Improvement of Structure and Properties of Polypropylene/Poly(ethylene-*co*-propylene) In-reactor Alloy by Modifying the Cocatalyst

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Summary: A series of polypropylene/poly(ethylene-*co*-propylene) in-reactor alloy were synthesized by a $TiCl_4/MgCl_2/SiO_2$/diester type Ziegler-Natta catalyst, using triethylaluminium (TEA), triisobutylaluminium (TIBA) or TEA/TIBA mixtures of different molar ratio as cocatalyst. Mechanical properties of the alloy are strongly influenced by the cocatalyst. Toughness-stiffness balance of the alloy synthesized using a 50/50 TEA/TIBA mixture as cocatalyst is much better than that of the alloy based on pure TEA cocatalyst. Changes in copolymer chain structure and composition distribution are thought to be the main reason for this improvement of properties.

Keywords: alloys; cocatalyst; polypropylene; Ziegler-Natta polymerization

Introduction

Polypropylene/poly(ethylene-*co*-propylene) (PP/EPR) in-reactor alloy is now produced in a scale of millions of tons per year by a continuous polymerization process that is mainly composed of two stages: propylene homopolymerization in the first reactor followed by tandem ethylene/propylene copolymerization in another reactor. $TiCl_4$/ID/$MgCl_2$ (ID = internal donor) type Ziegler-Natta catalysts are usually used in such process, and triethylaluminium (TEA) is the most frequently used cocatalyst.[1–4] In general, PP/EPR in-reactor alloys show much higher impact strength than a simple mechanical blend of PP with EPR at the same composition. This type of material is widely used in car and commodity industries for its high performances and low cost. However, there are very few literature studies that report any further improvement of PP/EPR in-reactor alloy through modification of the Ziegler-Natta catalyst.[5]

It is known for long time that PP/EPR in-reactor alloy presents a multi-phase physical structure where PP is the matrix (continuous phase) and EPR is the dispersed phase, acting as the toughening agent. It has been found that considerable segmented copolymer fractions exist in PP/EPR in-reactor alloys.[3,6–9] These segmented copolymers are believed to be miscible with both PP and EPR components and can thus act as the compatiblizer.[10,11] On the other hand, there is also a close relation between the sequence distribution of the random copolymer fraction and the impact strength of the alloy.[5] With this in mind, it is expectable that mechanical properties of the alloy can be greatly improved by regulating the microstructure of its EPR fractions.

In a previous work we have found that the amount and chain structure of the segmented copolymer fraction in EPR synthesized by supported Ti catalysts are strongly influenced by the type of cocatalyst.[12,13] In this article, the effects of cocatalyst on structure and mechanical properties of PP/EPR alloy synthesized by a $TiCl_4/MgCl_2/SiO_2$/diester type Ziegler-Natta catalyst are reported. It is found that using mixtures of TEA and triisobutylalu-

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minium (TIBA) as cocatalysts, the impact strength of the alloy can be markedly improved with only a small loss in stiffness of the materials.

Synthesis and Measurements

The PP/EPR alloys were synthesized in a 2 L autoclave equipped with mechanical stirrer. A high-yield $MgCl_2/SiO_2/TiCl_4$/diester type catalyst [14] (Ti content: 3 wt%) was used, with diphenyldimethoxysilane as external donor and TEA, TIBA or TEA/TIBA mixtures of different molar ratio as cocatalyst. At first propylene bulk polymerization was conducted in the autoclave for 1 h at 70 °C, with a total Al/Ti molar ratio 600 and Si/Ti molar ratio of 20. A small amount of hydrogen was added to the autoclave to regulate the molecular weight. After bulk polymerization, the propylene monomer was vented and gaseous ethylene/propylene mixture of 1:1 molar ratio was introduced to conduct gas-phase copolymerization at 9 bar for 40 min. Ethylene and propylene were continuously supplied to the autoclave under the control of an on-line regulation system so that monomer pressure in autoclave was kept constant and the ethylene/propylene molar ratio in the gas phase was kept at 1:1. Separate homopolymerization of propylene was conducted in a 1 L autoclave with the same catalyst systems in slurry mode, with *n*-heptane as the solvent. The reaction products were purified by washing with ethanol containing 5% HCl, filtering and washing with excess ethanol for three times, and then dried in vacuum at 65 °C for 12 h.

Each PP/EPR alloy sample was fractionated into three fractions using the following procedures: the sample was at first extracted with boiling *n*-heptane for 12 h. The insoluble part was the boiling *n*-heptane insoluble fraction (HI). The solution was cooled to room temperature to allow the boiling *n*-heptane soluble but room remperature insoluble fraction (HS) settle down, which was collected by filtration. The room remperature soluble fraction (RS) was collected from the filtrate. Isotacticity index of polypropylene was determined by extraction with boiling *n*-heptane for 12 h.

^{13}C NMR spectra of the polymer fractions were measured on a Varian Mercury Plus-300 NMR spectrometer at 75 MHz. *o*-Dichlorobenzene-d_4 was used as solvent and the concentration of the polymer solution was 15 wt%. The spectra were recorded at 120 °C, with hexamethyldisiloxane as internal reference. 2–3 mg of $Cr(acac)_3$ was added to each sample to shorten the relaxation time and ensure a quantitative result. Broadband decoupling with a pulse delay of 3 s was employed. Typically 3000 transients were collected.

The morphology of the impact fractured surface of PP/EPR alloy was observed using a scanning electron microscope (JSM-T20).

Notched Charpy impact strength of the alloy sample was measured on a Ceast impact strength tester according to ASTM D256. The flexural modulus was measured following ASTM D790 on a Shimadzu AG-500A electronic tester. The polymer granules were heat-molded at 170 °C into sheets, which were than cut into pieces, put into a 150 × 100 × 4 mm mold, and pressed under 14.5 MPa at 180 °C for 5 min. The sample plates were then slowly cooled to room temperature in the mold. Sample strips for the tests were cut from the plate following ASTM. For each test point five parallel measurements were made and the average values were adopted.

Propylene Homopolymerization

In a previous study, marked changes in polymer chain structure were found in ethylene-propylene copolymerization using a supported Ziegler-Natta catalyst when TEA cocatalyst was replaced by TEA/TIBA mixtures. [13] To see the effects of cocatalyst on propylene homopolymerization, slurry polymerization of propylene was carried out using different TEA/TIBA mixtures as cocatalyst, and the results are listed in Table 1.

Table 1.
Polymerization of propylene activated by TEA/TIBA mixture.

Run	TEA/TIBA (Molar ratio)	Activity (kg PP/g Cat · h)	I.I. [a] (%)	$M_w \times 10^{-4}$ [b]	PDI [c]
PP1	100/0	1.48	98	19.5	5.5
PP2	75/25	1.72	97	15.7	5.2
PP3	50/50	1.57	97	17.5	5.4
PP4	25/75	1.87	96	17.9	5.6
PP5	0/100	1.47	95	25.2	6.4

Polymerization conditions: Al/Ti = 150, Si/Ti = 7.5, $P_{Pr} = 5.6$ bar, $P_{H_2} = 0.5$ bar, 70 °C, 60 min.

[a] Isotacticity index;

[b] Weight average molecular weight determined by GPC;

[c] Polydispersity index.

It is seen that using TEA/TIBA mixtures of 75/25 or 50/50 molar ratios as cocatalyst caused only a slight decrease in isotacticity index of PP as compared with the commonly used TEA cocatalyst, and the activity was even slightly improved. Molecular weight and polydispersity of PP were almost unchanged. This means that, if these mixed cocatalysts are used in the preparation of PP/EPR alloys, the PP part of the alloy will have a very similar chain strcture as that prepared using pure TEA as cocatalyst. Using pure TIBA as cocatalyst will form PP with lower isotacticity and higher molecular weight.

Properties of PP/EPR In-reactor Alloy

A series of PP/EPR in-reactor alloys have been synthesized using the $MgCl_2/SiO_2/TiCl_4$/diester type catalyst activated by TEA, TIBA or TEA/TIBA mixtures, and the mechanical properties of the alloys were measured (see Table 2).

The polymerization activity became higher when a part of TEA was replaced by TIBA. The most interesting change after modifying the cocatalyst is a marked improvement of the impact strength at lower temperatures. Meanwhile, stiffness (flexural modulus) of the alloy was lowered with increasing TIBA in the cocatalyst. It is worth to note that, the flexural modulus of the sample synthesized with a 50/50 mixed cocatalyst is only about 15% lower than that of the sample synthesized using pure TEA, but the low temperature impact strength of the former is almost 90% higher than the later. In this sense it can be said that PP alloys synthesized based on mixed cocatalyst have better balanced toughness and stiffness.

The morphologies of impact fractured surfaces of PP/EPR alloy (fractured at 20 °C) are shown in Figure 1. The fracture surface of the alloy prepared based on pure TEA is rather smooth, but that of the alloy based on using a mixed cocatalyst is much coarser and has many regular pleats, which could be caused by shear yielding during

Table 2.
Mechanical properties of PP/EPR in-reactor alloys.

Cocatalyst (TEA/TIBA)	Activity (kg/g Cat · h)	Impact strength [a] (kJ/m^2)	Impact strength [b] (kJ/m^2)	Flexural strength (MPa)	Flexural modulus (MPa)
100/0	10.0	3.4	15.7	25.7	1100
75/25	10.9	4.7	18.1	21.7	960
50/50	12.9	6.4	24.4	20.3	950
0/100	12.4	7.7	N.B. [c]	18.7	530

[a] Measured at −20 °C;

[b] Measured at 20 °C;

[c] Not broken.

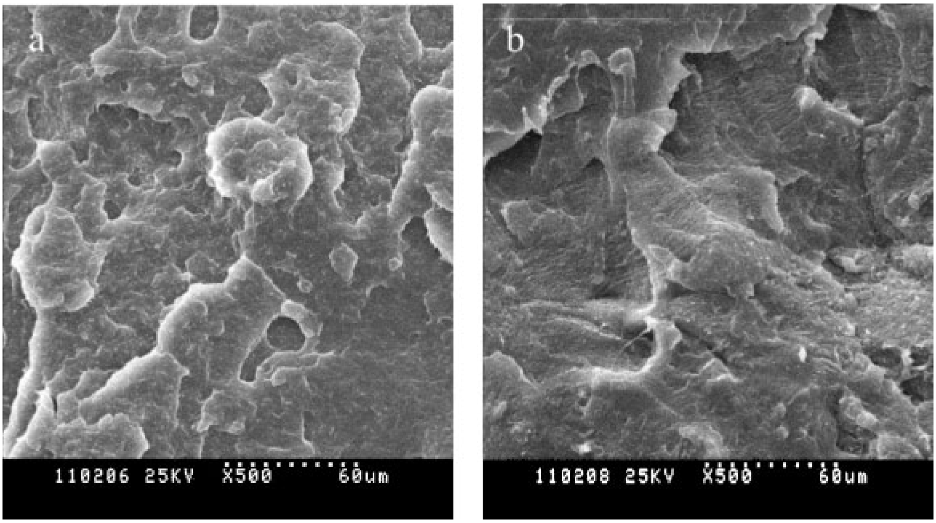

Figure 1.
SEM pictures of impact fractured surface of PP/EPR alloy (fractured at 20 °C) synthesized based on different cocatalysts. a. Pure TEA; b. 50/50 TEA/TIBA mixture.

ductile fracture of the materials. Though the room temperature impact strength of these samples are not much different, the toughening effect of the rubber phase seems to be much higher in the alloy based on using a mixed cocatalyst.

The morphologies of low-temperature (−20 °C) impact fractured surfaces of PP/EPR alloy are shown in Figure 2. On the surfaces of the two samples there are all many small cavities and globular particles, but the particles and cavities on the alloy based on using a mixed cocatalyst are smaller than those of the sample based on using a pure TEA activator, and there are fewer pulled out rubber particles on the

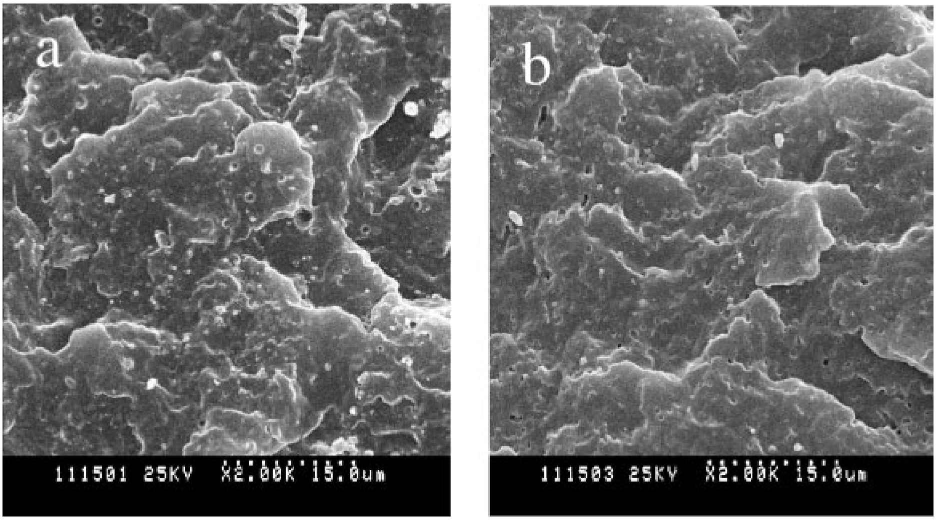

Figure 2.
SEM pictures of impact fractured surface of PP/EPR alloy (fractured at −20 °C) synthesized based on different cocatalysts. a. Pure TEA; b. 50/50 TEA/TIBA mixture.

surface of the modified alloy. This also indicates improvement of miscibility between PP and rubber phases by modifying the cocatalyst.

Chain Structure of PP/EPR In-reactor Alloy

The alloys synthesized using different cocatalysts were fractionated into three fractions: room temperature soluble fraction (RS), room temperature insoluble/ boiling *n*-heptane soluble fraction (HS) and boiling heptane insoluble fraction (HI). The influences of cocatalyst on fraction distribution of the alloy are shown in Figure 3. The amount of RS fraction (random copolymer) increased from 10 to 25% with increasing TIBA in the cocatalyst. The amount of HS fraction increased more clearly with increasing TIBA (from0.63% to 2.3%). Similar tendencies have also been found in EPR synthesized using

The same catalyst in a single copolymerization reaction.[13] However, it must be noted that about 2–3% of PP with low isotacticity is also soluble in boiling heptane.

Table 3.
Chain structure of room temperature soluble fraction.[a]

Sequence	TEA/TIBA molar ratio			
	100/0	75/25	50/50	0/100
E	47.7	47.0	53.8	34.2
EEE	22.1	23.6	25.8	11.9
EEP	16.8	16.1	17.5	15.1
PEP	8.8	7.3	10.5	7.2
EPE	9.3	11.0	12.8	7.9
PPE	17.9	20.8	10.2	11.9
PPP	25.2	21.2	23.3	46.0

[a] Conditions of sample synthesis are described in the part of "synthesis and measurements".

Because more than 95% of the EPR part is soluble in hydrocarbon solvents at 100 °C,[13] the amount of copolymer in the HI fraction is negligible. Therefore, only the chain structure of RS and HS fractions were analyzed by ^{13}C NMR, and the results are listed in Table 3 and Table 4, respectively.

The most notable change in RS fraction with the cocatalyst is increase in the amount of alternating sequences. In a sample prepared using a 50/50 mixed cocatalyst, the sum of (PEP + EPE) is almost 30% higher than that in the sample prepared using pure TEA. This improvement in

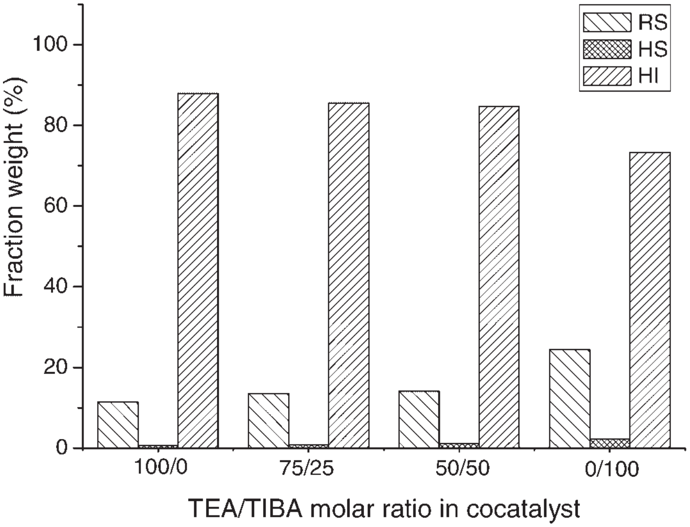

Figure 3.
Fraction distribution of PP/EPR alloys synthesized using different cocatalysts.

Table 4.
Chain structure of room temperature insoluble/heptane soluble fraction.[a)]

Sequence	TEA/TIBA molar ratio			
	100/0	75/25	50/50	0/100
E	78.9	84.3	85.5	71.0
EEE	68.7	74.2	72.3	59.1
EEP	9.9	9.9	11.4	9.9
PEP	0.3	0.2	1.8	2.0
EPE	4.4	6.1	6.2	4.6
PPE	0.7	1.6	1.1	1.2
PPP	15.9	8.0	7.2	23.2

[a)] Conditions of sample synthesis are described in "synthesis and measurements".

copolymer randomness may be an important reason for enhancement of impact strength, as elasticity of EPR strongly depends on its randomness of sequence distribution.[5]

The HS fractions are mixtures of segmented copolymer fraction and fraction of PP with medium sterogerularity. Because the PPP sequence in copolymer chains has been masked by PP fractions formed during the homopolymerization stage, it is difficult to tell the average length of PP sequence (n_p) in copolymer by the data in Table 4. In a previous study, we have found an increase in n_p of the segmented copolymer fraction by adding TIBA in the cocatalyst.[13] As the segmented copolymer plays the role of compatibilizer, increasing its n_p value will serve to improve its interfacial adhesion with the PP phase. The data in Table 4 also show that the sum of (PEP + EPE) increased by adding TIBA. This may serve to improve its adhesion with the rubber phase. Therefore, it can be said that changes in copolymer structure caused by modifying the cocatalyst are all beneficial to enhancing the miscibility of the PP and EPR phases.

These changes in copolymer structure and composition distribution caused by modification of cocatalyst are believed to be closely related to the chemical properties of TEA, TIBA and the products of their group exchange, which must exist in TEA/TIBA mixtures. Detailed studies on the mechanism of cocatalyst effects are underway.

Conclusions

Structure and properties of polypropylene/poly(ethylene-*co*-propylene) in-reactor alloys synthesized by a $TiCl_4/MgCl_2/SiO_2$/diester type Ziegler-Natta catalyst are strongly influenced by the cocatalyst. Toughness-stiffness balance of the alloy synthesized using a 50/50 TEA/TIBA mixture as cocatalyst is better than that of the alloy prepared using pure TEA cocatalyst.

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