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Structure and Properties of Isotactic Polypropylene/Polybutene-1 In-reactor Alloys

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Abstract The composition and structure of polymer largely determine the properties of its final products. As a novel polymer material, the composition, structure, and properties of the isotactic polypropylene/polybutene-1 in-reactor alloy (*i*PP/*i*PB alloy) synthesized by sequential two-stage polymerization with Ziegler-Natta catalyst were correlated for the first time in this work. The *i*PP/*i*PB alloy was fractionated by temperature rising elution fractionation (TREF) in a broad temperature ranged from -30°C to 140°C , and the chain microstructures and sequence distributions of isolated fractions were analyzed by DSC, GPC, ^{13}C -NMR, and FTIR. The *i*PP/*i*PB alloy was composed of five components, namely high isotactic PB (*i*PB, 85.8 wt%), medium isotactic PB (*m*PB, 5.1 wt%), poly((butene-1)-block-propylene) copolymers (PB-*b*-PP, 4.1 wt%) which contained PB and PP blocks with different lengths according to the isolation temperature, isotactic PP (*i*PP, 2.7 wt%), and atactic PB (*a*PB, 2.3 wt%). Compared to other commercial pipe materials, the *i*PP/*i*PB alloy presented outstanding thermal creep resistance and gas permeability resistance, high strength and low deformation at high temperature, and appropriate flexural strength. The roles of PP and PB-*b*-PP components in the alloy were interpreted. This work is expected to elucidate the potential application of *i*PP/*i*PB alloy as pipe materials and provide solutions for the design and synthesis of high performance pipe materials.

Keywords Polybutene-1; Alloy; Block copolymer; Structure; Property

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INTRODUCTION

Isotactic polybutene-1 (*i*PB) possessing excellent creep resistance, high toughness, and high thermal deformation temperature is widely used in hot-water pipe fields.^[1] *i*PB exhibits complex polymorphic behavior and can crystallize into hexagonal form I/I', tetragonal form II, or orthorhombic form III according to the crystallization situations.^[2–4] The kinetically favored metastable form II crystallized from molten state can transform into thermodynamically stable form I spontaneously and irreversibly, and finally *i*PB with significantly enhanced mechanical properties is obtained.^[5–11] However, this transformation usually takes more than one week and the long transition period inevitably increases the production cost of the *i*PB pipes. It was reported that mixing *i*PB with isotactic polypropylene (*i*PP) not only accelerated the II-I polymorphic transition, but also enhanced the strength of the final product.^[12–14] However, the *i*PP/*i*PB blend was a thermodynamically immiscible system and presented phase separated morphology,^[15–20] which led to unsatisfied properties of the *i*PP/*i*PB blends.^[21,22]

The *i*PP/*i*PB in-reactor alloys synthesized by sequential two-stage polymerization using MgCl_2 -supported Ziegler-Natta catalyst are proposed and expected to exhibit outstanding properties of *i*PB components without the above mentioned problems^[23–27] by the incorporation of *i*PP and PP-*b*-PB block copolymers. *i*PP might accelerate polymorphic transition of *i*PB from form II to form I,^[23] and the block copolymers might act as tie molecules to enhance the interfacial strength of *i*PP and *i*PB crystals and then contribute to higher impact resistance and higher tensile strength at higher temperature when compared with the mechanically blended *i*PP/*i*PB blends.^[24] However, the comprehensive properties of these alloys including the creep resistance, gas permeability, and water vapor permeability are not reported due to the small quantity of samples. Our previous works have reported that the *i*PP/*i*PB in-reactor alloys were analyzed by solvent extraction fractionation method and components including heptane soluble fraction (*i*PB), heptane insoluble fraction (*i*PP and block copolymers), and ether soluble fraction (atactic polymers) were obtained.^[25] Nevertheless, the accurate chain composition, chain sequence distribution, and fraction distribution of block copolymers in the *i*PP/*i*PB alloy and its influence on the properties of the alloy are not clear.

As an effective fractionation technique, temperature rising elution fractionation (TREF) has been used to fractionate semi-

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crystalline polymers such as polypropylene,^[28,29] polypropylene alloys,^[30,31] polyethylene/polypropylene alloys,^[32,33] *trans*-1,4-poly(isoprene-co-butadiene),^[34] and even poly(1-butene) copolymer^[35] according to the crystallizability of the polymer chains. In our recent work, a variety of copolymers containing various lengths of PB segments, PP segments, and poly(propylene-co-(butene-1)) segments were fractionated firstly by TREF to analyze the composition of the *i*PP/*i*PB alloys synthesized with varied vacuum treatment time between the propylene polymerization stage and butene-1 polymerization stage.^[36] However, the comprehensive properties of these alloys are not reported due to the small quantity of samples.

Herein, an *i*PP/*i*PB alloy synthesized with the 50 L autoclave was used to analyze the relationship between structure and properties of the multi-component alloy. Firstly, the alloy was fractionated by TREF within a broader elution temperature ranging from −30 °C to 140 °C. The chain microstructure and sequences distribution of main fractions were investigated by DSC, ¹³C-NMR, GPC, and FTIR techniques. The crystalline structures including the lamellae thickness of PB crystals in the alloy were studied by SAXS. The mechanical properties of the *i*PP/*i*PB alloy were characterized. The correlations between polymer chain structure, aggregation structure and mechanical properties of the *i*PP/*i*PB alloy were provided in this work. It was interesting to find that the *i*PP/*i*PB alloy with 93.2 wt% PB, 4.1 wt% PB-*b*-PP block copolymers and 2.7 wt% *i*PP showed excellent creep resistance, high strength, and low strain at high temperature, and enhanced gas permeability resistance, and had the potential application as hot-water pipe materials.

EXPERIMENTAL

Materials

The *i*PP/*i*PB alloy was synthesized by sequential two-stage polymerization in 50 L autoclave.^[25] As commercial pipe materials, *i*PB (PB4235, Lyondell Basell) and cross-linked polyethylene (PEX, Korea LG) were used as comparison to the *i*PP/*i*PB alloy. The physical parameters of these materials are summarized in Table 1.

Table 1 Physical parameters of the samples.

Sample	MFR ^a	$M_w^b \times 10^{-4}$	PDI ^b	Isotacticity ^c (wt%)	PP ^d (wt%)
<i>i</i> PP/ <i>i</i> PB alloy	0.48	79.0	7.8	97.8	13.8
<i>i</i> PB	0.54	73.0	5.1	97.4	—
PEX	—	—	—	—	—

^a Melt flow rate measured at 190 °C (2.16 kg) for *i*PP/*i*PB alloy and *i*PB; ^b Measured by high-temperature GPC; ^c Obtained by ¹³C-NMR; ^d Obtained by heptane extraction. No values for MFR and M_w of PEX due to cross-linking of this material.

Sample Preparation

The *i*PP/*i*PB alloy, *i*PB, and PEX sheets for the mechanical and physical property measurements were compression molded at 190 °C for 5 min under 10 MPa pressure, and then quenched at room temperature under 10 MPa pressure for 5 min. After room temperature aging for 10 days, the mechanical and physical properties of the sheets were tested.

Thin films of the fractions of *i*PP/*i*PB alloy for FTIR measurements were prepared by pressing on Specac GS03940 tabletting machine at 160 °C for 5 min under 20 MPa pressure.

P-TREF Experiment

Self-made preparative TREF (P-TREF) instrument with a broad temperature region (from −30 °C to 140 °C) was used to fractionate the *i*PP/*i*PB alloy. About 1.5 g of *i*PP/*i*PB alloy and 0.2 g of antioxidant (2,6-di-*tert*-butyl-4-methylphenol (264)) were added to xylene at 130 °C to get a clear solution with a concentration of 0.005 g/mL. Then the clear solution was quickly introduced into a glass elution column with 20 cm in length and 10 cm in diameter. The elution column stuffed with inert sea sands (0.3–0.6 mm size) was immersed in oil bath at 130 °C. Then the elution column was slowly cooled from 130 °C to −30 °C with a rate of 2 °C/h. The elution column was then heated up to a preprogrammed temperature from −30 °C to 140 °C with an interval of 10 °C at a rate of 1.0 °C/min, and synchronously eluted with xylene at the preprogrammed temperature for about 10 h after maintained at this temperature for 30 min. The elution solution was concentrated and precipitated by using plenty of ethanol and then filtered. The fractions were obtained by vacuum drying at 45 °C to constant weight. The fraction isolated at −30 °C was named as F−30°C and the fractions of other temperatures were all named according to this nomenclature.

Characterization

Differential scanning calorimetry (DSC) of polymer samples was carried out on DSC-8500 (PerkinElmer instruments) under the nitrogen flow. Firstly, about 5–10 mg of samples were heated from 30 °C to 200 °C with a rate of 10 °C/min. After maintained at 200 °C for 5 min to eliminate thermal history, the samples were cooled to 30 °C followed by reheating to 200 °C at 10 °C/min. The cooling and second heating curves of fractions of *i*PP/*i*PB alloy were recorded accordingly. The first heating curves of *i*PP/*i*PB alloy, *i*PB and PEX samples for mechanical tests were recorded. The relative crystallinity (X_c) of PB in *i*PP/*i*PB alloy was determined according to the Eq. (1) and the X_c of *i*PB and PEX was determined according to the Eq. (2).

$$X_c (\%) = \frac{\Delta H_m}{(1 - x_{pp})\Delta H_f^*} \times 100\% \quad (1)$$

$$X_c (\%) = \frac{\Delta H_m}{\Delta H_f^*} \times 100\% \quad (2)$$

where ΔH_m is the melting enthalpy tested from the first DSC heating curve, ΔH_f^* is the melting enthalpy of 100% crystallized PB (form I, 141 J/g) or PE (288 J/g),^[2,37] and x_{pp} is the weight percentage of PP in *i*PP/*i*PB alloy.

¹³C-nuclear magnetic resonance (NMR) measurements of the fractions were operated on 100 MHz Bruker AVANCE III spectrometer at 120 °C, and 1,2-dichlorobenzene-*d*₄ was used as the solvent. In the ¹³C-NMR spectra of PB, the characteristic signals at 40.3, 35.1, 27.8, and 10.8 ppm were ascribed to the main chain methylene, methyne, side chain methylene, and methyl, respectively. The concentration of pentad sequence [mmmm] of PB and PP was calculated from the CH₃ at 10.8 ppm and CH₃ at 21.8 ppm, respectively.^[38] In the ¹³C-NMR spectra of block copolymer fractions, signals at 42.6, 32.7 and

26.9 ppm were assigned to the butene-propylene sequence (BP), 30.0 and 23.4 ppm were assigned to PB and PB, respectively.^[36,39] The dyad sequence concentration [PP], [PB], and [BB] were calculated according to Eq. (3):

$$\begin{aligned} [\text{PP}] &= \frac{A_{28.9}}{A_{35.1} + A_{32.7} + A_{30.0} + A_{28.9}} \\ [\text{PB}] &= \frac{A_{32.7} + A_{30.0}}{A_{35.1} + A_{32.7} + A_{30.0} + A_{28.9}} \\ [\text{BB}] &= \frac{A_{35.1}}{A_{35.1} + A_{32.7} + A_{30.0} + A_{28.9}} \end{aligned} \quad (3)$$

where A represents peak area, and the subscript of A represents the chemical shift in ^{13}C -NMR spectrum.

The weight-average molecular weight (M_w) and polydispersity index (PDI) of fractions were determined on Waters GPC 2000 high-temperature gel permeation chromatography (GPC) at 150 ± 0.05 °C using 1,2,4-trichlorobenzene as the solvent. Polystyrenes were used as standards for all calibration curves.

Fourier transform infrared spectroscopy (FTIR) analyses of fractions were performed on Bruker TENSOR-II with 32 scans and a resolution of 4 cm^{-1} in the range of 400 cm^{-1} to 4000 cm^{-1} .

The wide-angle X-ray diffraction (WAXD) analyses of *i*PP/*i*PB alloy, *i*PB, and PEX samples were performed on a Rigaku/XRD-Uitima IV X-ray diffract meter with Cu K α radiation (wavelength $\lambda = 0.154\text{ nm}$) (40 kV, 40 mA) in a 2θ ranging from 5° to 40° with a scanning rate of $5^\circ/\text{min}$.

The small-angle X-ray scattering (SAXS) studies of *i*PP/*i*PB alloy, *i*PB, and PEX samples were carried out on Xenocs 2.0 equipment with incident X-ray Cu K α beam ($\lambda = 1.5418\text{ \AA}$) at room temperature. The distance from sample to detector was 2480 mm. Each pattern was collected within 60 s and then was background calibrated and normalized using the standard procedure. The long spacing d_{acr} , crystalline lamellae thickness d_c , and amorphous layer thickness d_a of these samples were calculated by the correlation function method.^[10]

Creep resistance was determined on a GT-7049 stress relaxation meter (GAOTIE Chemical Machinery, China) with 6.4 kg load (equivalent shear stress of 8 MPa) applied on the sample according to GB/T 11546.1-2008 at 70 °C for 600 min. Before the experiment, the samples were kept in measurement environment for 10 min to balance the temperature and humidity.

Gas permeability was measured on the i-Gastra 7100 differential pressure gas permeameter (Labthink Instruments Co., Ltd., China) according to GB/T 1038-2000. The measurement was carried out at 80 °C and 0% relative humidity with sample size of $110\text{ mm} \times 85\text{ mm} \times 2\text{ mm}$ (length $\times$ width $\times$ thickness) and effective measurement area of 38.48 cm^2 .

High temperature tensile strengths were tested with the A1-7000-S (GAOTIE Chemical Machinery, China) electrical tensile tester with a constant velocity of 50 mm/min according to HG/T 3868-2008 at constant temperature ranging from 20 °C to 100 °C.

Flexural strength was determined on the GT-TCS-2000 (GAOTIE Chemical Machinery, China) according to GB/T 9341-2008 at room temperature.

RESULTS AND DISCUSSION

TREF Fractionation and Fraction Analysis

In order to elucidate the exact fraction distribution as well as the structure and component of main fractions, the *i*PP/*i*PB alloy was fractionated step by step from -30 °C to 140 °C with TREF technology. Based on the fractionation principle, the crystallizability of the fractions increased with the increase in the elution temperature.^[35] The information of all fractions is summarized in Table 2. The main fractions were characterized with NMR, DSC, FTIR, and GPC.

Atactic PB components

The fractions isolated at rather low elution temperature normally have poor crystallizability.^[34,36] The BBBB sequences with 1,2-2,1-1,2-1,2-insertion of butene-1 monomers (a2 peak in Fig. 1A)^[40] and 36.7% pentad sequence concentration [mmmm] indicated the F-30°C was atactic PB (*a*PB). F-10°C and F0°C with rather weak melting temperature (T_m) peak (melting enthalpy about 0.7 J/g) (Fig. 2) were assigned to *a*PB. The rather weak bands at 923 cm^{-1} attributed to form I of *i*PB were observed in the FTIR spectra of F10°C and F20°C (Fig. 1B), indicating fractions including F10°C and F20°C were *a*PB. Therefore, the fractions eluted from -30 °C to 20 °C were *a*PB.

Medium isotactic PB components

Typical signals at 40.3, 35.1, 27.8, and 10.8 ppm representing the characteristic chemical shifts of main chain methylene, methyne, side chain methylene, and methyl of PB, respectively, were observed in the ^{13}C -NMR spectrum of F40°C with about 88.8% [mmmm] (Fig. 3).^[38] The relatively low T_c at about 60 °C (Table 2) and relatively low T_m at about 105 °C (Fig. 2) observed in F30°C and F40°C indicated these two fractions were medium isotactic PB (*m*PB).

High isotactic PB components

The F50°C, F60°C, and F70°C fractions showing typical chemical shifts of PB (Fig. 4) with 94.5%–94.8% [mmmm] (Table 2) and the high melting temperatures at about 113 °C (Fig. 2) were assigned to high isotactic PB (*i*PB).^[35]

Copolymer fractions

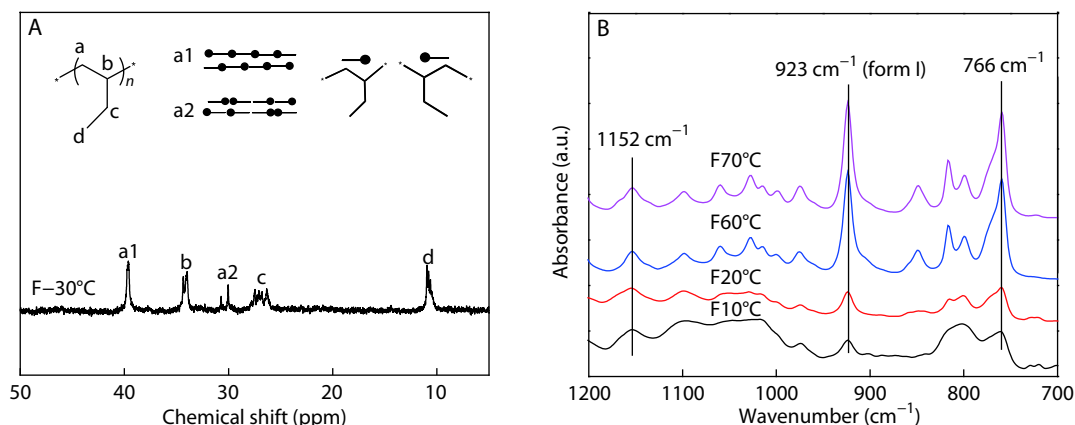
The fractions including F80°C–F110°C exhibited two T_m (Fig. 2) indicating the existence of both PB crystals ($T_m = 116$ °C) and PP crystals ($T_m = 145$ – 160 °C) in these fractions. Further, the 2.4 mol%–5.5 mol% propylene-butene dyad sequence concentration [PB] in F90°C, F100°C, and F110°C (Fig. 5, Table 2) proved that these fractions were copolymers with PB and PP blocks.^[39] The 93.4%–97.4% [mmmm] in the copolymers indicated the high isotacticity of both PB and PP blocks in these fractions.

However, the ^{13}C -NMR spectra of these fractions were totally different. Especially, the [PP]/[BB]/[PB] ratio in the fractions varied according to the fractionation temperature, indicating the exact chain sequence structures of these fractions were different. The propylene-propylene dyad sequence concentration [PP] increased from 22.7 mol% in F90°C to 50.3 mol% in F100°C, and then to 87.2 mol% in F110°C. Meanwhile, as the [PP] gradually increased with the increase of elution temperature, the T_m values of PP crystals in these fractions also increased from 145 °C to 161 °C, indicating much longer PP blocks formed more perfect crystals in fraction obtained at higher elution temperature. With the in-

Table 2 Characterization of the main fractions in *i*PP/*i*PB alloy.

Component	Fractionation temperature (°C)	Weight fraction (%)	Dyad sequence distribution (mol%)			[B] (mol%)	[P] (mol%)	PB sequence distribution (%)				PP sequence distribution (%)			
			[BB]	[PB]	[PP]			mmmm	mm	mr	rr	mmmm	mm	mr	rr
<i>a</i> PB	−30	1.85	100	0	0	100	0	36.7	78.9	19.6	1.5	—	—	—	—
	−20	0.04	—	—	—	—	—	—	—	—	—	—	—	—	—
	−10–0	0.20	100	0	0	100	0	—	—	—	—	—	—	—	—
	10–20	0.15	100	0	0	100	0	—	—	—	—	—	—	—	—
<i>m</i> PB	30	1.96	100	0	0	100	0	—	—	—	—	—	—	—	—
	40	3.15	100	0	0	100	0	88.8	91.1	6.7	2.2	—	—	—	—
<i>i</i> PB	50	76.56	100	0	0	100	0	94.5	96.9	0.7	2.4	—	—	—	—
	60	6.44	100	0	0	100	0	94.6	96.6	3.3	0.1	—	—	—	—
	70	2.84	100	0	0	100	0	94.8	95.6	3.9	0.5	—	—	—	—
PB- <i>b</i> -PP copolymer	80	0.28	—	—	—	—	—	—	—	—	—	—	—	—	—
	90	0.50	74.9	2.4	22.7	76.1	23.9	97.4	98.5	1.1	0.4	—	—	—	—
	100	0.59	44.2	5.5	50.3	46.9	53.1	94.4	96.7	1.0	2.3	93.4	94.7	3.5	1.8
	110	2.72	9.8	3.0	87.2	11.3	88.7	—	—	—	—	96.5	97.6	1.7	0.7
<i>i</i> PP	120	2.64	0	0	100	0	100	—	—	—	—	96.7	97.3	1.1	1.6
	130–140	0.08	0	0	100	0	100	—	—	—	—	—	—	—	—

Component	Fractionation temperature (°C)	$M_w \times 10^{-4}$	M_w/M_n	PB thermal properties			PP thermal properties			Chain structure model Butene-1 ● Propylene ○
				T_c (°C)	T_m (°C)	H_m (J/g)	T_c (°C)	T_m (°C)	H_m (J/g)	
<i>a</i> PB	−30	—	—	None	None	None	—	—	—	
	−20	—	—	—	—	—	—	—	—	
	−10–0	—	—	—	104	0.7	—	—	—	
	10–20	—	—	—	—	—	—	—	—	
<i>m</i> PB	30	—	—	62.8	106	16.6	—	—	—	
	40	—	—	54.2	105.2	21.4	—	—	—	
<i>i</i> PB	50	72.0	6.7	73.6	113.4	21.5	—	—	—	
	60	77.3	5.7	77.4	113.1	25.0	—	—	—	
	70	67.9	5.3	77.3	112.6	24.1	—	—	—	
PB- <i>b</i> -PP copolymer	80	77.8	4.3	79.0	116.3	18.6	98.9	144.9	10.2	
	90	—	—	84.5	116.5	21.5	104.1	151.4	10.7	
	100	—	—	83.5	116.2	9.4	114.0	159.2	39.0	
	110	15.7	3.0	84.8	114.3	2.6	115.5	161	58.5	
<i>i</i> PP	120	36.5	3.5	—	—	—	115.6	164.6	74.3	
	130–140	—	—	—	—	—	—	—	—	

**Fig. 1** ¹³C-NMR spectrum of F-30°C (A) and FTIR spectra of fractions (B).

crease in elution temperature, the butene-butene dyad sequence concentration [BB] decreased from 74.9 mol% in F90°C to 44.2 mol% in F100°C and then to 9.8 mol% in F110°C, while T_m of the PB crystals dropped from 116 °C to 114 °C, indicating that the much shorter PB block in F110°C did not affect the perfection of PB crystals greatly. According to the DSC and ¹³C-NMR results, these fractions F80°C–F110°C were

deemed as poly((butene-1)-block-propylene) (PB-*b*-PP) copolymers containing different length, of PB blocks and PP blocks.

High isotactic PP components

Fractions including F120°C, F130°C, and F140°C presenting one melting peak at 164.6 °C (Fig. 2), typical chemical shifts at 46.5, 28.9, and 21.8 ppm assigned to the main chain methylene,

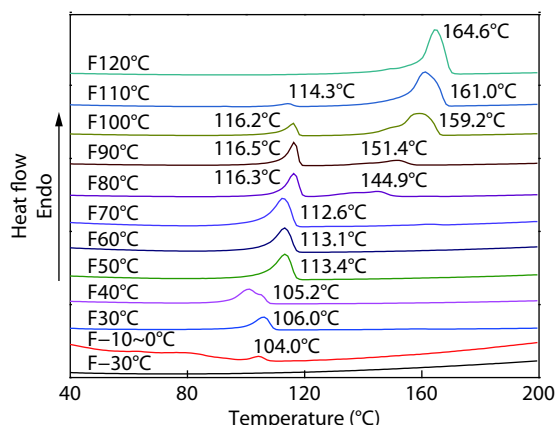


Fig. 2 The second scanning DSC curves of fractions isolated at different elution temperatures. The curve of F-10~0°C refers to the mixture of F-10°C and F0°C.

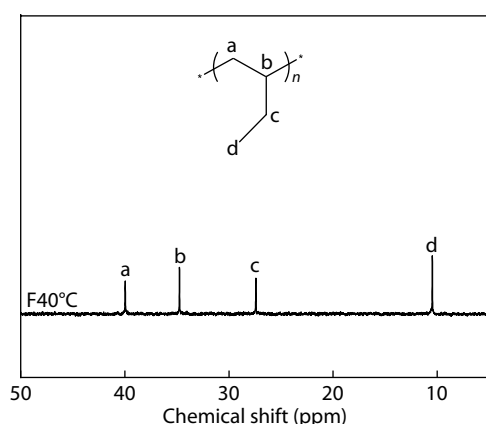


Fig. 3 ^{13}C -NMR spectrum of F40°C.

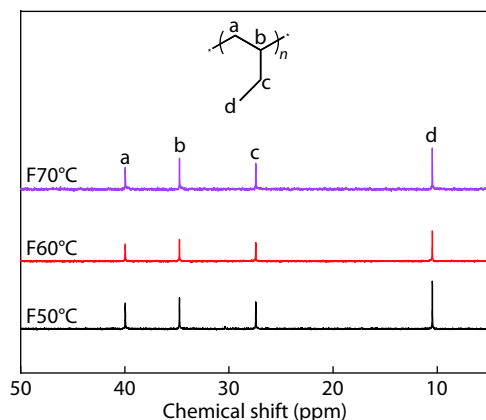


Fig. 4 ^{13}C -NMR spectra of F50°C, F60°C, and F70°C.

methyne and side chain methyl of PP (Fig. 6),^[38] and 96.7% [mmmm] (Table 2) were high isotactic PP (*i*PP) component.

The component distribution of *i*PP/*i*PB alloy including the chain sequence structure and weight-average molecular weight of copolymer fractions are summarized in Fig. 7 and Table 2. Based on the above analysis, the *i*PP/*i*PB alloy was composed of *i*PB (85.8 wt%, [mmmm] > 94%), *m*PB (5.1 wt%), PB-*b*-PP copolymers (4.1 wt%), *i*PP (2.7 wt%, [mmmm] > 96%)

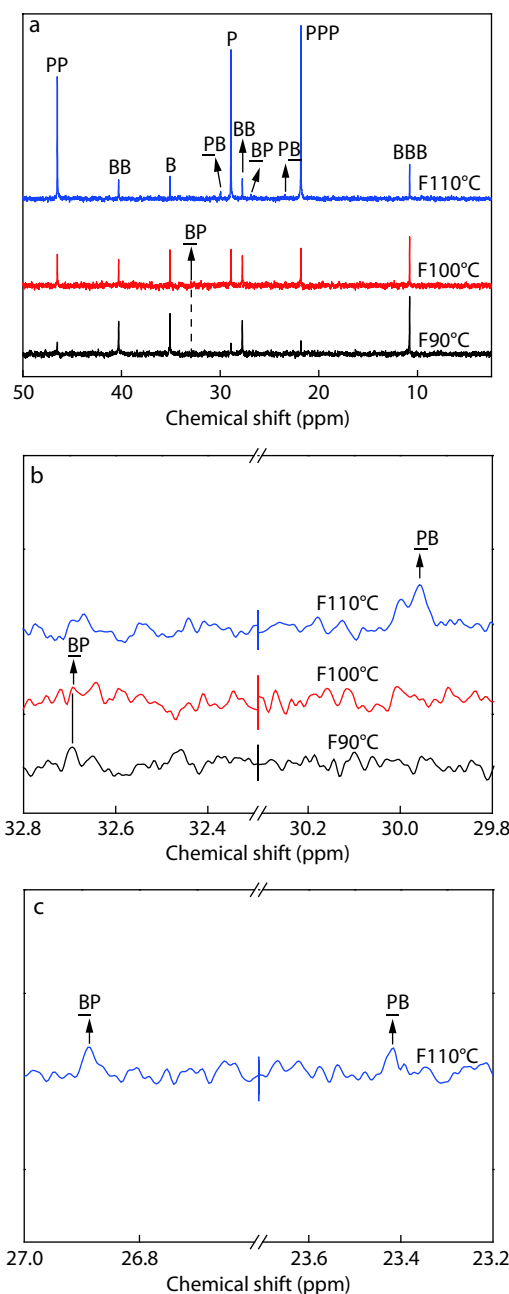


Fig. 5 ^{13}C -NMR spectra (a) and enlarged ^{13}C -NMR spectra (b, c) of F90°C, F100°C, and F110°C.

and *a*PB (2.3 wt%). PB component including *i*PB and *m*PB fractions as the major component occupied 90.9 wt% of the alloy. The length of PP blocks in PP-*b*-PB copolymers increased with the increase in elution temperature (Fig. 7b). The weight-average molecular weight (M_w) of *i*PP component obtained in the first polymerization stage was about 36.5×10^4 , while M_w of *i*PB component obtained in the second polymerization stage was in the range of 67.9×10^4 – 79.3×10^4 . M_w of block copolymers F80°C and F110°C was 77.8×10^4 and 15.7×10^4 , respectively, reflecting the active centers producing F80°C and F110°C might lie in different locations in the PP particles and have different sensitivities to the chain transfer agents.

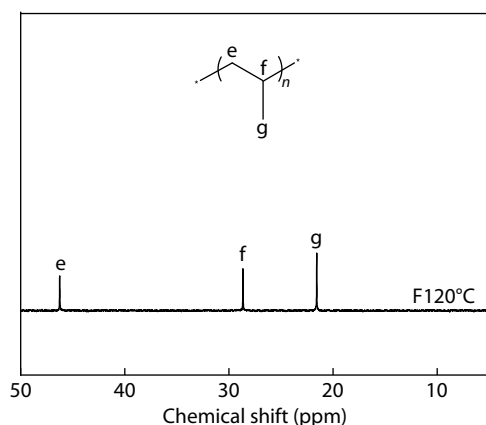


Fig. 6 The ^{13}C -NMR spectrum of F120°C.

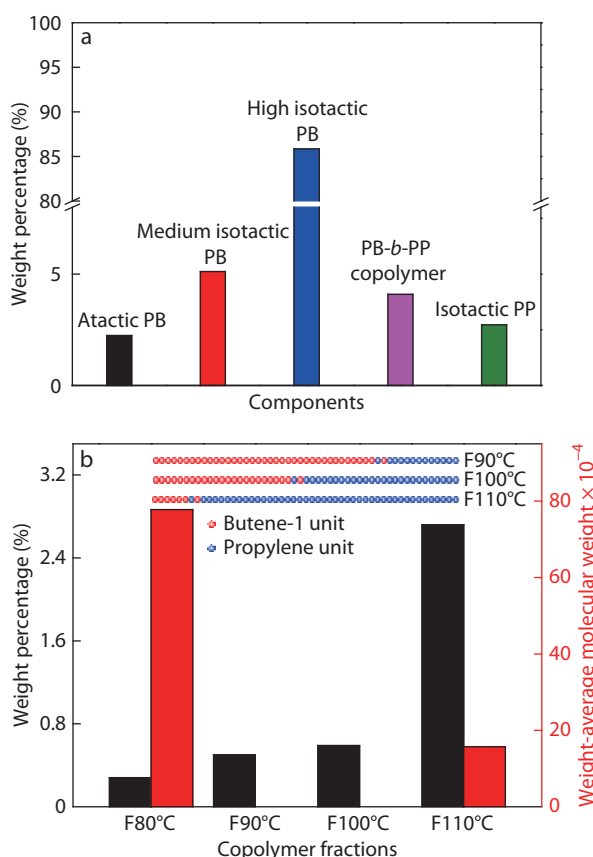


Fig. 7 Component distribution of *i*PP/*i*PB alloy (a), chain sequence structure and weight-average molecular weight of block copolymer fractions (b).

Properties of the *i*PP/*i*PB Alloy Compared with Other General Pipe Materials

DSC and WAXD

For comparison, the crystalline structures of *i*PP/*i*PB alloy and two commercial polymers including *i*PB and PEX were studied. The *i*PP/*i*PB alloy after aging at room temperature for more than one week showed a melting peak at 129.2 °C (Fig. 8a) assigned to form I of PB (Fig. 8b) with crystallinity (X_c) of 52.2%,^[2] which was very close to the commercial *i*PB ($T_m = 129.6$ °C, $X_c = 50.2\%$)

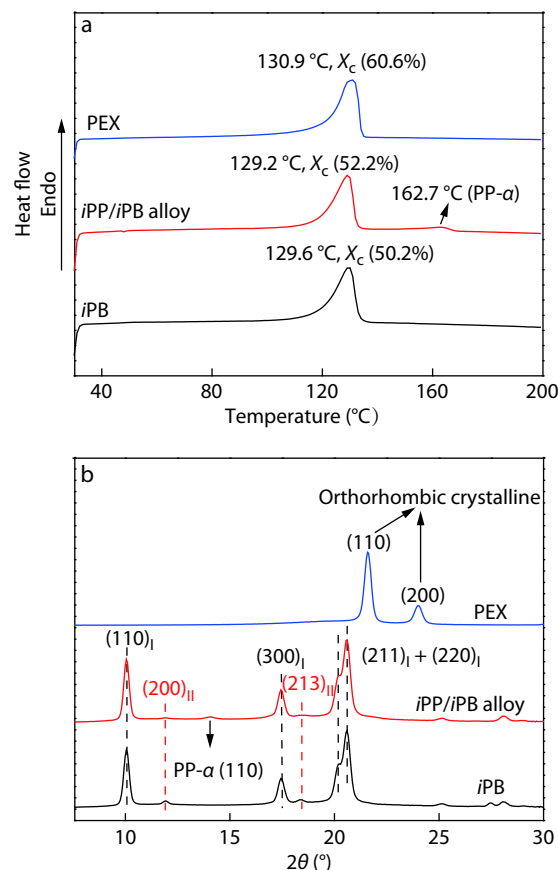


Fig. 8 The first heating DSC curves (a) and WAXD patterns (b) of *i*PP/*i*PB alloy, *i*PB, and PEX.

and PEX ($T_m = 130.9$ °C, $X_c = 60.6\%$) (Figs. 8a and 8b).^[37] However, the *i*PB after aging at room temperature for more than one week showed residue and weak diffraction peak of form II, which almost disappeared in the pattern of *i*PP/*i*PB alloy (Fig. 8b). This result indicated that the *i*PP/*i*PB alloy had much higher form II-I transformation rate and higher relative fraction of the form I ($X_I = 0.93$) than that in *i*PB ($X_I = 0.89$).^[10] The weak melting peak at 162.7 °C observed in the *i*PP/*i*PB alloy in Fig. 8(a) was assigned to α -PP crystal as proved by the weak diffraction peak at $2\theta = 14.1^\circ$ in Fig. 8(b).

SAXS

Two ordered scattering peaks were observed in one-dimensional scattering intensity distribution curves (Fig. 9a), indicating the formation of regular stacked layered crystal structures in these samples.^[7] The values of d_{ac} , d_c , and d_a of PB form I in *i*PB and *i*PP/*i*PB alloy calculated by resultant correlation function curves of Fig. 9(b) are shown in Fig. 9(c).^[41] The d_c of *i*PP/*i*PB alloy was 19.0 nm, which was a little larger than that of *i*PB (18.3 nm) and much larger than that of PEX (12.6 nm). The crystalline structures of the semi-crystalline polymers determine the properties and applications of the products. The highest crystalline lamellae thickness of PB in the *i*PP/*i*PB alloy was expected to contribute to the increased stiffness, modulus (E), yield stress (σ_y), chemical resistance and dimensional stability, and decreased yield strain (ϵ_y).^[42] In addition, dense chain packing in the crystalline phase reduced the free volume of the

gas transportation and thus improved the gas resistance of the *i*PP/*i*PB alloy.^[43]

Creep resistance

Creep resistance as one of the most important properties was used to characterize the size stability at high temperature for materials as pipe application. *i*PB as the polyolefin with the best creep resistance was used as comparison to evaluate the creep behavior of *i*PP/*i*PB alloy.^[1] Fig. 10 clearly illustrates that *i*PP/*i*PB alloy containing a small amount of *i*PP and block copolymer components showed excellent thermal creep properties at 70 °C

with much smaller deformation than that of *i*PB. Therefore, the incorporation of 2.7 wt% *i*PP and 4.1 wt% block copolymer components did improve the creep resistance of the alloy.

Permeability resistance

As another important parameter to evaluate the pipe material, permeabilities including gas permeability (Fig. 11a) and water vapor permeability (Fig. 11b) of samples were investigated. It can be seen that CO₂ permeability was the highest and the air

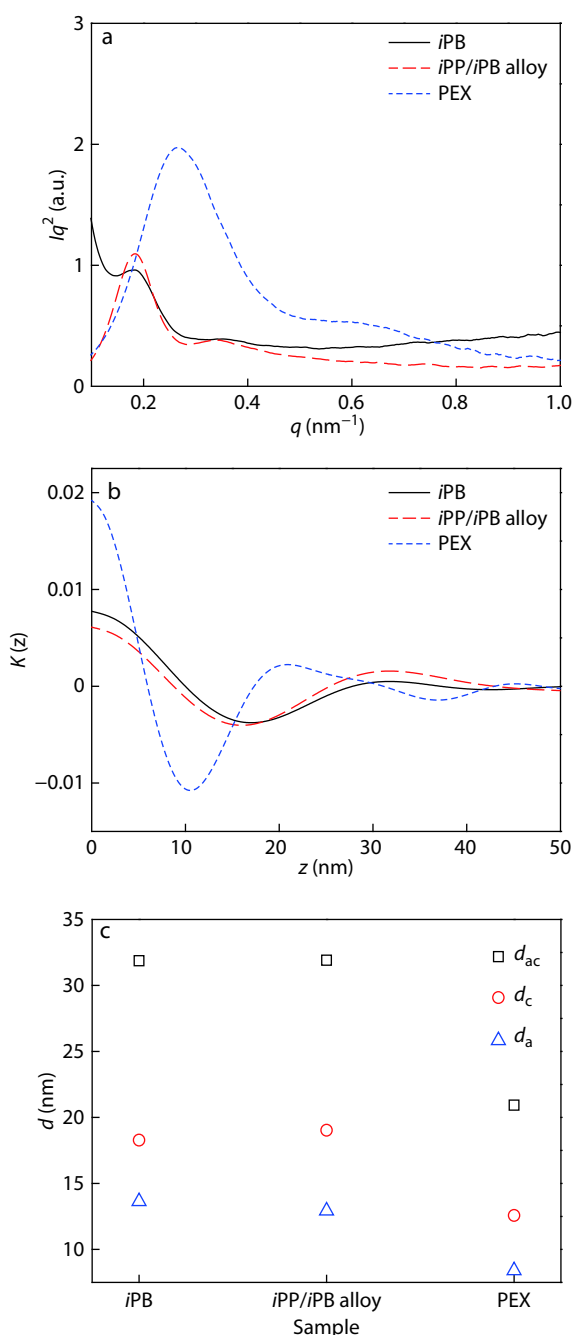


Fig. 9 Evolution of one-dimensional scattering intensity distribution (a), $K(z)$ curves calculated by correlation function (b), and crystalline parameters (d_{ac} , d_c , d_a) (c) of *i*PP/*i*PB alloy, *i*PB, and PEX.

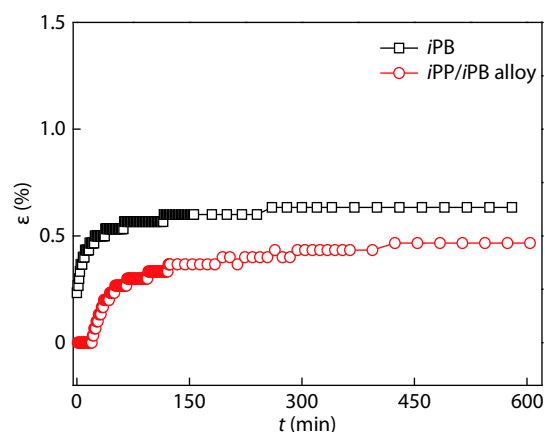


Fig. 10 Creep behaviors of *i*PP/*i*PB alloy and *i*PB at 70 °C.

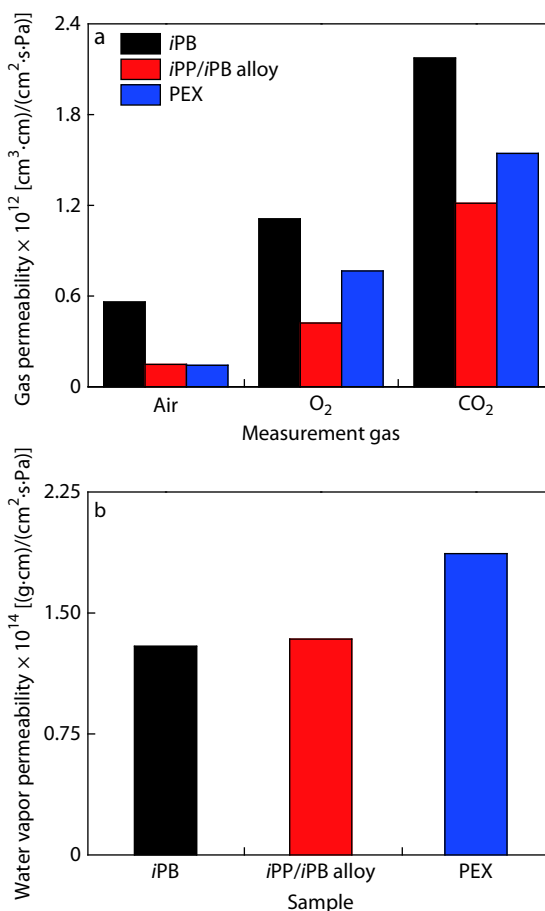


Fig. 11 Gas permeability (a) and water vapor permeability (b) of *i*PP/*i*PB alloy, *i*PB, and PEX.

permeability was the lowest for all three materials (Fig. 11a). The permeability is mainly influenced by the molecular size, solubility in the membrane, and condensation temperature of the gas molecules.^[44] Compared with other gases, CO₂ with higher solubility in the membrane and small molecular size showed higher permeability.^[44] It was worth noticing that *i*PP/*i*PB alloy showed the lowest permeability for air, O₂, and CO₂, and much lower than that of *i*PB, indicating the *i*PP/*i*PB alloy had much better gas permeability resistance when compared with *i*PB. The water vapor permeabilities of *i*PP/*i*PB alloy and *i*PB were almost similar (Fig. 11b), both lower than that of PEX. The higher water vapor permeability resistance of these materials when compared with that of gas was due to the polarity of water vapor providing high difficulty in permeability.^[45]

Tensile tests

The mechanical properties including strengths at different deformations (10%, 100%) at constant temperature ranging from 20–100 °C are represented in Fig. 12. It can be observed that the strengths of all samples decreased and the elongations at break increased with increasing test temperature, which resulted in the gradual melting of the crystals and movements of the polymer chains. *i*PB and *i*PP/*i*PB alloy showed the similar strength at 10% and 100% elongation. Although the strengths at 10% elongation of PEX at 20–60 °C were higher than those of *i*PB and *i*PP/*i*PB alloy, the strengths of PEX at 80–100 °C

became lower than those of *i*PB and *i*PP/*i*PB alloy (Fig. 12a). The higher strength at the high temperature of *i*PP/*i*PB alloy was attributed to its thicker lamellae thickness, which provided the integrity of the aggregation structure and then higher thermal stability of the *i*PP/*i*PB alloy at the higher temperature. The strengths at 100% elongation of *i*PP/*i*PB alloy and *i*PB were higher (Fig. 12b), and the elongations at break of *i*PP/*i*PB alloy and *i*PB (Fig. 12c) were lower than those of PEX at all testing temperatures. The *i*PP/*i*PB alloy possessed excellent size stability under higher temperature. Flexural strength of *i*PP/*i*PB alloy was around 15 MPa (Fig. 12d), which is similar to those of *i*PB and PEX, and can meet the requirements of winding, installation, and debugging of pipes, sheets, etc. in actual production.^[1]

Discussion on the Relations for Composition, Structure and Properties of the *i*PP/*i*PB Alloy

The superior properties of semi-crystalline materials are naturally attributed to their structural advantages, which are mainly reflected by the microstructure and crystal structure of the materials.^[46] Our previous work has proved that *i*PP/*i*PB blends showed the low critical solution temperature (LCST)-like phase-separated structure.^[20] However, compared with the *i*PP/*i*PB blends containing the same PP content by mechanical blending method, the *i*PP/*i*PB alloy exhibited phase-separated structure with much smaller PP domains, which was attributed to the compatibilization of block copolymers.^[24] As shown in Fig. 13,

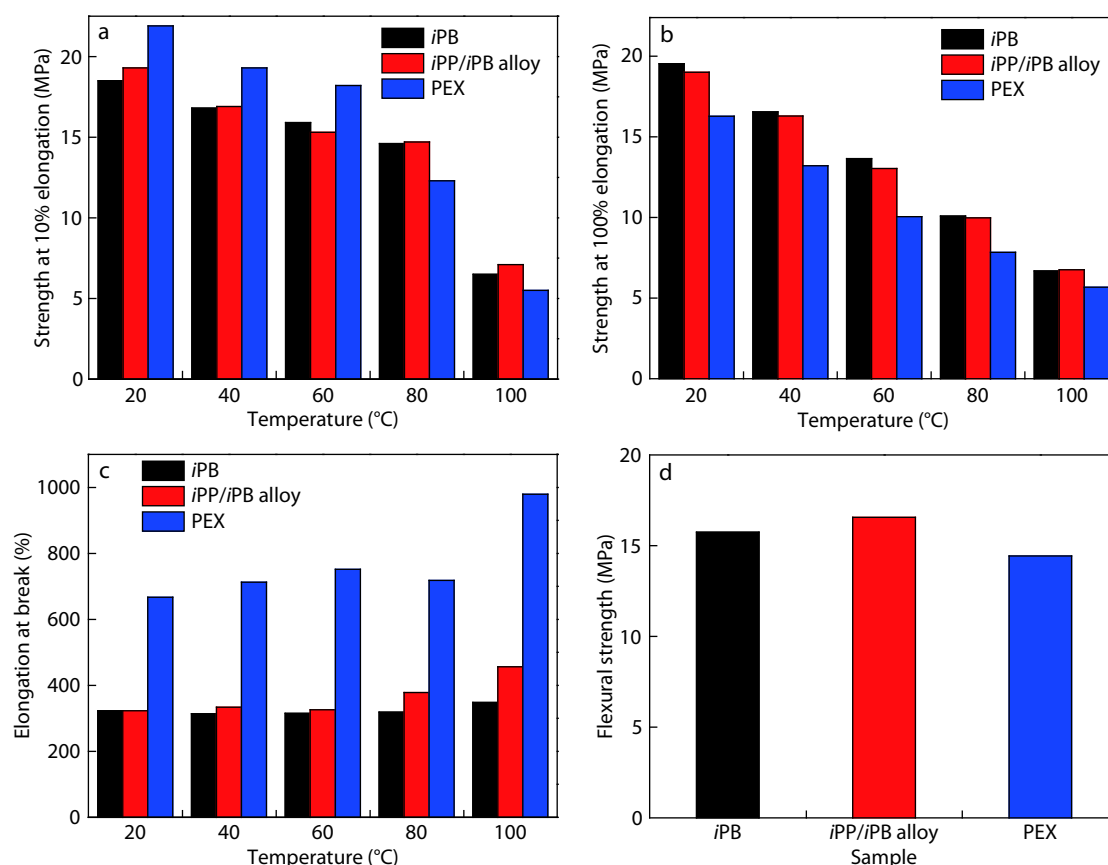


Fig. 12 Strength at 10 % elongation (a) and 100 % elongation (b), elongation at break (c), and flexural strength (d) of *i*PP/*i*PB alloy, *i*PB and PEX. The tensile properties were tested at constant temperature ranging from 20–100 °C and flexural strength were tested at room temperature.

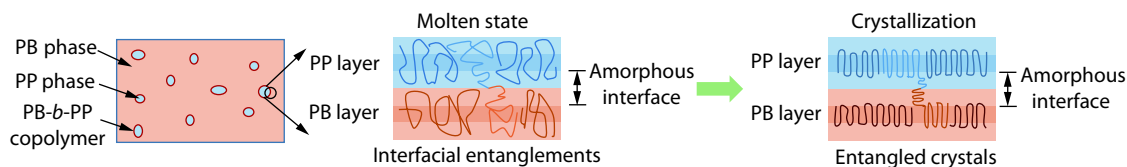


Fig. 13 Schematic illustration of the aggregation structures in *iPP/iPB* alloy.

the block copolymers in the *iPP/iPB* alloy may act as a tie molecule to enhance the interfacial entanglements between the PB and PP domains in the molten state.^[24] The subsequent cooling and crystallization led to the stronger interfacial interaction between the PB and PP crystals, which could promote the stability of molecular chains and effectively constrain the mobility of polymer chains, resulting in higher mechanical properties of the *iPP/iPB* alloy, including excellent creep resistance and high strength at higher temperature.^[24,47,48] The PP component in *iPP/iPB* alloy not only significantly accelerated the transformation of form II-I, but also acted as nucleating agents to induce PB to crystallize at a higher temperature than that of neat *iPB*,^[24] and resulted in much thicker PB lamellae in *iPP/iPB* alloy.^[2] The thicker lamellae of PB in the *iPP/iPB* alloy could provide the integrity of the aggregation structure and higher thermal stability at higher temperature, which contributed to a higher strength at high temperature and improving the gas resistance.^[49]

CONCLUSIONS

The *iPP/iPB* in-reactor alloy synthesized by sequential two-stage polymerization using MgCl_2 -supported Ziegler-Natta catalyst was mainly composed of 85.8 wt% *iPB*, 5.1 wt% *mPB*, 2.7 wt% *iPP*, 4.1 wt% PB-*b*-PP, and 2.3 wt% *aPB*. The minor PP component in *iPP/iPB* alloy not only accelerated the transformation of form II-I, but also benefited the increase in PB lamellae thickness without destroying the integrity of PB aggregate structures. The PB-*b*-PP block copolymers acting as the tie molecules improved the interfacial interactions between PP and PB crystals. Consequently, the resultant *iPP/iPB* alloy with thicker PB lamellae and improved interfacial interactions between PP and PB crystals presented the greatly satisfied mechanical properties including improved creep resistance and gas permeability resistance, tensile strength at high temperature compared with other general pipe materials.

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