

Chain Structure and Mechanical Properties of Polyethylene/Polypropylene/Poly(ethylene-co-propylene) In-Reactor Alloys Synthesized with a Spherical Ziegler–Natta Catalyst by Gas-Phase Polymerization

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ABSTRACT: Two polyethylene/polypropylene/poly(ethylene-co-propylene) in-reactor alloy samples with a good polymer particle morphology were synthesized by sequential multistage gas-phase polymerization with a spherical Ziegler–Natta catalyst. The alloys showed excellent mechanical properties, including both toughness and stiffness. With temperature-gradient extraction fractionation, both alloys were fractionated into five fractions. The chain structures of the fractions were studied with Fourier transform infrared, ¹³C-NMR, and thermal analysis. The alloys were mainly composed of polyethylene, polyethylene-*b*-polypropylene block copoly-

mer, and polypropylene. There also were minor amounts of an ethylene–propylene segmented copolymer with very low crystallinity and an ethylene–propylene random copolymer. The block copolymer fraction accounted for more than 44 wt % of the alloys. The coexistence of these components with different structures was apparently the key factor resulting in the excellent toughness–stiffness balance of the materials. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 640–647, 2005

Key words: alloys; chain; mechanical properties

INTRODUCTION

The toughening modification of polypropylene (PP) has been widely studied in both science and application.^{1–6} Among the ways of toughening PP, the in-reactor blending of PP with other polyolefins (e.g., an ethylene–propylene random copolymer) by sequential multistage polymerization has been proved superior with respect to both polymer properties and production cost.^{7–9} A polypropylene/poly(ethylene-co-propylene) (PP/EPR) in-reactor alloy has been industrialized on a large scale. However, because there is more than 10% random copolymer (EPR) with a low modulus in this PP/EPR in-reactor alloy, this kind of toughened PP suffers from a significant drop in the flexural modulus in comparison with the PP homopolymer. A possible way of overcoming this drawback is to add polyethylene (PE) to the alloy, as PE is a crystalline polymer with moderate rigidity. Until now, there has been no literature on polyethylene/

polypropylene/poly(ethylene-co-propylene) (PE/PP/EPR) in-reactor alloys synthesized by multistage polymerization, and their chain structure and properties have never been reported either.

Since the 1990s, the main progress in the production of PP in-reactor alloy has come from the use of a spherical Ziegler–Natta catalyst.^{10,11} A PP/EPR alloy synthesized by the catalyst is in the form of regular, spherical granules and shows better mechanical properties than alloys synthesized with other common catalyst systems. The polymerization process also benefits from the spherical shape of the polymer granules, as risks of scaling and fouling in the reactor can be lowered. However, the preparation of a PE/PP/EPR in-reactor alloy with a spherical Ziegler–Natta catalyst has not been reported in the literature.

Recently, we have reported the synthesis and chain structure of a PE/PP in-reactor alloy with a superactive spherical Ziegler–Natta catalyst.¹² The in-reactor alloys show much improved impact strength, and the flexural modulus is only slightly lower than that of the PP homopolymer. Such good balance between toughness and rigidity is very important for applications as high-performance structural materials. However, the impact strength of a PE/PP two-component alloy is still not high enough for applications that require high toughness. Adding a certain amount of an ethylene–propylene random copolymer to a PE/PP alloy may further improve the toughness of the materials. In this

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article, we report the synthesis and chain structure of a new type of PE/PP/EPR in-reactor alloy, which is prepared by the polymerization of ethylene in the first stage, by the polymerization of propylene in the second stage, and by ethylene-propylene copolymerization in the third stage in a sequential reaction mode. Our experimental results show that the granules of this PE/PP/EPR alloy are mostly spherical, and the stiffness-rigidity balance of the alloy is better than that of the conventional PP/EPR in-reactor alloy.

EXPERIMENTAL

Synthesis of the PE/PP/EPR alloy

The PE/PP/EPR in-reactor alloy was synthesized in a four-stage polymerization process. In the first stage, or the prepolymerization stage, the slurry polymerization of propylene was conducted in a well-stirred glass reactor for 30 min. A high-yield spherical Ziegler-Natta catalyst, $\text{TiCl}_4/\text{MgCl}_2 \cdot \text{ID}$ (where ID is an internal donor), kindly donated by the Beijing Research Institute of Chemical Industry (Beijing, China), was used in the polymerization. The catalyst had a Ti content of 3 wt %. $\text{Al}(\text{C}_2\text{H}_5)_3$ (Fluka) was used as the cocatalyst ($\text{Al}/\text{Ti} = 60$), and $\text{Ph}_2\text{Si}(\text{OCH}_3)_2$ was used as the external donor ($\text{Al}/\text{Si} = 25$). Petroleum ether (30 mL; bp = 60–90°C) was used as the solvent. Propylene pressure in the prepolymerization stage was 1 atm, and the temperature was 50°C. A catalyst efficiency of 15–20 g of PP/g of catalyst was obtained in the prepolymerization stage. After the prepolymerization, the slurry containing the prepolymerized catalyst was transferred to a Büchiglasuster 0.5-L jacketed autoclave (Flawil, Switzerland). The propylene in the slurry was removed by the evacuation of the autoclave to 5 mmHg for 3 s, and ethylene was added to the autoclave to 0.6 MPa. Ethylene homopolymerization was carried out for 1 h at 60°C. After about 20 min of ethylene polymerization, all the solvent in the reactor was thoroughly absorbed into the polymer granules, so the polymerization could be regarded as a gas-phase process. At the end of this stage, ethylene was removed by evacuation to 5 mmHg for 3 min, and propylene was added to the autoclave and then continuously supplied to the reactor at 0.7 MPa for 2 h at 60°C. After the gas-phase PP polymerization stage, propylene was removed by evacuation to 5 mmHg for 3 min, and an ethylene-propylene mixture of a constant composition (ethylene/propylene = 1) was continuously supplied to the autoclave at 60°C. The pressure of the ethylene-propylene mixture for the HEPR sample was 0.7 MPa, and that for LEPR was 0.4 MPa. After ethylene-propylene copolymerization for 1 h, the reaction was terminated, and the product was washed with ethanol and dried *in vacuo*. The total catalyst efficiency for the four-stage polymerization

fell in the range of $3.4\text{--}4.5 \times 10^3$ g of polymer/g of catalyst.

Fractionation of the PE/PP/EPR alloy

A modified Kumagawa extractor (Hangzhou, China) was used to carry out a temperature-gradient extraction fractionation (TGEF) of the polymer.¹³ *n*-Octane was used as the solvent to successively extract samples at different controlled temperatures. Five fractions were collected at 25, 90, 110, 120, and >120°C from each alloy; the >120°C fraction was the residual sample after the extraction. The fractions were named the 25°C fraction, 90°C fraction, 110°C fraction, 120°C fraction, and >120°C fraction, respectively. The purified fractions were obtained after the extract solutions were concentrated, the polymer was precipitated, and the fractions were washed and dried *in vacuo*.

Measurements

Fourier transform infrared (FTIR) spectra of the alloys and fractions were recorded on a Bruker Vector-22 spectrometer (Karlsruhe, Germany). Thin films of the polymer prepared by hot pressing were used as samples.

¹³C-NMR spectra of the fractions were measured on a Bruker AMX400 NMR spectrometer at 100 MHz. *o*-Dichlorobenzene-*d*₄ was used as the solvent to prepare a 20 wt % polymer solution. The spectra were recorded at 120°C, with hexamethyldisiloxane as the internal reference. Broadband decoupling and a pulse delay of 5 s were employed. Typically, 1000 transients were collected. The ethylene content of the samples was determined on the basis of the peak area.

A differential scanning calorimetry (DSC) analysis of the fractions was carried out with a PerkinElmer Pyris 1 thermal analyzer (Wellesley, MA) under a nitrogen atmosphere. About 5 mg of a sample was sealed in an aluminum sample pan, heated to 180°C for 30 min, and annealed at 130, 120, 110, 100, 90, 80, 70, and 60°C for 12 h at each temperature. Then, the DSC scan was recorded at a heating rate of 5°C/min from 30 to 180°C. Multistep annealing of the samples ensured that the PE and PP segments of different lengths formed lamellae of different thicknesses; thus, the DSC melting curve could reflect the presence of these different lamellae.

The intrinsic viscosity ($[\eta]$) of the polymer fractions was measured with an Ubbelohde viscometer at 135°C with decahydronaphthalene as the solvent.

Mechanical properties

The notched Charpy impact strength of the alloy samples was measured on a Ceast impact strength tester (Chengteh, China) according to ASTM Standard D

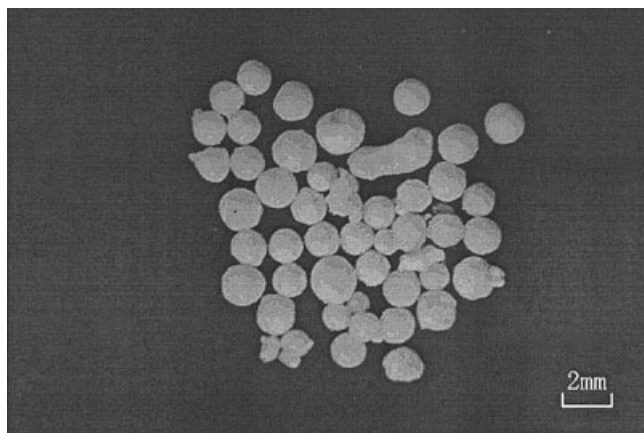


Figure 1 Morphology of the PE/PP/EPR in-reactor alloy granules.

256. The flexural modulus and flexural strength were measured according to ASTM Standard D 709 on a Reger 2000 electronic tester (Shenzhen, China). Sample plates (150 × 150 × 4 mm) for mechanical property measurements were prepared via compression molding at 180°C for 5 min under a pressure of 20 MPa. The samples were then cooled to room temperature in about 2 h. The sample strips for the tests were cut from the plates according to the ASTM standard.

RESULTS AND DISCUSSION

Overall structure and mechanical properties of the alloys

Two PE/PP/EPR alloy samples containing different amounts of ethylene were synthesized in this work. Figure 1 shows the morphology of the PE/PP/EPR in-reactor alloy granules. Most of the granules were spherical, and the size distribution of the granules was rather narrow. This feature is beneficial to for the large-scale production of PE/PP/EPR alloys in an industrial process.

In Table I, the ethylene contents and main mechanical properties of the two samples are listed. Both samples showed an excellent balance between toughness and stiffness. The values of the impact strength were much higher than that of a conventional isotactic polypropylene (iPP) homopolymer (ca. 4 kJ/m²). Meanwhile, the flexural modulus of the alloys was just

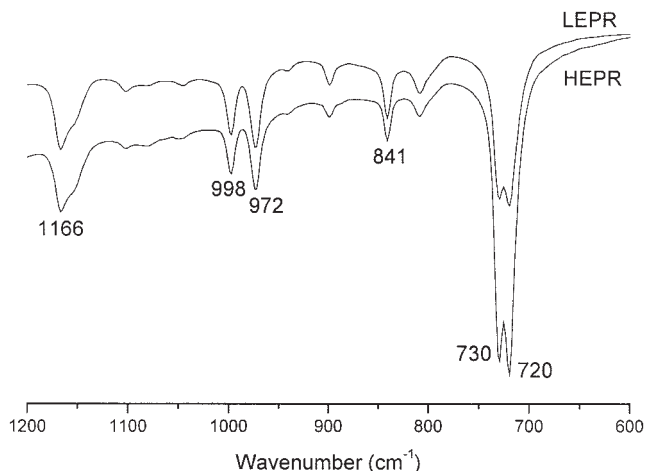


Figure 2 IR spectra of HEPR and LEPR.

a little lower than that of iPP (ca. 1600 MPa). There were also some differences in the mechanical properties for these two alloys. HEPR exhibited better impact properties but poorer rigidity than LEPR.

Figure 2 shows the FTIR spectra for these two PE/PP/EPR samples. The doublet at 720–730 cm⁻¹ is present for both samples, and this means that both samples contained crystalline PE chains or segments. The bands at 998 and 841 cm⁻¹, which represent iPP chains, are also present for both samples. Therefore, the PE/PP/EPR alloys were mainly composed of PE and iPP chains or segments. According to our previous work, there are a lot of PE-*b*-PP block copolymer chains present in a PP/PE in-reactor alloy.¹⁴ These block copolymer chains can act as compatibilizers between the PE and PP phases. To explore whether such a block copolymer also exists in PE/PP/EPR alloys, the two samples were fractionated into five fractions by TGEF.

Fractionation results

Table II lists the results of TGEF fractionation. The fraction distributions were quite different for these two samples. The main difference was in the amounts of the 90 and 110°C fractions. The sample containing a higher ethylene content (HEPR) had a markedly larger amount of the 90°C fraction but a smaller amount of the 110°C fraction.

TABLE I
Ethylene Content and Mechanical Properties of HEPR and LEPR

Sample	C ₂ (mol %)	Impact strength (kJ/m ²)	Flexural strength (MPa)	Flexural modulus (MPa)	[η] (dL/g)
HEPR	80.00	NB	10.8	1113.9	9.3
LEPR	71.62	111.3	14.0	1503.2	10.3

NB = not broken.

TABLE II
Fraction Distribution and Ethylene Content in Every Fraction

	Fraction (°C)									
	LEPR					HEPR				
	25	90	110	120	>120	25	90	110	120	>120
Fraction content (wt %)	5.7	4.9	33.4	44.7	11.3	7.0	14.2	22.9	47.7	8.2
C ₂ (mol %)	27.55	43.91	97.28	76.96	8.87	46.18	61.97	96.99	94.83	6.36

FTIR spectra of the fractions are shown in Figure 3. The doublet bands at 720–730 cm⁻¹, caused by the crystallization of PE segments of the 25°C fraction, are very weak. This shows that the PE segments were too short to crystallize. The doublet bands at 720–730 cm⁻¹ of the 90°C fraction are visible, and this indicates that some of the PE segments were long enough to form crystalline lamellae. For the other three fractions, the doublet bands at 720–730 cm⁻¹ can be clearly seen. Meanwhile, the bands at 998 and 841 cm⁻¹ are also detectable for these fractions. This means that both ethylene and propylene segments in these three fractions were crystallizable.

On the basis of the relative intensities of the characteristic IR bands of PE and PP, the change in the ethylene content in the fractions with the extraction temperature can be rationalized. The relative intensity of the PE bands increased gradually in the first three fractions, and this showed that the ethylene content increased with the extraction temperature. However, the intensity of the PE bands in the last fraction was very weak, and this meant few ethylene units in this fraction. This shows that both the composition and the microstructure, that is, the monomer distribution, affected the fractionation result by TGEF. The relative ethylene contents in the fractions extracted at the same temperature from the two different alloys can also be compared. The 25, 90, and 120°C fractions of HEPR contained more ethylene units than the corresponding fractions of LEPR, but the >120°C fraction of HEPR contained fewer ethylene units.

NMR analysis

To further explore the chain structures of the different fractions, ¹³C-NMR spectra of the 25, 90, 110, 120, and >120°C fractions from HEPR and LEPR were recorded and are shown in Figure 4.

The spectra of the two 25°C fractions are quite similar. They are typical spectra of a random ethylene-propylene copolymer. This random copolymer was mainly produced in the stage of ethylene-propylene copolymerization. Unavoidably, a little of the random copolymer was made during the switching of the monomers because there was a little ethylene left in the reactor (e.g., ethylene dissolved in the polymer granules) after the monomer switch from ethylene to

propylene. The spectra of the two 90°C fractions are quite similar too. There is a strong peak at 28.1 ppm that is the methylene signal of long PE sequences. Meanwhile, there are several peaks corresponding to the PPP sequence, such as P_{ββ} at 20.0 ppm, T_{ββ} at 26.8 ppm, and S_{αα} at 44.6 ppm; this means that there were long PP segments in the polymer chain. The peaks at 35.7–36.0 (S_{αδ} and S_{αγ}), 31.3 (T_{δδ}), 25.4 (S_{βδ}), 22.9 (S_{ββ}), and 18.1 ppm (P_{δδ}) indicate that there were also sequences such as PPEE, EEPEE, and PEP in the polymer chain.¹⁵ This shows that the 90°C fractions were segmented copolymers of ethylene and propylene. In combination with the FTIR results, we infer that some of the ethylene and propylene segments were long enough to crystallize. The peaks at 12.2, 21.0, and 30.3 ppm could be ascribed to high-boiling-point hydrocarbons, which may have come from the TGEF solvent.

The spectra of the 110°C fractions can be viewed as the mixed spectra of large amounts of PE and small amounts of PP. The peaks at 35.7–36.0 (S_{αδ} and S_{αγ}), 31.3 (T_{δδ}), 25.4 (S_{βδ}), 22.9 (S_{ββ}), and 18.1 ppm (P_{δδ}) are also visible in the spectra and indicate that there were also sequences such as PPEP, PPEE, EPE, and PEP in the chain.¹⁵ In our previous work,¹⁴ we found that PE homopolymer fractions could be eluted at a temperature lower than 120°C in temperature rising elution fraction, and PP chains of high isotacticity were extracted by TGEF only at temperatures higher than 120°C. The possibility that these fractions were PE/PP mixtures could be ruled out. Therefore, the PP segments were chemically linked with the PE segments, and an ethylene-propylene block copolymer existed in the 110°C fractions. However, the presence of the PE homopolymer could not be excluded. Considering the nonliving characteristic of the coordination polymerization and the wide extraction temperature range, we believe that the 110°C fractions were mixtures of PE and a PE-*b*-PP copolymer with very long PE segments and relatively short PP segments.

The two 120°C fractions also showed ¹³C-NMR signals typical of PE and PP. In the spectra of the two 120°C fractions, trace amounts of a junction structure between the PE segments and PP segments, represented by the S_{αδ}, S_{βδ}, or T_{βδ} peaks, can be detected. This is evidence that the PE and PP segments actually connected to form a block copolymer, and both blocks

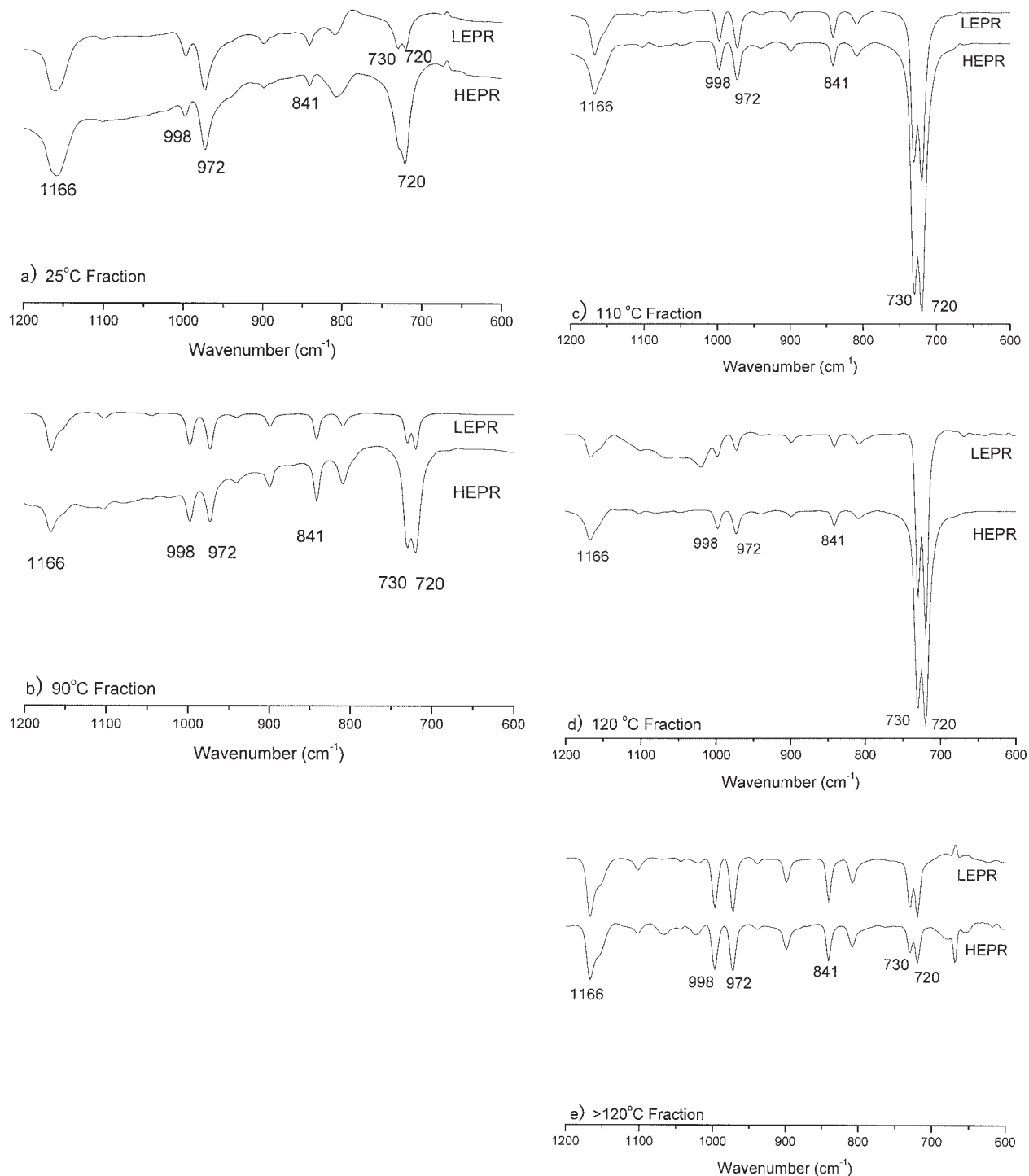


Figure 3 IR spectra ($1400\text{--}600\text{ cm}^{-1}$) of fractions of HEPR and LEPR: (a) 25°C fraction, (b) 90°C fraction, (c) 110°C fraction, (d) 120°C fraction, and (e) $>120^\circ\text{C}$ fraction.

were very long. The 120°C fraction from HEPR had a lower propylene content than LEPR.

The ^{13}C -NMR spectra of the two $>120^\circ\text{C}$ fractions are quite similar. In our previous work,¹² we found that the $>120^\circ\text{C}$ fraction of an alloy prepared in three stages (prepolymerization, ethylene homopolymerization, and propylene homopolymerization),

namely, a PE/PP alloy with a low ethylene content, was actually pure iPP. In these two ^{13}C -NMR spectra, a trace amount of $S_{\beta\delta}$ carbon can also be detected, and we concluded that the fractions extracted at $>120^\circ\text{C}$ were mixtures of pure iPP and a PE-*b*-PP block copolymer with very long PP segments and short PE segments.

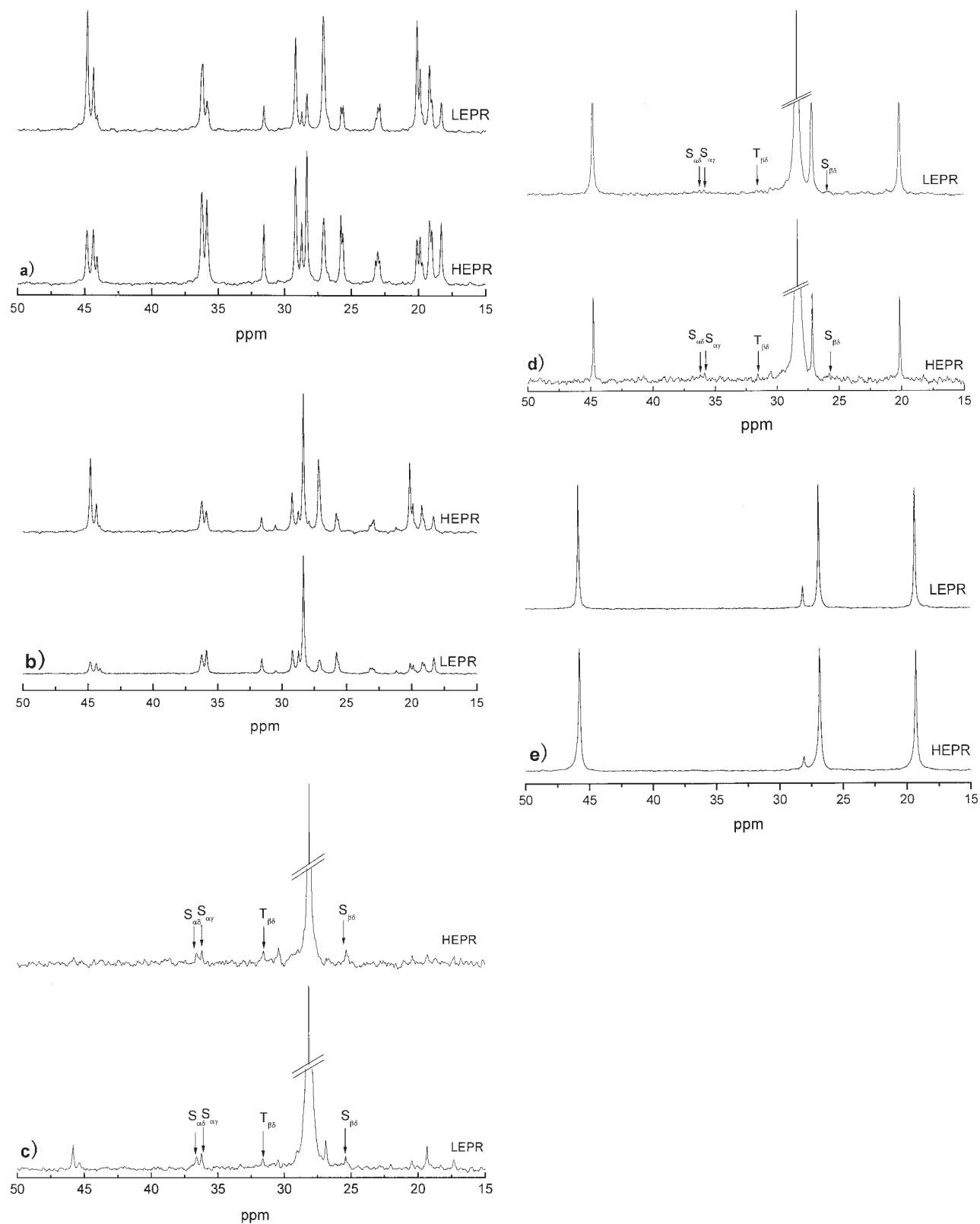


Figure 4 ^{13}C -NMR spectra of four fractions extracted at 25, 90, 110, 120, and $>120^\circ\text{C}$ in LEPR and HEPR: (a) 25°C fraction, (b) 90°C fraction, (c) 110°C fraction, (d) 120°C fraction, and (e) $>120^\circ\text{C}$ fraction.

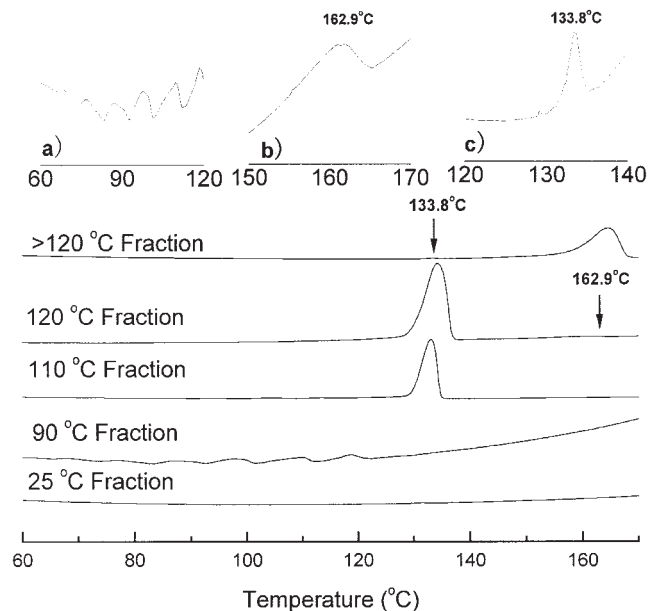


Figure 5 DSC curves of the five fractions from HEPR: (a) the inserted part of the DSC curve of the 90°C fraction at 60–120°C, (b) the inserted part of the DSC curve of the 120°C fraction at 150–170°C, and (c) the inserted part of the DSC curve of the >120°C fraction at 120–140°C.

Thermal analysis

A thermal analysis of annealed samples was also conducted to verify the chain structures of the different fractions. Multistep annealing of the samples ensured that PE and PP segments of different lengths formed lamellae of different thicknesses, and so the DSC melting curves could reflect the presence of these different lamellae. As shown in Figure 5, DSC melting curves of the five fractions from HEPR are very different. The room-temperature fraction was completely amorphous, and this agreed with the random structure detected by ^{13}C -NMR and invisible splitting bands caused by crystallization in FTIR.

The 90°C fraction shows several weak endothermic peaks in the range of 60–120°C. By comparing the results of ^{13}C -NMR and FTIR analysis, we concluded that these endotherms were mainly caused by the melting of PE lamellae of relatively short thickness. This means that the PE segments in this fraction were long enough to form crystals, but there were also many short PE segments, as the fusion enthalpy was much smaller than that of a PE homopolymer. This agreed with the segmented structure proved by ^{13}C -NMR.

The DSC curve of the 110°C fraction shows a strong melting peak at 133.1°C, which is close to the melting temperature of the PE homopolymer. From the ^{13}C -NMR results, we know that the 110°C fraction was a mixture of PE/PE-*b*-PP. The thermal analysis showed that the PE homopolymer accounted for the major part of this fraction.

The melting curve of the 120°C fraction shows two melting peaks at temperatures similar to those of PE and PP. However, the peak at 162.9°C is very weak. Comparing the results of ^{13}C -NMR analysis, we found that this fraction was mainly composed of a PE-*b*-PP block copolymer with very long PE and PP segments. Finally, the >120°C fraction also shows two peaks at 133.8 and 165.0°C, but the peak at the temperature similar to that of PE is very weak. This means that it was mainly composed of pure PP, in addition to a little PE-*b*-PP block copolymer with very long PP segments and short PE segments.

By combining the results of IR, NMR, and DSC analysis, we obtained a clear map of the chain structure and structure distribution of the PE/PP/EPR alloy. In both samples, the PE homopolymer was mainly found in the 110°C fraction, and the PP homopolymer existed in the >120°C fraction. The 120°C fraction was mainly composed of a block copolymer with very long PE and PP segments. These three fractions constituted more than 70% of the alloy. Two other components, an ethylene-propylene random copolymer and an ethylene-propylene segmented copolymer, were also present in the PE/PP/EPR alloys. The PE, PP, and EPR components had distinct mechanical properties, and the presence of the segmented copolymer and PE-*b*-PP block copolymer ensured high interfacial strength among the different phases. This unique chain structure of the PE/PP/EPR alloys led to the excellent balance between stiffness and toughness. On the other hand, there were some differences in the fraction distributions and compositions of the fractions for these two PE/PP/EPR alloys. LEPR had more 110°C fraction (PE) and >120°C fraction (PP) but less 25°C fraction (EPR), 90°C fraction (segmented copolymer), and 120°C fraction (block copolymer) than HEPR. The 25, 90, and 120°C fractions of LEPR had less ethylene than the corresponding fractions of HEPR. The data in Table I show that LEPR had a higher flexural modulus and flexural strength but a lower impact strength than HEPR. Because PP segments mainly contributed to the flexural modulus and PE segments and EPR mainly contributed to the impact properties, HEPR had more PE segments than LEPR, and this may be one of the reasons that the impact properties of HEPR were better than those of LEPR. Hence, we can conclude that the weight percentage of the PP homopolymer and the composition of the ethylene-propylene block copolymer were the major factors affecting the mechanical properties of the PE/PP/EPR alloys.

CONCLUSIONS

Two PE/PP/EPR in-reactor alloy samples were synthesized by multistage gas-phase polymerization with a spherical Ziegler-Natta catalyst. The alloys had ex-

cellent mechanical properties, including both toughness and rigidity. Both samples were fractionated by TGEF according to the chain structure of the fractions. The 110, 120, and $>120^{\circ}\text{C}$ fractions constituted more than 70% of the alloys. By FTIR, ^{13}C -NMR, and thermal analysis, it was proved that the alloys were mainly made up of PE, PE-*b*-PP block copolymer, and PP. The alloys also included a lot of an ethylene-propylene segmented copolymer with very low crystallinity and an ethylene-propylene random copolymer. The block copolymer fraction accounted for more than 44 wt % of the alloys. The coexistence of these components with different structures is believed to be the key factor resulting in the excellent toughness-rigidity balance of the materials.

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