CHARACTERIZATION OF IMPACT POLYPROPYLENE COPOLYMERS BY SOLVENT FRACTIONATION[*]

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Abstract The compositional heterogeneity of two impact polypropylene copolymers (IPCs) was studied by a combinatory investigation of temperature rising elution fractionation (TREF) and solvent fractionation. The chain structures and composition of fractions obtained from solvent fractionation were examined in detail. The TREF results shows that there are much more E-P segmented copolymer and more uniform distribution of ethylene sequence in IPC-1, which is responsible for its better comprehensive mechanical performance. The fractions from hexane and heptane are ethylene-propylene rubber phase and E-P block copolymers respectively. The result of solvent fractionation method also shows that custom hexane or heptane extractions can not extract the E-P copolymer completely.

Keywords: Fractionation; Impact polypropylene copolymer; Composition; Chain structure.

INTRODUCTION

Polypropylene (PP) is a semi-crystalline polymer widely used in packaging, textile and automobile industries because of its good processability and properties. Nevertheless, its applications are limited because of the poor toughness at low temperatures. In the past several decades, research on improving PP impact resistance aroused the interests of many researchers[1–8]. Generally, there are two ways to improve the toughness of PP: one is by physical blending it with variety of elastomers such as ethylene-propylene random copolymer (EPR), ethylene-propylene-diene terpolymer (EPDM) and so on[1–4]; the other is in-reactor blending by catalloy process with Ziegler-Natta or metallocene catalyst[5–8]. The latter method has been proved to be efficient in improving the inherently poor impact properties of polypropylene with the developments of catalyst technology and polymerization process[9–15]. Moreover, impact polypropylene copolymers (IPCs) or the so called in-reactor blends have been widely used as matrix components in automobile parts, appliances and other industrial uses in the last two decades because of the excellent mechanical properties and relatively low production cost[16]. However, the typical IPC is a complicated multiphase system because of heterogeneity of inter- and/or intrachain structure, which makes it difficult to find an easy way to characterize. Many approaches have been developed to analyze its multi-scaled structures, for example, nuclear magnetic resonance (NMR)[17–19], infrared spectrometry-Fourier transform (FTIR)[17, 20, 21], differential scanning calorimetry (DSC)[19, 22–26], solvent fractionation[27–29] and temperature rising elution fractionation (TREF)[18, 30–33]. It is believed that common solvent extractions, such as hexane extraction and heptane extraction, are effective methods to analyze homo-polypropylene, and they are not fit for polypropylene copolymers analysis. So far, no one can tell why these

solvent fraction methods are not effective for polypropylene copolymers, and what these fractions are composed of in detail. In this paper, the compositions and chain structures of two IPCs were examined by gel permeation chromatography (GPC), TREF and NMR. Two different fractions were obtained by hexane and heptane extraction and the composition and chain structure of each fraction was examined by NMR, FTIR and DSC in detail. The results show that there are much more E-P segmented copolymer and more uniform distribution of methyl sequence length (MSL) (or ethylene sequence) in IPC-1, which is responsible for its final properties. It was found that the fractions from hexane and heptane were ethylene-propylene rubber phase and E-P block copolymers, redpectively, and that custom hexane or heptane extraction can not extract the E-P copolymer completely form IPC.

EXPERIMENTAL

Materials

The two impact polypropylene copolymers (IPC-1 and IPC-2) used in the present work are commercial products. The two products can be used as special material for thin-wall injection moulding. The mechanical properties reported by the supplier were summarized in Table 1.

Table 1. Properties of two impact polypropylene copolymers

Item	$M_w \times 10^{-4}$	M_w/M_n	MI (g/10min)	E_b (GPa)	σ_t (MPa)	Izod NIS (kJ·m^{-2})	
						23°C	−20°C
IPC-1	12.55	12.4	25	1.37	29.4	7.35	3.92
IPC-2	16.59	8.6	29	1.32	24.5	5.4	2.25

MI: melt index；E_b: bending modulus；σ_t: tensile yield strength；Izod NIS: Izod notch impact strength; M_w: weight-average relative molecular mass and molecular weight distribution were obtained by GPC and the other data are from the product specification.

Methods

TREF experiments

The analytical TREF experiments were carried out on a commercial TREF instrument (model 300, Spain, Polymer Char Company). In TREF analysis, about 50 mg of polymer was dissolved in 20 mL of *o*-dichlorobenzene (*o*-DCB) containing 2,6-di-*tert*-butyl-4-methylphenol (0.025%, mass ratio) at 150°C for 90 min and stabilized at 135°C for 45 min. The solution was deposited on a steel column packed with an inert support, and the column was cooled down to room temperature at a rate of 0.5 K/min. The polymer crystallized during the cooling process was then eluted with *o*-DCB at a heating rate of 1 K/min, and the concentration of the eluted solution at a 0.5 mL/min flow rate was monitored on-line at the exit by an IR detector.

GPC experiments

Gel permeation chromatography (GPCIR, Polymer Char) was used to measure the molecular weight and its distribution with solvent 1,2,4-trichlorobenzene for each PP sample at 145°C. The sample for the calibration curve was standard polystyrene (PS).

Solvent fractionation

Hexane and heptane were used for solvent fractionation. The typical fractionating procedure is as follows. The sample of IPC was dissolved in xylene at 130°C, and then the solution was gradually cooled to room temperature. Powder sample was obtained by precipitating the solution using a great deal of ethanol and removing residual solvent under vacuum. The powder sample was extracted by boiling hexane for about 24 h. From the hexane solution, the first fraction (A) was obtained. After being extracted by boiling hexane, the retained precipitate was dried under vacuum, then extracted by boiling heptane, the retained precipitate was separated into 2 fractions, the fraction dissolved in heptane (B) and the fraction insoluble (C) in heptane.

NMR experiments

^{13}C-NMR spectra were measured on a Bruker dmx300 NMR spectrometer at a resonance frequency of

75.5 MHz. Then, 20 wt% homogeneous polymer/*o*-DCB solutions were prepared before test. The spectra were recorded at 120°C and typically 3000 transients were collected.

FTIR experiments

A Nicolet 6700 (Thermo Fisher Scientific) FTIR spectrometer was used to measure the spectra of all samples with a resolution of 2 cm and 32 scans for each sample. Samples were prepared by fusing a scrap of the sample placed between 2 cover glasses. After melting at 230°C for 5 min, the sample was compressed into film with a thickness of about 200 μm.

RESULTS AND DISCUSSION

The two impact polypropylene copolymers (IPCs), used as special material for thin-wall injection moulding, were produced by ethylene-propylene copolymerization. The molecular weights and their distribution of the two IPCs were measured. The M_w and polydispersity index of IPC-1 are 12.55×10^4 and 12.4 respectively. The M_w of IPC-2 is higher (16.59×10^4) compared with that of IPC-1, and it has a narrower molecular weight distribution index of 8.6. The mechanical performance of the two IPCs is much different. The Izod notch impact strength and tensile yield strength σ_t of IPC-1 are both larger than those of ICP-2, while their bending modulus E_b is almost the same. In view of the complicated components of IPCs, the intrachain or interchain compositional heterogeneity is believed to be responsible for the difference in mechanical properties. The composition of the two IPCs was characterized by NMR and TREF first. In order to explore facile and effective methods for characterizing the two IPCs and further understanding the difference in structure between the two IPCs, we expected to divide IPCs into three fractions, *ca*. rubber phase, E-P copolymers and homo-polypropylene by applying custom solvent fractionation (hexane and heptane extraction). The compositions of different factions were examined by FTIR, NMR and DSC in detail.

^{13}C-NMR spectroscopy measurement was performed to characterize the chain structure and ethylene content of the two IPCs. The peak assignments of different carbon atoms along the molecular chain in NMR spectra were done according to the Ref. [34], and the calculated results are summarized in Table 2.

Table 2. ^{13}C-NMR data for sequence distribution of IPCs and their different fractions from solvent fractionation

Sample	E	P	EE	EP	PP	EEE	EEP	PEP	EPE	PPE	PPP
IPC-1	20.4	79.6	14.7	11.7	73.7	11.6	6.4	2.6	1.9	4.2	73.4
IPC-2	15.3	84.7	11.1	7.8	80.8	8.4	4.9	2.0	1.8	2.7	80.3
IPC-1-A	58.4	41.6	37.5	40.4	21.4	25.2	23.3	9.2	7.7	15.5	18.4
IPC-1-B	61.4	38.6	45.3	33.1	22.1	36.8	17.2	7.2	6.8	13.3	18.5
IPC-2-A	47.1	52.9	26.3	40.9	32.5	16.7	18.8	11.6	8.8	20.8	22.4
IPC-2-B	61.6	38.4	48.2	26.4	25.4	40	15.3	6.3	6.0	12.3	20.1

The monomer content of E in IPC-1 is 20.4 mol%, much higher than that (*ca*. 15.3 mol%) in IPC-2. The content of EEE in IPC-1 is also much higher than that in IPC-2. These results indicate that there are more crystalline ethylene sequences in IPC-1. At the same time, the contents of triads EEP, PEP, EPE and PPE in IPC-1 are all higher than their counterparts in IPC-2. That means there are more E-P copolymers in IPC-1 than in IPC-2, which will be proved by TREF results (see the following section). The content of triad PPP is 80.3 mol% in IPC-2, much higher than that in IPC-1, the same with the case of the monomer content of P.

TREF Fractionation Analysis

In order to find the difference in chemical structure and compositional heterogeneity between IPC-1 and IPC-2, the analytical TREF experiments were carried out on a TREF instrument (see Fig. 1). The experiment data (obtained from Fig. 1) shown in Table 3, indicate that the composition of the two IPCs is much different. The content of the rubber phase of IPC-1 and IPC-2 is 16.3 wt% and 14.2 wt%, respectively, while the content of crystallizable E-P copolymer in IPC-1 is 32.1 wt% (the fraction during 35−110°C), much higher than that of crystallizable E-P copolymer (13.1 wt%, the fraction during 35−110°C) in IPC-2. Generally, the higher the

content of rubber, the better the impact resistance. The crystallizable ethylene-propylene block polymer serving as compatibilizer between rubber phase and the PP matrix is a key factor to determine the comprehensive performance of IPCs. High content of crystallizable ethylene-propylene block polymer in IPC-1 would act as compatibilizer during the forming process of aggregation state structures, which makes the two incompatible components (rubber and polypropylene) become compatible, which endows IPC-1 with good impact resistance while retaining good rigidity. The fraction (> 110°C) is mainly composed of homo-polypropylene. The content of homo-polypropylene in IPC-2 is 72.7 wt%, much higher than that in IPC-1 (51.6 wt%). In addition, the difference in content of the high temperature (120–130°C) eluting fraction between IPC-1 and IPC-2 is obvious. During the elution temperature range of 120–130°C, the fraction is mainly composed of polypropylene with high isotacticity. The contents of this fraction in IPC-1 and IPC-2 are 11.6 wt% and 39.6 wt%, respectively, which result in the difference in melt and crystallization temperature obtained in DSC scan curves. The sample with higher content of polypropylene with high isotacticity usually has a higher melt point and a higher crystallization temperature.
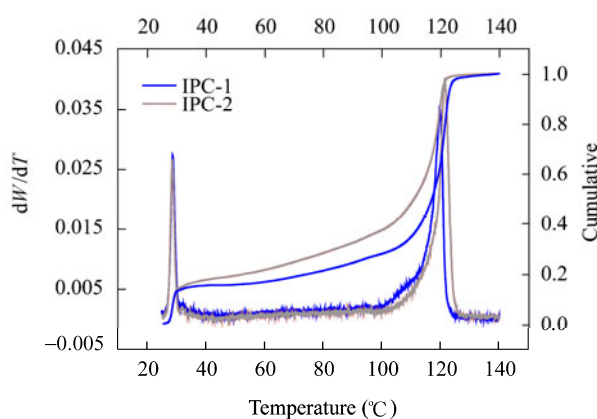

**Fig. 1** TREF curves of the two impact propylene copolymers

Table 3. Content of fractions obtained by temperature rising elution fractionation (TREF)

Sample name	Fraction (≤ 35°C, wt%)	Fraction (35–90°C, wt%)	Fraction (90–100°C, wt%)	Fraction (100–110°C, wt%)	Fraction (110–120°C, wt%)	Fraction (120–130°C, wt%)
IPC-1	16.3	16.0	5.2	10.9	40.0	11.6
IPC-2	14.2	2.2	3.5	7.4	33.1	39.6

FTIR Analysis of Fractions

The infrared spectra of the different fractions are shown in Fig. 2. As we know[27, 35], the absorptions at about 998 and 841 cm^{-1} are due to methyl rocking modes and are associated with the threefold helix of isotatic PP, which is the characteristic structure of PP crystal. The band at 972 cm^{-1} is associated with methyl rocking vibrations of amorphous PP. The band at 720 cm^{-1} is due to $-(CH_2)_n-$ ($n \geq 5$) rocking vibrations. The doublet at 720–740 cm^{-1} indicates the presence of a crystalline polyethylene (PE) block. When the crystallinity of PE is low, the band at 730 cm^{-1} of the doublet will be reduced to a shoulder of the band at 720 cm^{-1}. In Fig. 2, only the absorption of PP amorphous band (973 cm^{-1}) and band at 720 cm^{-1} can be observed in the spectra of IPC-1-A and IPC-2-A. It indicates that the propylene units and ethylene units in fraction A can not crystallize and fraction A is mainly composed of ethylene-propylene rubber. Because atactic polypropylene is soluble in hexane and heptane, atactic polypropylene in IPC-1 and IPC-2 should be included in fraction A and fraction B. That was proved by FTIR results shown in Fig. 2. The doublet at 720–740 cm^{-1} can be observed in the spectra of IPC-1-B and IPC-2-B. That indicates the presence of crystalline polyethylene (PE) blocks in the fraction B. At the same time, the absorption of PP amorphous band (973 cm^{-1}) can also be observed and the absorptions at

998 and 841 cm^{-1} due to PP crystals are very weak. This means that the fraction B is mainly composed of E-P block copolymer with long ethylene sequence, and the majority of E-P copolymers with long propylene sequence were not included in fraction Bs. We can observe the characteristic absorption peaks of PP crystals and absorption peak of weak $-(CH_2)_n-$ ($n \geq 5$) rocking vibrations clearly in the infrared spectra of fraction C. Therefore, it indicates that the insoluble fraction in heptane contains not only homo-polypropylene but also a small quantity of E-P copolymers with long propylene sequence.
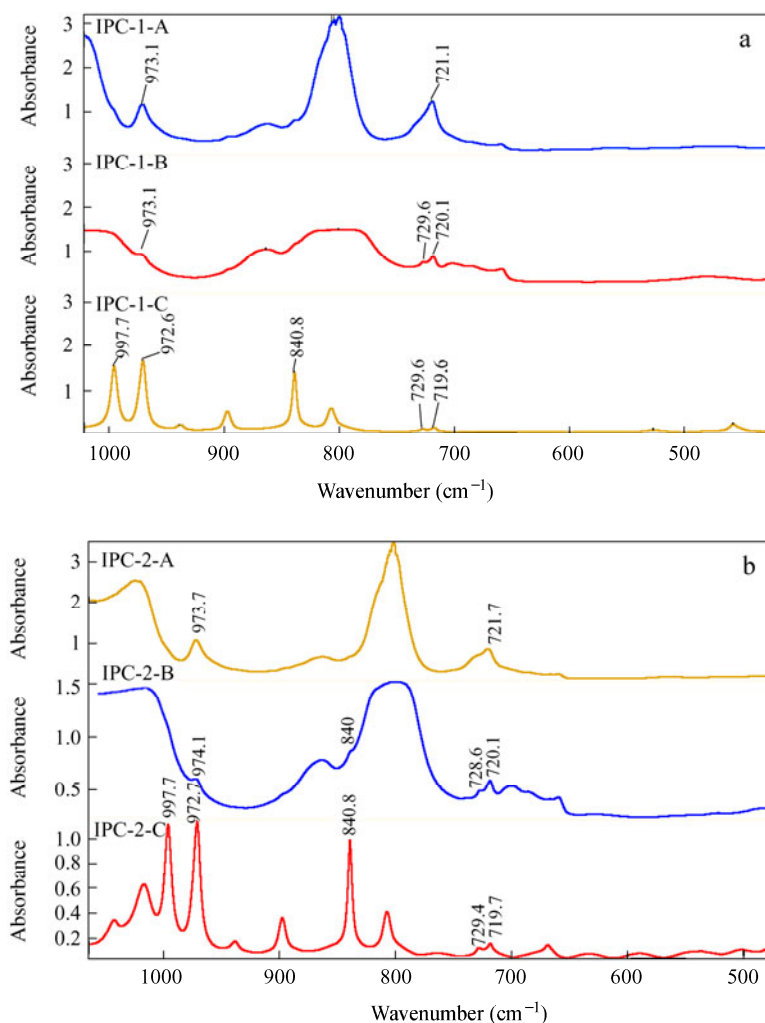

Fig. 2 The infrared spectra of the different fractions: (a) IPC-1 and (b) IPC-2

NMR Study of the Fractions

In order to further confirm the chain structure and composition of fraction A and fraction B of the two IPCs, ^{13}C-NMR spectroscopy measurements were performed, shown in Fig. 3, and the calculated results are summarized in Table 2. For the fraction A of the two IPCs, both propylene and ethylene sequence distributions in all triads are relatively homogeneous. This confirms that fraction A is EP rubber. For the two fraction Bs, the content of E is much higher than that of P, while the content of EP decreases. The content of EEE in two fraction Bs is also much higher than that of fraction As. These results indicate that there are crystalline ethylene sequences in fraction Bs, which are E-P segmented copolymers. This means that the fractions Bs are segmented copolymer with long ethylene sequences indeed, the same as results obtained by FT-IR. It is also interesting to find that the content of E change gradually from fraction A to fraction B for these IPCs. For example, the

content of E in IPC-1 changes from 58.4 mol% (in IPC-1-A) to 61.4 mol% (IPC-1-B) and the content of EEE changes from 25.2 mol% (in IPC-1-A) to 36.8 mol% (IPC-1-B). Moreover, propylene sequence distribution and ethylene sequence distribution change more continuously between fractions of IPC-1 than between fractions of IPC-2. More continuous change in propylene sequence distribution and ethylene sequence distribution means better compatibility and better comprehensive mechanical performances[35, 36].
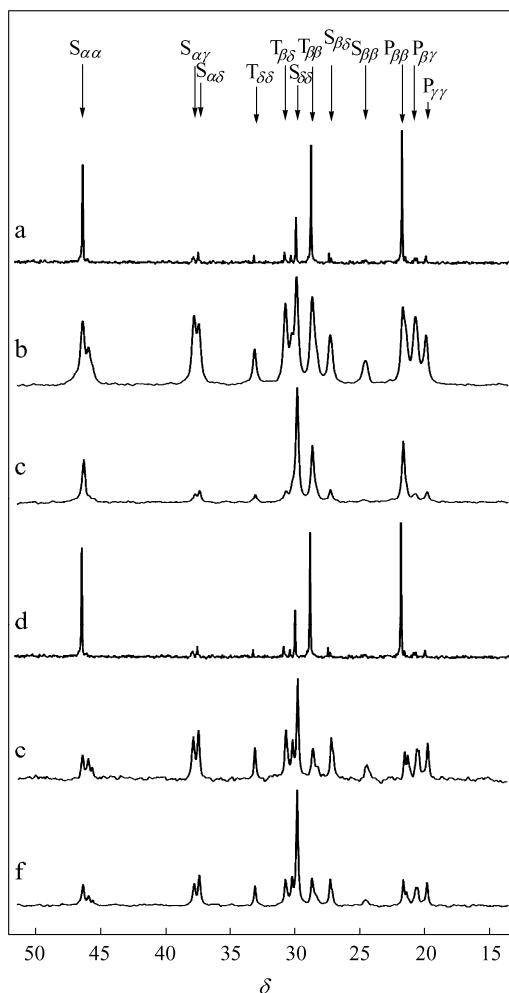

Fig. 3 ^{13}C-NMR spectra of different fractions from solvent fractionation (a) IPC-1,
(b) IPC-1-A, (c) IPC-1-B, (d) IPC-2, (e) IPC-2-A and (f) IPC-2-B

According to FTIR and NMR results, it can be concluded that boiling heptane can not extract E-P block copolymer completely, and a small quantity of E-P block copolymers with long ethylene sequence and (or) with long propylene sequence still can not be dissolved in boiling heptane.

DSC Analysis

The thermal properties of the three fractions obtained from solvent fractionation were determined by DSC, shown in Fig. 4. The soluble fraction in hexane (fraction A) was mainly rubber phase. Glass transition temperatures (T_g) of IPC-1-A and IPC-2-A are −50.2°C and −46.6°C respectively. It indicates that when the content of rubber phase is the same, the impact resistance of IPC-1 would be better than that of IPC-2. Because there is more rubber phase in IPC-1 than in IPC-2 (see TREF data), the toughness of IPC-1 is better than that of IPC-2 indeed, shown in Table 1. After the sample was extracted by boiling hexane, the retained precipitate was

separated into 2 fractions, the fraction dissolved in heptane (fraction B) and the fraction insoluble (fraction C) by heptane extraction. We also examined thermal properties of the soluble fractions in heptane (IPC-1-B, IPC-2-B). According to previous reports[27, 32, 35], the fraction B is believed to be composed of crystallizable ethylene-propylene copolymer with different structure regularity. The results show that the fraction soluble in heptane is composed of crystallizable ethylene-propylene copolymer with different structure regularity. Moreover, according to the positions of the melting peak, it was found that the fraction Bs were mainly composed of E-P copolymers with long ethylene sequence. The DSC heating scan of insoluble fractions showed that they were basically isotactic polypropolene. It is because that their melt and crystallization temperatures are almost the same with *i*PP. The molecular weight and its distribution are responsible for the minor difference of peak data between these two samples.
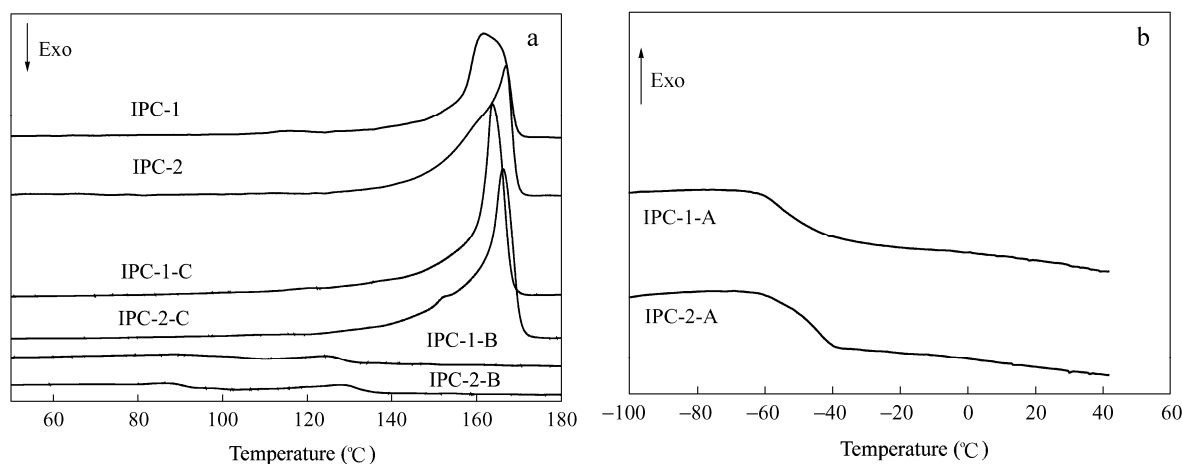
Fig. 4 DSC curves of IPC-1, IPC-2, fractions B and C from solvent fractionation (a) and fraction A from solvent fractionation (b)

CONCLUSIONS

The compositional heterogeneity of two impact polypropylene copolymers was studied by a combinatory investigation of TREF and solvent fractionation. The chain structures and composition of fractions obtained from solvent fractionation were examined in detail. The TREF results show that there are much more E-P segmented copolymers and more uniform distribution of methyl sequence length (MSL) in IPC-1, which are responsible for its better comprehensive mechanical performance. The fraction A from hexane extraction is mainly composed of ethylene-propylene rubber and the fraction B from heptane extraction is E-P block copolymers. The fraction C is mainly composed of homo-polypropylene with small quantity of E-P block copolymers. The results of solvent fractionation method also show that custom hexane or heptane extraction can not extract the E-P copolymer completely form IPC.

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