of in-situ blends of different structural heterogeneity was measured, and the results show that increasing the amount of segmented copolymer has a positive effect on the impact strength. The segmented copolymer portion alone is found to increase the impact strength at room temperature greatly, while the low temperature impact strength can be markedly enhanced only when random copolymer coexists with the segmented copolymer.

Keywords: iPP/EPR in-situ blend; Structural distribution; Impact strength

1. Introduction

It is well known that the poor low-temperature impact properties of isotactic polypropylene (iPP) can be improved by blending with poly(ethylene-*co*-propylene) (EPR) [1,2]. The iPP/EPR blends are called toughened polypropylene or high-impact polypropylene, which find wide applications in the consumer and automotive industry. In comparison to iPP/EPR blends formed by mechanical blending, blends prepared by in-situ or in-reactor blending techniques have been proved to be superior both in mechanical properties and production costs [3–5]. Because the rubber phase can reach a high degree of dispersion in the in-situ blends, they are also called iPP/EPR alloys. A typical in-situ blend is prepared by sequential homopolymerization of propylene in the first reactor, followed by ethylene/propylene copolymerization in a second reactor. In the particular, Montell company developed an in-reactor blending technique named as Catalloy [6,7], which uses a spherical superactive $TiCl_4/MgCl_2$ based catalyst to prepare multiphase, multipolymer PP alloys with spherical shape. The use of spherical catalyst allows a wider range of rubber content in the alloy and better control over phase structure to be achieved. The resulted spherical resin can be directly processed, eliminating the need of pelleting. This technique was considered as the main progress since the PP in-reactor blend was first developed in the 60s [6]. However, there are almost no reports on the microstructure, structural distribution and structure-properties relationship of iPP/EPR alloy based on spherical catalysts. During the formation of EPR in the iPP spherical particles, the rubber phase is found to be uniformly dispersed in the particle, resulting in a more intimate interaction between the matrix and the rubber phase. Therefore, the structure and properties of spherical iPP/EPR alloy is expected to be different from those of traditional in-situ blends based on non-spherical catalysts. In the later case, large portion of EPR is expected to be formed on the surface of the small and irregular particles.

The compositional heterogeneity and chain structure of traditional iPP/EPR in-situ blends, which are also called propylene–ethylene block copolymer, have been studied by many researchers [3,8–10]. Fractionation of the blends by successive solvent extraction [3] or by temperature-rising elution fractionation [9]has been reported. Through characterization of the fractions by ^{13}C NMR, DSC and wide-angle X-ray diffraction, the blends are found to be mainly composed of three parts: ehtylene–propylene random copolymer, block copolymer with different lengths of ethylene and propylene segments, and iPP. It has been

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considered that the block copolymer functions as compatilizer between the iPP and EPR phases, resulting in improvement of mechanical properties [4,11–13]. However, possible synergistic effects between the random copolymer EPR and the block copolymer have not been thoroughly evaluated.

In this paper, the chain structure and structural distribution of an iPP/EPR in-situ blend based on a spherical $TiCl_4$/$MgCl_2$ catalyst is studied by temperature gradient extraction fractionation combined with ^{13}C NMR, FT-IR, DSC and WAXD. The functions of main components in the blend will be discussed based on the mechanical properties of blends with different structures.

2. Experimental part

2.1. Preparation of iPP/EPR in-situ blend

A high-yield, spherical $TiCl_4/MgCl_2 \cdot ID$ (ID = internal donor) catalyst (DQ-1, donated by the Beijing Research Institute of Chemical Industry) was used in the polymerization reactions, with $Al(C_2H_5)_3–Ph_2Si(OCH_3)_2$ as a cocatalyst. The polymer was synthesized in a two-stage reaction process, in which the first stage is propylene homopolymerization in liquid propylene at 70°C in an autoclave, and the second stage is successive gas-phase ethylene–propylene copolymerization in a stirred-bed reactor. In the first stage, spherical iPP granules of 1–3 mm diameter were produced, and residual propylene in the particles was completely removed before transferring the granules to the second reactor. In the copolymerization stage, an ethylene–propylene mixture of constant composition was continuously supplied to the gas-phase reactor at constant pressure. The final product after two stages of reaction is still free-flowing, spherical granules. This means that most of the copolymer has been formed inside the granules. Ethylene content of the in-situ blend can be adjusted by changing the conditions of copolymerization. The samples studied in this paper were synthesized by copolymerizing ethylene–propylene in the second stage at 60°C and 0.5 MPa monomer pressure for 2 h. Ethylene content in the feed gas was in the range of 20–60 mol% (for sample A, ethylene content in the feed gas was 60 mol%).

2.2. Fractionation of the in-situ blend

A modified Kumagawa extractor was used to carry out a temperature-gradient extraction fractionation of the polymer [14]. *n*-Octane was used as the solvent to successively extract the sample at different controlled temperatures, from room temperature to around 120°C. Eight fractions were collected by extracting 5 g of sample A at 20, 50, 70, 80, 90, 100, 110 and >110°C, respectively. Purified fractions were obtained after concentrating the extract solutions, precipitating the polymer, washing and drying the fractions in vacuum.

2.3. Separation of random copolymer from the in-situ blend

Extraction by boiling *n*-heptane has been adopted to remove only the ethylene–propylene random copolymer and block copolymer containing relatively short segments from the blend. About 10 g of blend sample was extracted in a Kumagawa extractor by boiling *n*-heptane for 12 h. The dissolved polymer was precipitated by ethanol and dried in vacuum. The weight percentage of soluble part was used as a measure of the content of random copolymer in the blend.

To remove the random copolymer from large amount of samples, extraction of the blends by *n*-heptane at 30°C was conducted. First the in-situ blend particles were broken up into fine powder, and then stirred in *n*-heptane at 30°C for 12 h. The solution was filtered out, and the insoluble part was washed with *n*-heptane and dried in vacuum.

2.4. Characterization of polymer structure

Fourier-transfer infrared spectra of the fractions were recorded on a Nicolet 5DX FT-IR spectrometer. Thin film of the sample was prepared by hot-pressing. An empirical equation has been used to estimate ethylene content based on IR spectrum:

$$\ln A_{1150}/A_{720} = 2.98 - 0.060 \times C_2$$

(C_2—mole percent of ethylene in the polymer).

The equation was calibrated by ethylene content data measured by ^{13}C NMR.

^{13}C NMR spectra of the fractions were measured on a Bruker AMX400 NMR spectrometer at 100 MHz. *o*-Dichlorobenzene-d_4 was used as a solvent to prepare the polymer solution of 20 wt%. The spectra were recorded at 120°C, with hexamethyldisiloxane as internal reference. Broadband decoupling and a pulse delay of 5 s were employed. Typically 3000 transients were collected.

2.5. Thermal analysis

Differential scanning calorimetry analysis of the fractions were made on a Perkin–Elmer DSC-7 thermal analyzer under N_2 atmosphere. About 5 mg of sample was sealed in aluminum sample pan and annealed at 130, 120, 110, 100, 90 and 80°C, respectively, each for 12 h. Then the DSC scan was recorded at a heating rate of 5°C/min.

2.6. WAXD analysis

WAXD analysis of the fractions was carried out on a Rigaku Max-rA X-ray diffractometer using Ni-filtered Cu K_α radiation at room temperature. The sample plate was prepared by hot pressing at 200°C, then annealing at 130, 100 and 80°C for 1 h, respectively.

2.7. Intrinsic viscosity of the polymer

The intrinsic viscosity of the polymer fractions was measured using an Ubbelohde viscometer at 135°C with decalin as solvent.

2.8. Measurement of mechanical properties

The notched Izod impact strength of the polymer sample was measured on a Ceast impact strength tester according to ASTM D256. Flexural modulus values were measured following ASTM D790 on a Shimadzu AG-500A electronic tester. The sample plates were heat-molded into sheets, which were than cut into pieces, put into a $150 \times 150 \times 4\ \text{mm}^3$ mold, and pressed under 25 MPa at 180°C for 5 min. The sample was than cooled to room temperature in the mold. Sample strips for the tests were cut from the plate following ASTM.

3. Results and discussion

3.1. Fractionation of a typical in-situ blend

A typical sample (Sample A) of iPP/EPR alloy was fractionated by TGEF into eight fractions. The weight distribution of the fraction in the sample is shown in Fig. 1. It can be seen that the fraction extractable at room temperature (20°C) and the fractions soluble at ≥110°C constitute the main portion of the blend, but the fractions extracted at medium temperatures (50–100°C), which account for about 13 wt% of the blend, may not be omitted. As reported in previous works [14], polyolefins can be fractionated by TGEF according to the crystallinity of the fractions. So the room temperature fraction should be amorphous copolymer, and the last two fractions are isotactic polypropylene.

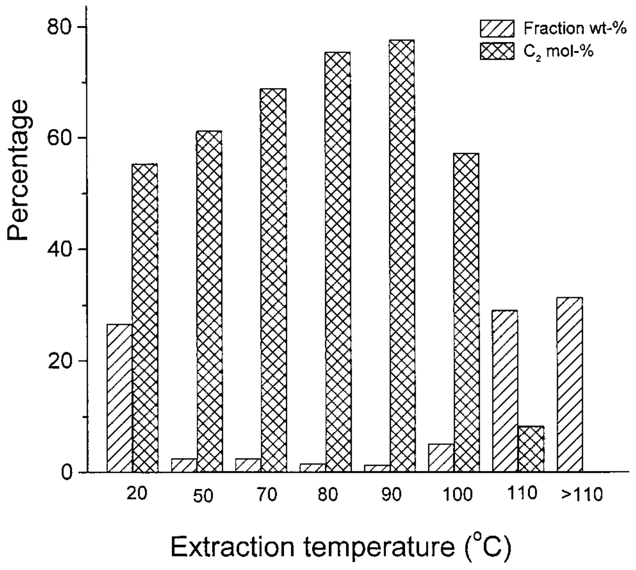

Fig. 1. Weight distribution of the fractions and ethylene content in the fractions.

3.2. Chain structure of the fractions

All the eight fractions of sample A were analyzed by FT-IR, and the spectra are shown in Fig. 2. The spectrum of the 20°C fraction is characteristic of a random copolymer, in which both PP segments and PE segments are too short to crystallize. The spectra of fractions obtained at 50–80°C are similar to that of the 20°C fraction, but there is a gradual increase of ethylene content with temperature, as indicated by the increase of the 720 cm^{-1} absorption. In the fractions of 90°C and 100°C, the absorption at 998 and 841 cm^{-1} clearly show that there are long PP segments that can crystallize. Meanwhile the PE segments are also highly crystalline, as indicated by the doublet at 720–740 cm^{-1}. The spectra of the last two fractions are formed by crystalline PP with small amount of PE segments. Using the equation described in the experimental part, the ethylene content of each fraction was determined and shown in Fig. 1. It can be seen that there is a gradual increase of ethylene content with extraction temperature in the range of 20–90°C, and then it drops to almost zero in the last fraction.

^{13}C NMR spectra of some fractions were also measured to further confirm the chain structure. As shown in Fig. 3, the spectrum of 20°C fraction is typical of ethylene-propylene random copolymer produced by titanium catalyst, which shows almost no propylene inversion and very low stereo irregularity [15]. This is consistent with the high isospecificity of the catalyst (the isotacticity index of polypropylene synthesized at the same condition is about 98.2%). The spectrum of 90°C fraction shows a high content of long PE segments and a relatively large amount of long PP segments, but a very small amount of PEP and EPE segments (the peaks of these sequences are located at 22.8 and 31.3 ppm) [16]. This means that it contains segmented copolymer chains with almost no isolated ethylene units and a small amount of isolated propylene units. The presence of propylene homopolymer of low stereoregularity in this fraction can be ruled out, as there were no peaks in the range of 19.5–18 ppm that can be assigned to the mmmr, mmrr and rrrr pentads. Considering the very high isotacticity of the polypropylene part, the amount of polypropylene with low and medium isotacticity in the 20–90°C fractions will be negligible. The presence of ethylene homopolymer may also be ruled out, as polyethylene can only be extracted at a temperature much higher than 90°C. Therefore, the 90°C fraction is mainly composed of a segmented ethylene-propylene copolymer. This multi-block structure is consistent with the coexistence of PE and PP crystals as disclosed by IR analysis. Finally, the 110°C fraction is composed of highly isotactic PP, interrupted by small amount of long PE segments. But, the EEE segments appeared in this spectrum may also represent PE homopolymer mixed in iPP. To rule out this possibility, we have also studied crystalline structure of the fractions by DSC and WAXD analysis.

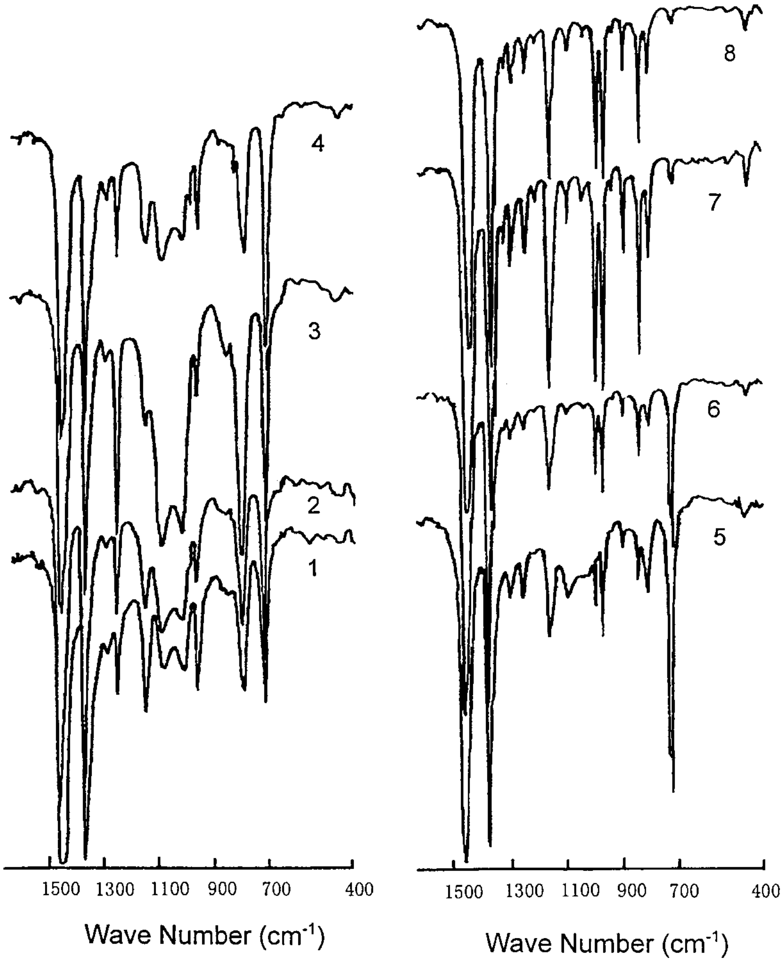

Fig. 2. FT-IR spectra of the fractions of sample A. Extraction temperature of the fractions (°C): (1) 20; (2) 50; (3) 70; (4) 80; (5) 90; (6) 100; (7) 110; (8) >110.

3.3. Crystalline structure of the fractions

The DSC heating scanning curves and WAXD graphs of the fractions are shown in Figs. 4 and 5, respectively. In the DSC graphs, the 50 C fraction shows a very small endothermic peak at about 90°C. Its WAXD graph shows weak peaks at $2\theta = 21$ and 23, which are diffractions of the PE crystal planes (110) and (200). There are also very weak peaks at 17 and 14, which correspond to the (110) and (040) planes of PP crystal. Therefore, in this fraction there are very small amount of PE and PP segments that can form imperfect crystals. As the extraction temperature rises to 80°C, the WAXD peaks from PE become stronger, while the PP crystallinity is only slightly increased. In the 90°C fraction the PE diffraction becomes the strongest, which is consistent with its high ethylene content. As the extraction temperature rises to >110°C, only peaks from iPP crystalline are observed in the WAXD graph.

In the DSC curves, more and more peaks appear as the extraction temperature rises from 50°C to 90°C, and the positions of the peaks move to a high temperature. The multiple endothermic peaks appeared in the range of 80–130°C may be resulted by lamellae of different thickness, which are mainly formed by PE segments of different length. As indicated by the WAXD results, small amount of imperfect PP crystals may also show their peaks in this range, making the curve more complicated. Fully annealing of the DSC samples enabled the growth of different lamellae independently. In these fractions the main component should be an ethylene–propylene copolymer which contains many long PE segments, and the length of PE segments is distributed in a rather broad range.

In the 90°C fraction, a small endothermic peak at 140°C also appeared. This peak shifted to around 150°C in the 100°C fraction and finally shifted to 160°C in the last two fractions. By conferring the WAXD graphs, it can be concluded that this peak is the melting peak of iPP crystals. In the last two fractions the multiple DSC peaks in 80–130°C disappeared, reflecting their low ethylene content. The DSC and WAXD graphs of the 100°C fraction show that it is mainly composed of a multi-block copolymer with both PE and PP segments long enough to crystallize. The low melting temperature of its PP blocks reflects the imperfection of the crystal, which is an indication that the movement of PP segments is limited by the PE segments. The results of WAXD and DSC analysis are extremely

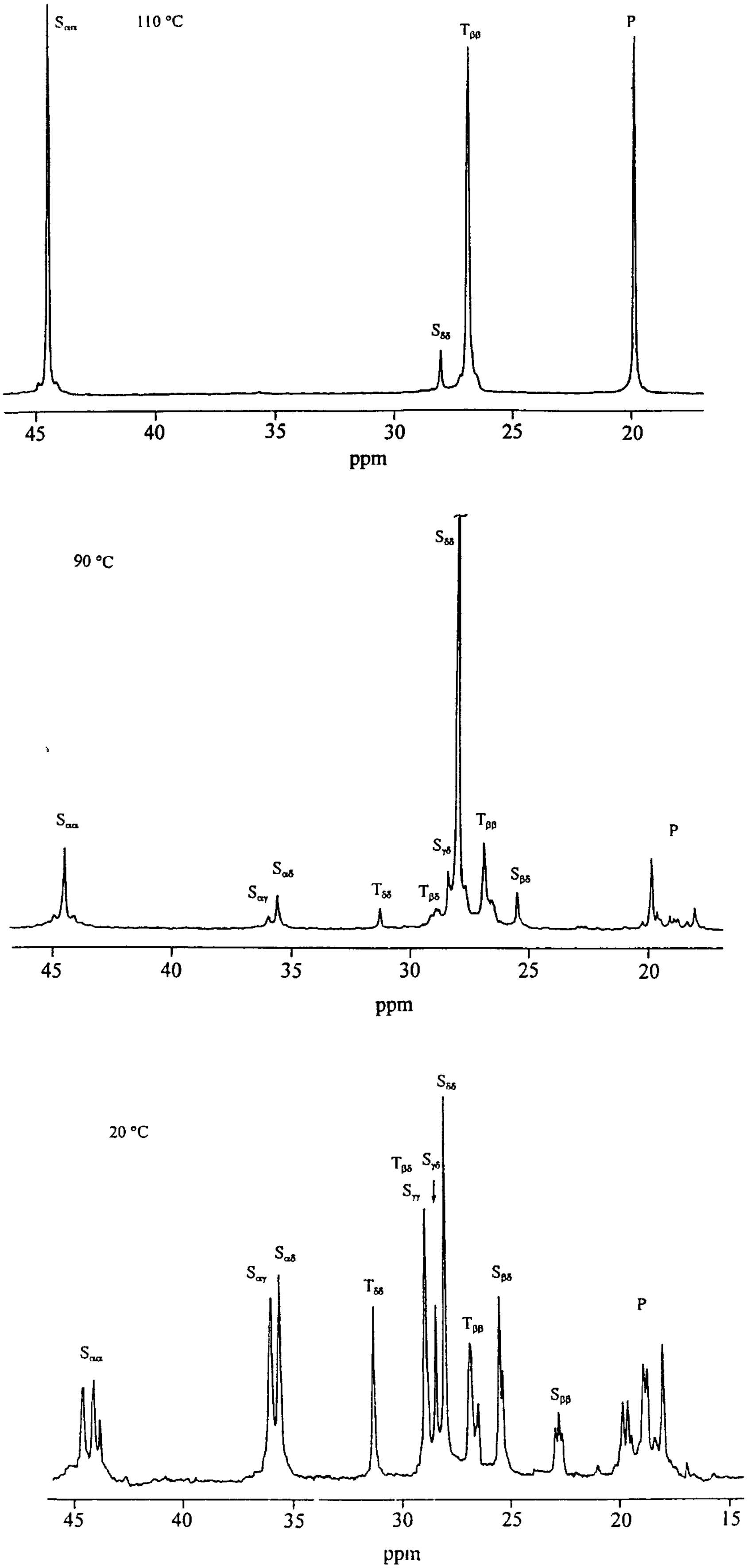

Fig. 3. ^{13}C NMR spectra of three fractions extracted at 20, 90 and 110°C.

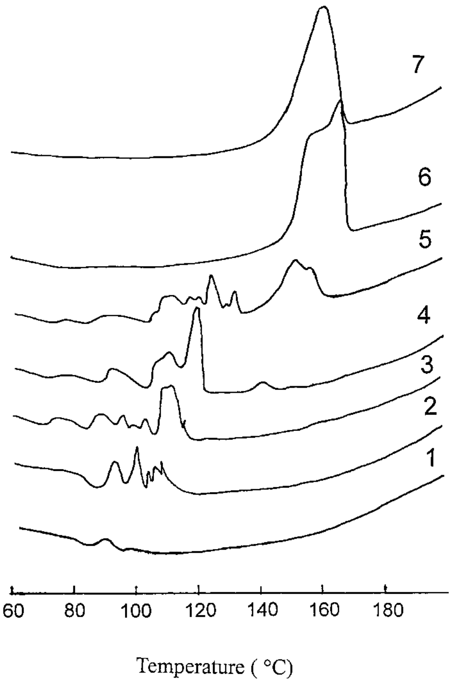

Fig. 4. DSC heating scanning curves of the fractions. Extraction temperature of the fractions (°C): (1) 50; (2) 70; (3) 80; (4) 90; (5) 100; (6) 110; (7) >110.

consistent with the chain structures disclosed by FT-IR and ^{13}C NMR analysis.

At this point it becomes quite clear that the in-situ blend is composed of three portions: (1) ethylene–propylene random copolymer which can not form any crystals; (2) segmented ethylene–propylene copolymers with PE and PP segments of different length; (3) nearly pure iPP.

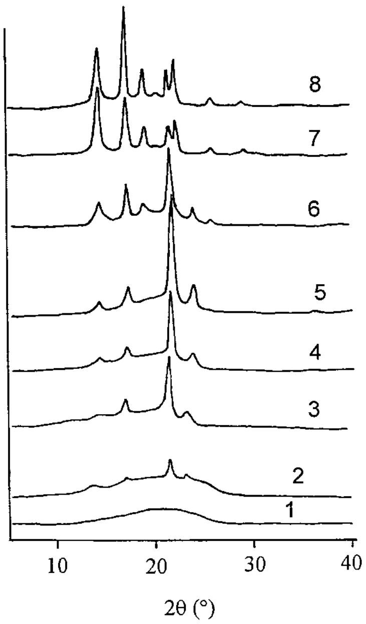

Fig. 5. WAXD graphs of the fractions. Extraction temperature of the fractions (°C): (1) 20; (2) 50; (3) 70; (4) 80; (5) 90; (6) 100; (7) 110; (8) >110.

The formation of the random copolymer is easy to understand, as the main active centers on $TiCl_4/MgCl_2$ based catalysts can catalyze the statistical copolymerization of ethylene and propylene. However, the formation of the small amount of block copolymer should be attributed to some special active centers which have a product of reactivity ratios ($r_E \times r_P$) much higher than 1. In our previous study on propylene/1-hexene copolymerization, broad distribution of chain structure has been identified among the copolymer fractions, ranging from a completely random copolymer to highly segmented copolymers [17]. So the multiplicity of active centers is the direct source of the broad structure distribution.

3.4. Mechanical properties of the in-situ blend

To determine the effects of different components of the in-situ blend on the mechanical properties, we measured the notched Izod impact strength and flexural modulus of some in-situ blend samples of different structure. To simplify the experiments, the structure distribution of the samples were determined and expressed in a simple way. The blends were extracted by boiling *n*-heptane, and the weight percentage and ethylene content of the soluble and insoluble parts were determined, respectively. As the actual working temperature of *n*-heptane extraction is about 90°C, and *n*-heptane has physical properties very similar to *n*-octane, the *n*-heptane soluble part will be similar to the sum of 20–90°C fractions from TGEF, and the insoluble part may represent the sum of 100, 110 and >110°C fractions. Thus, the amount of *n*-heptane soluble part is a rough measure of the random copolymer content, and ethylene content of the insoluble part is a measure of segmented copolymer with long PE and PP segments.

In Table 1 the mechanical properties of four samples are compared. Sample A and B have similar ethylene content, and their heptane soluble parts have similar ethylene content and molecular weight, but the heptane insoluble part of sample A contains more ethylene than that of sample B. This means that sample A contains more segmented copolymers than sample B, or the segmented copolymer in sample A has longer ethylene segments than sample B. The molecular weight of *n*-heptane insoluble part of both samples ($M_v = 60\text{–}100 \times 10^3$) is high enough to prevent a big difference in impact strength. Therefore, the higher impact strength of sample A than sample B means that the segmented copolymer has positive effects on the impact properties. The comparison of sample C with D also supports this point. These samples have a very similar content of random copolymer, but the one contains a higher amount of segmented copolymer, sample C, shows better impact property, especially at low temperature.

On the other hand, when the amount of ethylene in segmented copolymer keeps the same, increasing the amount of random copolymer also has positive effects on the impact strength. Sample A and sample C have a similar

Table 1
Mechanical properties of the in-situ blends

Sample	n-C_7 soluble part[a] (wt%)	C_2 content[b] (mol%)	C_2 in C_7 soluble part[c] (mol%)	C_2 in C_7 in-soluble part[d] (mol%)	[η] (dl/g)		Impact strength (J/m)		Flexural modulus (MPa)
					C_7 soluble part	C_7 insoluble part	23°C	−30°C	
A	34.2	35.0	66.5	15.0	1.43	1.16	NB[e]	680	608
B	51.2	34.1	53.6	10.1	1.50	0.67	NB[e]	510	329
C	25.2	22.5	41.4	15.5	1.41	0.95	653	347	757
D	23.5	18.9	46.7	9.1	1.67	0.82	559	60	800

[a] Weight percent of the boiling n-heptane soluble part.
[b] Mole percent of ethylene in the whole sample determined by FTIR.
[c] Mole percent of ethylene in the boiling n-heptane soluble part.
[d] Mole percent of ethylene in the boiling n-heptane insoluble part.
[e] The sample was not broken in the test.

amount of segmented copolymers (reflected by ethylene content in the heptane insoluble part), but sample A, which contains more random copolymer, shows higher impact strength. Therefore, both the random copolymer and the block copolymers are necessary for improving the impact properties of iPP/EPR blends.

The flexural modulus of the samples seems to be influenced mainly by the content of random copolymer. As shown in Table 1, the sample containing more random copolymer (like sample B) shows lower flexural modulus. In other words, random copolymer will make the material soft.

To study the possible synergistic effects between the random copolymer and block copolymers in the blend, we removed the random copolymer from some of the samples by extraction at 30°C using n-heptane, and measured the impact strength of the insoluble part. In Table 2 the impact strength of both the whole polymers and samples without random copolymer are compared, either at room temperature (23°C) and low temperature (−30°C). It can be seen that the room temperature impact strength is only slightly lowered after removing the random copolymer, but the low temperature impact strength strongly relies on the random copolymer. In other words, incorporating only the segmented copolymer into the iPP matrix can result in great improvement in the room temperature impact strength, but the random copolymer is necessary for improving low temperature impact strength.

Improvement in impact strength by the segmented copolymer may be caused by the finely dispersed PE phase in iPP, because PP segments in the segmented copolymer is highly compatible with the iPP matrix, and thus can force the PE segments to form very small domains. As PE has much higher impact strength than iPP at room temperature, the impact strength of the whole material will be improved. On the other hand, the crystalline morphology of the material may also be changed by the segmented copolymer. The size of iPP spherulites may be reduced, and even the spherulite structure may be destroyed. These changes can also help to enhance the impact strength. This should be a mechanism different from that of typical rubber toughening of brittle polymer.

However, at low temperatures the segmented copolymer itself will become brittle, as the glass transition temperature (T_g) of PP segments should be close to T_g of neat iPP (about −10°C). In this case, the segmented copolymer will not be able to toughen the material, and highly elastic random copolymer becomes necessary.

The lower T_g of EPR (−50°C) should be an important fact to increase the low temperature impact strength. But according to the studies of L. D'Orazio et al. [18], mechanical

Table 2
Impact strength of in-situ blends with and without random copolymer portion

Sample	Ethylene content (mol%)		Amount of the extract[c] (wt%)	Ethylene content in the extract (mol%)	Impact strength (J/m)			
	Before extraction[a]	After extraction[b]			Before extraction[a]		After extraction[b]	
					23°C	−30°C	23°C	−30°C
E	9.8	8.5	3.6	36.1	522	82	480	17.5
D	18.9	14.6	11.7	39.9	610	117	559	31.3
F	25.2	15.2	23.0	47.2	620	260	594	32.3

[a] The original sample without extraction by n-heptane.
[b] Sample with no random copolymer, which is the n-heptane insoluble part after extraction at 30°C for 12 h.
[c] Percentage of random copolymer extracted by n-heptane at 30°C for 12 h.

blends of iPP and EPR show only slightly higher impact strength than iPP at −30°C. This means that, the presence of only the random copolymer can not ensure great enhancement of impact strength. The excellent impact properties of the in-situ blends at low temperature are likely to be resulted by the synergistic effects of random copolymer and segmented copolymer in the blend.

Such synergistic effects may be understood based on the compatilizer function of the segmented copolymer. Long PP segments in PP-PE segmented copolymer are highly compatible with iPP, and the PE segments are compatible with the PE segments in random copolymer. So the segmented copolymer acts as a compatilizer between the rubber phase and the matrix, resulting in strong interactions between the two phases. At low temperature, such interphase interactions become very important for effective absorption of energy by the rubber phase. The superior impact properties of in-situ blends over the mechanical blends can thus be explained by the synergistic effects of segmented copolymer in the former systems.

4. Conclusions

An iPP/EPR in-situ blend synthesized by spherical Ziegler–Natta catalyst was fractionated by TGEF. The fractions were characterized by FTIR, ^{13}C NMR, DSC, and WAXD. The in-situ blend was found to contain mainly three portions: an ethylene–propylene random copolymer, a series of ethylene–propylene segmented copolymer with PE and PP segments of different length, and propylene homopolymer. The DSC study clearly shows that, PE segments of different lengths in the segmented copolymer fractions can form crystalline lamellae of different thickness. The segmented copolymer accounts about 10 wt% of the whole polymer.

The impact strength of in-situ blends of different structural heterogeneity was measured, and the results show that, increasing the amount of ethylene in segmented copolymer portion has a positive effect on the impact strength. Further study on the impact strength of polymer samples with and without random copolymer portion shows that, the segmented copolymer portion alone is able to increase the impact strength at room temperature greatly, while the low temperature impact strength can be markedly enhanced only when random copolymer coexists with the segmented copolymer. The synergistic effect between random copolymer and segmented copolymer is a key factor for high impact strength at low temperature.

Acknowledgements

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