

Influence of Catalyst Residues on Thermo-oxidative Aging and Thermal Stability of Poly(butene-1)*

Bao-yu Sun, Lei Cui, Xiu-bo Jiang, Bai-yu Jiang, Wei Yao** and Ai-hua He**

Key Laboratory of Rubber-Plastics, Ministry of Education/Shandong Provincial Key Laboratory of Rubber-Plastics, School of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

Abstract Isotactic poly(butene-1) (*i*PB) with spherical morphology was synthesized successfully with bulk precipitation polymerization without post-treatment of the products. The bulk precipitation polymerization process made it possible for *i*PB to be used as general plastic due to the acceptable decreased cost compared with the solution polymerization process. The influence of catalyst residues on the aging and thermal stability of *i*PB synthesized by bulk precipitation polymerization method was investigated by gel permeation chromatography, mechanical performance testing, thermogravimetric analysis and infrared spectroscopic analysis. Commercial *i*PB and the lab-made *i*PB with varied catalyst residue contents were studied. The results demonstrated that the catalyst residues played an important role in the aging process of the *i*PB. A possible mechanism of aging promotion by catalyst residues was proposed.

Keywords: Catalyst residues; Poly(butene-1); Aging; Thermal stability.

INTRODUCTION

Isotactic poly(butene-1) (*i*PB) is a semicrystalline polyolefin with some attractive mechanical properties, such as excellent resistances to creep and environmental stress cracking, good impact resistance, high-temperature resistance, high tear strength and outstanding elastic recovery^[1–3], which is considered as the best candidate for the application as hot-water pipes.

Generally, industrial *i*PB was synthesized *via* solution or gas phase polymerization with MgCl₂-supported TiCl₄/AlEt₃ catalysts^[2, 3]. Recently, our research group has successfully worked out a new bulk precipitation technology for butene-1 polymerization with supported Ziegler-Natta catalysts^[4–6]. Bulk precipitation technology showed some advantages including relatively low polymerization viscosity, no solvents, and simple post-processing without solvent recycle, purification and pelleting. Due to the fact that *i*PB is easy to dissolve in the butene-1 monomer, a low polymerization temperature is required to ensure the separation of *i*PB from its monomer during the bulk precipitation process, which inhibits the catalytic activity of the supported Ziegler-Natta catalyst. So the catalyst residues in the final *i*PB products should not be neglected based on the present bulk precipitation technology.

The catalyst residues, containing Ti, Mg, and Al metallic elements, led to jamming of the processing equipment and the drop of the performance of the materials. For polypropylene (PP) fiber production, the ash content in PP should be lower than $\delta = 100$ ^[7].

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** Corresponding authors: Wei Yao (姚薇), E-mail: yaowei@qust.edu.cn

Ai-hua He (贺爱华), E-mail: aihuahe@iccas.ac.cn

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Attentions have been paid to the aging property and aging mechanism of PP and *i*PB^[8–17]. Recently, the aging property of PB pipes under different internal pressures has been discussed. And the diffusion coefficient was constant through the pipe wall. It has also been suggested that the chlorine caused the oxidation. The lifetime of the pipe was significantly shortened even at relatively low chlorine contents in water^[8–10]. In addition, thermal and photo oxidation played an important part in the aging of polyolefin, a series of triazines were studied and introduced in the polyolefin materials as antioxidants^[11–17]. Photo-oxidative degradation of *i*PB in the presence and absence of copper (II) bis-(1,3-diphenyl triazine-N-oxide) (CPTO) chelate has been studied by Regional Engineering College. The experiment result indicated that CPTO could retard the photo-oxidative degradation of *i*PB and showed similar aging-resistant mechanism with PP due to the similar structure of PB and PP^[16, 17]. Gijsman *et al.*^[18] studied the influence of catalyst residues on the oxidation rate of PP at different temperatures. Epacher *et al.*^[19] found the content of the double bonds on aged PP increased with the increment of catalyst residues with or without addition of stabilizer.

In this study, the influence of catalyst residues on the aging and thermal stability of *i*PB synthesized by bulk precipitation polymerization was evaluated. Four kinds of *i*PB samples (the commercial and the lab-made ones) with different catalyst residue contents were characterized by GPC, mechanical performance testing, TG and FTIR. The work provided a basic aging understanding based on different catalyst residue contents of *i*PB to explore the commercial application of *i*PB synthesized by bulk precipitation polymerization.

EXPERIMENTAL

Materials

Four poly(butene-1) samples included a commercial *i*PB one (P5050N) labeled as *i*PB-1 and three lab-made *i*PB labeled as *i*PB-2, *i*PB-3 and *i*PB-4, respectively. The physical parameters of these *i*PB samples are shown in Table 1. The *i*PB samples were plasticized by an SK-160B two roll rubber mixing mill at 110 °C, then hot pressed at 140 °C for 10 min and then cold pressed at room temperature for 6 min by an XQLB-350 × 350 vulcanizing press to obtain the *i*PB sheets. The *i*PB sheets were aged at room temperature for a week to provide the samples enough time to finish the crystal transformation from metastable phase II to stable phase I. Finally the aged *i*PB sheets were used for the following characterization.

Table 1. Physical parameters of the *i*PB samples

Samples	Isotactic content ^a (%)	MFI ^b (g/10 min)	Ti ^c (mg/kg)	Al ^c (mg/kg)	Mg ^c (mg/kg)
<i>i</i> PB-1 (Mitsui P5050N)	97.0	0.52	0.2	6.5	2.8
<i>i</i> PB-2 (Lab-made)	96.5	0.27	0.8	48.5	7.7
<i>i</i> PB-3 (Lab-made)	96.0	0.40	2.0	285.5	24.7
<i>i</i> PB-4 (Lab-made)	95.4	0.36	8.0	569.7	113.4

^a The isotactic content of *i*PB was measured by boiling ether extraction for 48 h;

^b Melt flow index was tested at 190 °C with a load 2160 g (ASTM D1238);

^c The *i*PB samples were treated under high temperature in a quartz crucible and the finally obtained ash was dissolved in acid solvent for the metallic ions measurement with a IRIS Intrepid II XSP plasma spectrometer (Thermo Fisher, USA)^[20].

Tensile Test

The tensile properties were evaluated by a tensile tester (GT-AI-7000M) according to GB/T 1040.2-2006. The testing speed was 50 mm/min.

Aging Test

The *i*PB sheet samples were put in a thermal-oxidative aging oven (401A) at 70 °C for 7 days. After thermo-oxidative aging, all the samples were transferred to atmosphere at room temperature for another week before the following measurements.

GPC Test

The molecular weight and the polydispersity index (PDI) of *i*PB were measured by gel permeation chromatography (GPC, PL-GPC220) in 1, 2, 4-trichlorobenzene at 150 ± 0.05 °C. Narrow molecular weight polystyrene (PS) samples were used as standards for calibration.

TGA

Thermogravimetric analysis (TGA) was performed with a Netzsch TG209 thermogravimetric analyzer at a heating rate of 10 K/min under nitrogen atmosphere.

FTIR Measurement

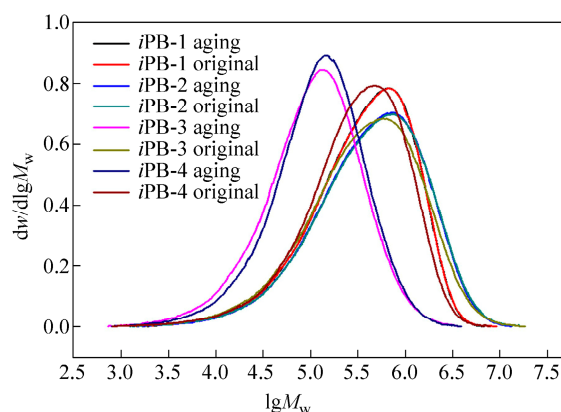
Fourier-transform infrared (FTIR) spectra were recorded on a Magna-IR Spectrometer750 instrument using ATR (ZnSe cell) at a resolution of 4 cm^{-1} by 32 scans. ATR corrections were used and pressure was applied to the samples.

RESULTS AND DISCUSSION**Molecular Weight and Molecular Weight Distribution of the *i*PB**

The effects of the catalyst residues on the molecular weight and molecular weight distribution of *i*PB were investigated, and the results are shown in Table 2 and Fig. 1.

Table 2. GPC test of samples before and after aging

Samples	Original <i>i</i> PB		<i>i</i> PB after aging	
	$M_w \times 10^{-5}$ (g/mol)	M_w/M_n	$M_w \times 10^{-5}$ (g/mol)	M_w/M_n
<i>i</i> PB-1	6.35	5.0	6.31	4.9
<i>i</i> PB-2	8.80	6.7	8.54	6.2
<i>i</i> PB-3	7.89	6.9	1.64	4.2
<i>i</i> PB-4	5.46	5.1	2.07	3.8

**Fig. 1** GPC curves of all samples before and after aging

As Table 2 showed, almost no changes in M_w were observed for *i*PB-1 and *i*PB-2 after thermal-oxidative aging process. This indicated that both *i*PB-1 (Mitsui P5050N) and *i*PB-2 (lab-made) samples possessed excellent aging resistant performance. While for *i*PB-3 and *i*PB-4 with increased catalyst residues, great changes of the molecular weights were observed, as shown in Table 1. The GPC peaks of *i*PB-3 and *i*PB-4 after thermal-oxidative aging shifted to longer elution time obviously (as shown in Fig. 1), which indicated that the *i*PB-3 and *i*PB-4 samples after thermal-oxidative aging degraded assuredly and their molecular weight decreased accordingly. The *i*PB-3 with higher molecular weight degraded more obviously. From Table 1, the molecular weight distribution of *i*PB-3 and *i*PB-4 after thermal-oxidative aging became much narrower compared with the original samples, and M_w/M_n changed from the original value 6.9 and 5.1 to 4.2 and 3.8, respectively. This was due to the fact that more degradation reactions occurred in high-molecular-weight fractions of polymers.

Mechanical Properties

The mechanical properties of original and aged samples are shown in Table 3 and the retention rate of mechanical property and aging coefficient are shown in Table 4. As we all knew, the high aging coefficient and retention rate of mechanical properties represented a better aging resistant performance.

Table 3. The mechanical properties of the original and the thermal-oxidative aging samples

Samples	Original samples			After aging		
	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)
<i>iPB</i> -1	22.5	27.2	233	22.4	25.9	207
<i>iPB</i> -2	35.1	36.5	357	31.4	34.5	347
<i>iPB</i> -3	19.9	19.7	180	12.3	12.3	18
<i>iPB</i> -4	31.2	33.3	330	15.3	16.1	113

Table 4. The retention ratio^a of mechanical properties and aging coefficient^b

Samples	Retention ratio of yield strength (%)	Retention ratio of tensile strength (%)	Retention ratio of elongation at break (%)	Aging coefficient (%)
<i>iPB</i> -1	99.6	95.2	89.0	84.7
<i>iPB</i> -2	89.5	94.5	97.2	91.9
<i>iPB</i> -3	61.8	62.4	10.1	6.3
<i>iPB</i> -4	49.0	48.3	34.4	16.6

^a Retention ratio of mechanical properties was defined as the properties after aging/the properties before aging;

^b Aging coefficient = (the tensile strength after aging × the elongation at break after aging)/(the tensile strength before aging × the elongation at break before aging)

As shown in Table 3, the mechanical properties of *iPB*-1 and *iPB*-2, such as yield strength, tensile strength and elongation at break, changed little after thermal-oxidative aging. While for *iPB*-3 and *iPB*-4, obvious differences were observed. For the thermal-oxidative aging samples, all values like yield strength, tensile strength, elongation at break decreased greatly.

Table 4 summarized the retention ratio of yield strength, tensile strength and elongation at break and the aging coefficient for the *iPB* samples. The retention ratio of yield strength of *iPB*-2 was slightly lower than that of *iPB*-1, which might be attributed to no addition of the additives such as antioxidant in lab-made *iPB*-2. The higher retention ratio of elongation at break for *iPB*-2 was due to the relatively higher molecular weight of *iPB*-2. With the increase in the catalyst residue, as shown in *iPB*-3 and *iPB*-4, the retention ratio of yield strength and tensile strength decreased gradually. For comprehensive consideration, aging coefficients were calculated and listed in Table 4. From Table 4, it can be seen that *iPB*-2 showed the highest aging coefficient, while *iPB*-3 showed the lowest aging coefficient.

TGA Measurements

The starting thermal decomposition temperature (T_{ons}), the temperature of maximum degradation rate (T_{max}) and the decomposition temperature interval ($T_{0.95}-T_{\text{ons}}$) were obtained through TGA measurements, and the results are shown in Table 5. The original *iPB*-1 has the onset decomposition temperature at 420.7 °C. With the increase in the catalyst residue, the T_{ons} value of the original *iPB* samples decreased, and for the original *iPB*-4, the T_{ons} value was decreased to 416.5 °C. The T_{max} values changed little for all original *iPB* samples. That meant the higher content of catalyst residue induced the thermal decomposition occurring at lower temperatures. When the *iPB* samples were treated in the thermal-oxidative aging oven, all the values of T_{ons} and T_{max} were lower than those of the original ones and the $T_{0.95}-T_{\text{ons}}$ values were broader than the original ones, which indicated the samples after aging showed worse thermal stability than the original ones.

Table 5. Thermogravimetric analysis of the *i*PB samples

Samples	Original samples (°C)			After aging (°C)			ΔT_{ons}	ΔT_{max}	$\Delta(T_{0.95}-T_{\text{ons}})$
	T_{ons}	T_{max}	$T_{0.95}-T_{\text{ons}}$	T_{ons}	T_{max}	$T_{0.95}-T_{\text{ons}}$			
<i>i</i> PB-1	420.7	445.0	38.1	419.1	444.2	39.5	1.6	0.8	1.4
<i>i</i> PB-2	419.4	447.0	41.3	417.4	446.3	42.8	2.0	0.7	1.5
<i>i</i> PB-3	417.3	444.2	41.7	411.6	442.7	45.2	5.7	1.5	3.5
<i>i</i> PB-4	416.5	444.9	43.5	411.0	442.2	47.3	5.5	2.7	3.8

T_{ons} : the onset temperature of degradation; $T_{0.95}$: the temperature of 95% weight loss;

T_{max} : the temperature of the maximum degradation rate; $\Delta T_{\text{ons}} = T_{\text{ons}}$ (original *i*PB)– T_{ons} (aged *i*PB);

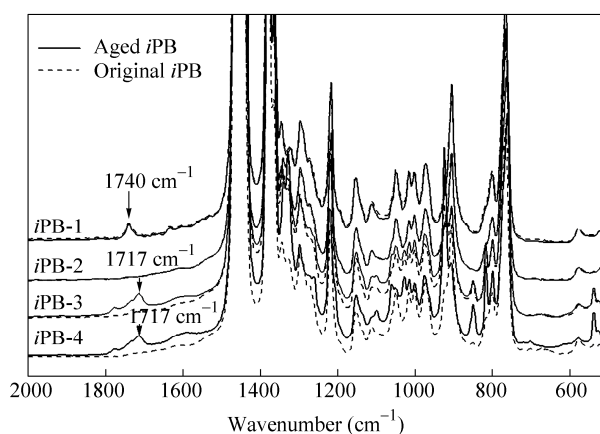
$\Delta T_{\text{max}} = T_{\text{max}}$ (original *i*PB)– T_{max} (aged *i*PB); $\Delta(T_{0.95}-T_{\text{ons}}) = (T_{0.95}-T_{\text{ons}})_{\text{aged } i\text{PB}} - (T_{0.95}-T_{\text{ons}})_{\text{original } i\text{PB}}$

All the temperature difference values (ΔT_{ons} , ΔT_{max} and $\Delta(T_{0.95}-T_{\text{ons}})$) between original and aging samples are listed in Table 5 and showed more clearly the distinction in the thermal stability performance of these samples.

The samples *i*PB-1 and *i*PB-2 containing lower catalyst residues had lower values (ΔT_{ons} , ΔT_{max} in Table 5) than *i*PB-3 and *i*PB-4, which indicated *i*PB-1 and *i*PB-2 possessed better thermal stability performance. And the difference values of the decomposition temperature interval, $\Delta(T_{0.95}-T_{\text{ons}})$, of *i*PB-4 was the highest one, which was due to the facile decomposition behavior of *i*PB-4 containing higher catalyst residue content. The values of ΔT_{ons} , ΔT_{max} and $\Delta(T_{0.95}-T_{\text{ons}})$ for lab-made *i*PB-2 (Table 5) were very close to those of commercial *i*PB-1, which indicated *i*PB-2 synthesized by bulk precipitation technology can be comparable with the commercial product (*i*PB-1) according to their thermal stability.

FTIR Measurements

Infrared spectra were effective tools to characterize the chemical structure of polymers. As shown in Fig. 2, obvious carbonyl (C=O) vibrating peaks at 1717 cm^{-1} were observed for aged *i*PB-3 and *i*PB-4 samples, which indicated carbonyl (C=O) groups generated during the aging process of *i*PB. However, there were no peaks observed in the same position for *i*PB-1 and *i*PB-2, indicating the two samples showed good aging resistant performance. There was a peak at 1740 cm^{-1} observed for *i*PB-1 perhaps due to some unknown additives in commercial *i*PB-1. And the intense peaks of *i*PB-3 and *i*PB-4 at $800\text{--}900\text{ cm}^{-1}$ did not come from the polybutene-1 and should be due to the contribution of high-content catalyst residues.

**Fig. 2** The infrared spectra of all samples before and after aging

The Aging-promoted Mechanism of Catalyst Residues

The metal residues in polypropylene contributed a lot to the oxidation degradation such as acceleration to decomposition of peroxides and inhibition to antioxidants^[17].

PB was similar to polypropylene in chain structures, and half of the carbons in polymer backbone chains were tertiary carbon atoms, so the oxidative aging mechanism should also be similar. The aging mechanism of

PP could perhaps be borrowed to explain that of PB and shown as follows:

Chain initiation reaction:



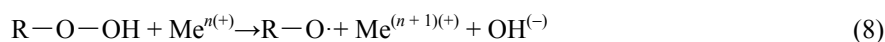
Chain propagation reaction:



Chain termination reaction:



No matter what happened in chain initiation reaction, free radicals would react with existed oxygen to form hydroperoxides (Eqs. (3) and (4)), and in the presence of metal ions, hydroperoxides were decomposed *via* redox reactions (Eq. (8)), which led to generation of new radicals:



Unstable coordination complexes were formed when the metal ions met with ROOH. Then numerous RO· and R-O-O· radicals generated accompanying with the decomposition of ROOH, which accelerated the aging process. Thus the aging resistant properties of polymers dropped obviously in the presence of metal impurities.

CONCLUSIONS

Via the analysis of GPC, mechanical performance testing, TGA and FTIR, the lab-made *i*PB-2 synthesized by bulk precipitation technology showed excellent aging resistant performance, which can be comparable with the commercial product (*i*PB-1).

After the thermal-oxidative aging, the molecular weight of the *i*PB reduced and molecular weight distribution became narrow. The catalyst residues indeed accelerated the aging process and made the mechanical properties of the samples worse. During the aging process, carbonyl groups generated as the catalyst residues in samples increased. Thus for *i*PB, metal residues played an important role in aging-promotion of polymer materials. Although the catalyst residues in the final products should not be neglected, the lab-made *i*PB-2 prepared by the bulk precipitation technology showed good aging resistant properties comparable with the commercial *i*PB-1 (Mitsui).

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