

i*-PP/EPR REACTOR ALLOY PREPARED THROUGH ETHYLENE/PROPYLENE SLURRY COPOLYMERIZATION CATALYZED BY METALLOCENE SUPPORTED *i*PP PARTICLES

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Abstract *i*-PP/m-EPR reactor alloy were prepared through ethylene/propylene slurry copolymerization catalyzed by metallocene (*rac*-Et(Ind)₂ZrCl₂) supported on porous *i*PP particles. Polar monomer (dihydromyrcene alcohol) treated with triethylaluminum was added in the preparation of porous *i*PP particles to introduce hydroxyl groups and thus enhance the ability for chemically supporting the metallocene catalyst. The effects of MAO/Zr ratio and monomer composition in feed on the reaction activity and property of polymer were investigated. DSC analysis results imply that EPR prepared by metallocene supported PP particles showed much more obvious features of random copolymer compared with that prepared with conventional Z-N catalyst. Under appropriate reaction conditions, well separated spherical particles of *i*PP/m-EPR reactor alloy containing up to about 40 wt% m-EPR were obtained. SEM analysis results showed that m-EPR microphases smaller than 2 μm in size were uniformly distributed in PP matrix after blending the *i*PP/m-EPR reactor alloy.

Keywords: Reactor alloy; Ethylene/propylene copolymerization; Metallocene.

INTRODUCTION

Polypropylene (PP) had been widely used in a variety of applications because of its advantages, such as low cost, low density, high softening point, easy processing, as well as outstanding tensile properties. However, its poor impact strength, especially at low temperature, hindered its application as an engineering thermoplastic^[1, 2]. A conventional way to cover the shortage was to blend the polymer with its compatible elastomer. To produce toughened PP, various elastomers had been applied, such as ethylene-propylene rubber (EPR)^[3–5], styrene-butadiene-styrene (SBS) copolymer^[6], butyl rubber^[7], and ethylene-propylene-diene rubber (EPDM)^[8, 9]. Among these rubbers, EPR and EPDM were considered as the most effective impact modifiers. However, it has been found in our recent work that the ethylene-propylene-diene rubbers polymerized by metallocene catalyst (m-EPDM) is much better than conventional EPDM for toughening PP^[10]. The PP/m-EPDM blended polymer had a lower critical rubber content when the brittle-ductile transition occurred and the brittle-ductile transition interval of PP/m-EPDM blends is much narrower. And also, the elongation at break of PP/m-EPDM blends was longer than PP/EPDM blends.

It was well known that conventional Ziegler-Natta (Z-N) catalysts had multiple active sites exhibiting a range of reactivity and producing a spectrum of composition and molecular weight. Ethylene-propylene copolymers synthesized by Z-N catalyst contained a large portion of blocky copolymers, which were not as

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effective as random copolymers on improving low temperature impact strength of PP. In contrast, metallocene catalysts were generally single site catalysts, meaning that all catalytic sites were identical. This feature yielded products with extremely uniform composition and molecular weight. And also, the metallocene catalysts were generally more effective than conventional Z-N catalysts in incorporating high levels of a wide variety of olefin comonomers^[11–13].

On the other hand, it has been proved that the *i*PP/rubber alloys prepared by *in situ* or reactor granule technology were much better than that formed by mechanical blending both on mechanical properties and production costs^[14–18], since there were strong interaction between PP and rubber and the rubber could reach a high content in the reactor alloy. In order to prepare the *i*PP/m-EPR reactor alloy, Galli *et al.*^[19] devised a multicatalyst process in which the metallocene was impregnated onto PP particles. However, the physical absorption of metallocene resulted in a poor linking between PP and rubber. Up to now, the preparation and commercialization of *i*PP/m-EPR reactor alloy through multi-steps with combination of Z-N and metallocene type catalyst are still faced with many challenges.

In the present work, functional polypropylene granules were synthesized through propylene copolymerization with protected dihydromyrcene alcohol by a spherical Z-N catalyst ($\text{TiCl}_4/\text{MgCl}_2/\text{SiO}_2$). The functional polypropylenes performed effectively as supports in anchoring the metallocene catalysts (*rac*- $\text{Et}(\text{Ind})_2\text{ZrCl}_2$), and then were applied in the slurry copolymerization of ethylene and propylene to produce *i*PP/m-EPR reactor alloy.

EXPERIMENTAL

Materials

Spherical $\text{TiCl}_4/\text{MgCl}_2/\text{SiO}_2$ -ID (where ID was an internal donor) catalyst, in which Ti content is 2.22 wt% and Mg/Si weight ratio is 0.67, was donated by Beijing Research Institute of Chemical Industry, Beijing, China. Triethylaluminum (TEA) and cyclohexylmethyldimethoxysilane (CHMDMS) were selected as a cocatalyst and external donor respectively in propylene polymerization reactions. Metallocene catalyst *rac*- $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ is purchased from Sterm Chemicals Company. Methylaluminoxane (MAO) from J&K Chemical Company was used as received. Polymerization-grade ethylene and propylene from Yangzi Petrochemical Chemical Engineering Company, China were purified by passing through CuO and 0.5 nm molecular sieves. Toluene (anhydrous grade, from Hangzhou Chemical Reagents Factory, China) was refluxed over potassium for 24 h prior to use.

Preparation of Functional PP Particles

Copolymerization of propylene with dihydromyrcene alcohol treated by TEA was conducted to prepare functional PP particles. Toluene (600 mL) was introduced to a nitrogen-purged autoclave equipped with a mechanical stirrer and a temperature probe. The toluene was stirred vigorously (100 r/min) and kept at the polymerization temperature, and then trialkylaluminum and dihydromyrcene alcohol were added. After 20 min, Z-N catalyst, TEA and external donor (CHMDMS) were introduced into the reactor, and immediately the feeding of propylene gas was started. The polymerization was conducted at 50°C for 6 h. Finally, the polymer was washed several times with toluene and dried under vacuum at 60°C. ¹H-NMR was used to determine the polar monomer content in the obtained polymer.

The above polymer was immersed in acidic methanol solution for 5 h with stirring for alcoholysis, then washed several times with methanol and dried under vacuum at 60°C.

Supporting Metallocene Catalyst on Functional PP Particles

The flask was added with 20 g of functional PP particles, 80 mL of toluene and 20 mL of MAO in succession. The temperature was brought up to 60°C and the reaction proceeded for 3 h, then filtered and washed 3 times with toluene. Then 80 mg of *rac*- $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ in toluene solution was added, and the supporting reaction was conducted at 60°C for 5 h. The resulting slurry was washed eight times with toluene, and finally dried under vacuum.

Copolymerization of Ethylene and Propylene

Quantitative toluene, metallocene supported PP particles and MAO were introduced into autoclave equipped with a magnetic stirrer under a flow of nitrogen. After evacuating the nitrogen in the reactor by a vacuum pump, the copolymerization was initiated by introducing the mixture of ethylene and propylene with an appointed composition, and conducted at 45°C at a constant pressure. The copolymerization was finally terminated by adding excess amount of hydrochloric acid solution diluted with ethanol.

Characterization

High temperature ^1H -NMR spectra were recorded on a Bruker AMX400 NMR spectrometer in *o*-dichlorobenzene- d_4 at 120°C. The concentration of Zr (in *rac*-Et(Ind) $_2$ ZrCl $_2$) on the PP supports were determined by inductively coupled plasma atomic emission spectroscopy using a IRIS Intrepid II XSP type ICP.

The intrinsic viscosity of polypropylene and EPR was measured with an Ubbelohde in decalin solution at 135°C. Viscosity-average molecular weights (M_η) of PP and EPR were estimated from the intrinsic viscosity data using the Mark-Houwink equation. Isotacticity (I.I) of polypropylene was determined as the weight fraction of polymer insoluble in boiling heptane. The iPP/m-EPR reactor alloy was extracted by boiling heptane for 24 h, and EPR dissolved in boiling heptane was obtained by removing the solvent. Apparent morphology of samples was examined by scanning electron microscopy (model Hitachi S-4800). Differential scanning calorimetry analysis of the samples was made on a DSC Q100 V9.5 Build 288. The sample was heated from -100°C to 180°C at a heating rate of 10 K/min, and kept at 180°C for 5 min, then cooled to -100°C at 10 K/min for recrystallization; this was followed by reheating from -100°C to 180°C at 10 K/min.

RESULTS AND DISCUSSION

The Functional PP Particles

Figure 1 illustrated the process for preparation of functional PP particles. Copolymerization of propylene and dihydromyrcene alcohol treated by triethylaluminium was conducted with Z-N catalyst system, followed by hydroxylation with acidic methanol, leading to the production of functional PP particles containing hydroxyl in side chains (B in Fig. 1).

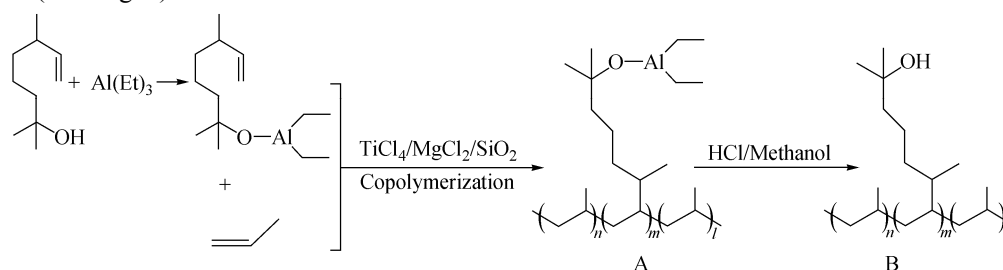


Fig. 1 Scheme for synthesis of functional polypropylene particles

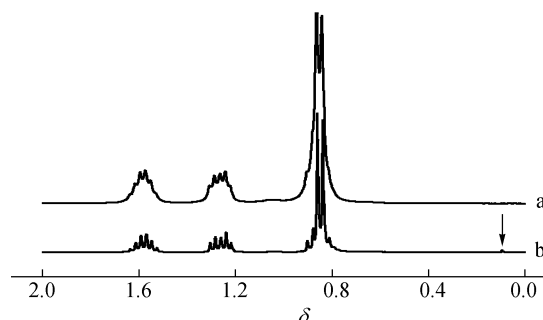
It was seen from Table 1 that the addition of dihydromyrcene alcohol treated by triethylaluminium in the polymerization of propylene increased the activity of Z-N catalyst slightly as compared with the propylene homo-polymerization case and the polar monomer reached a high conversion level of 66.3%. The functional polypropylene particles showed almost the same basic properties as neat PP.

Figure 2 showed the ^1H -NMR spectra of neat PP and copolymer A. For the copolymer A, in addition to the three major peaks at $\delta = 0.86$, 1.26, and 1.57 corresponding to the CH_3 , CH_2 , and CH protons in the PP backbone, there was a minor peak at $\delta = 0.1$ (marked by arrows) corresponding to the protons of methylene in $-\text{Al}-\text{CH}_2-\text{CH}_3$ on the side group of PP backbone. The polar monomer content in copolymer A was then calculated by comparing the integrated intensity of the peak at $\delta = 0.1$ with that of the sum of the peaks at $\delta = 0.86$, 1.26, 1.57 based on the number of protons each chemical shift embodied. Comonomer content in copolymer A was 1.33 mol%, indicating the satisfactory insertion of polar monomer into PP backbones.

Table 1. Preparation and characterization of neat PP and functional PP^a

Run ^b	Alcohol ^c (mmol)	Yield (g)	Activity (kg PP/(mol Ti·h))	Conv ^d (%)	CC ^e (mol%)	M_n ($\times 10^4$)	T_m ^f (°C)	ΔH_f ^f (J/g)	I.I. (%)
1	0	84.3	151.9	—	0	64.5	161.8	88.9	98.0
2	42	89.0	160.4	66.3	1.33	63.3	160.8	87.9	97.2

^a Conditions: Z-N cat. = 100 mg, TEA/Ti = 300, Si/Ti = 30, t = 6 h, T = 50°C, pressure = 0.202 MPa, amount of toluene = 600 mL; ^b Run 1 is neat PP, run 2 is copolymer A in Fig. 1; ^c Dihydromyrcene alcohol was treated with TEA (TEA/alcohol mol ratio = 1.2) before Z-N catalyst system was added; ^d Conversion of dihydromyrcene alcohol; ^e Comonomer (dihydromyrcene alcohol) content in the polymer determined by ¹H-NMR; ^f Determined by DSC measurement

**Fig. 2** ¹H-NMR spectra of (a) neat PP and (b) copolymer A

Copolymerization of Ethylene and Propylene

The obtained functional polypropylene granules with porous structure were used as supports to chemically bond *rac*-Et(Ind)₂ZrCl₂ as mentioned in the experimental section. Inductively coupled plasma (ICP) results showed that the content of Zr in the thus-prepared metallocene supported PP particles was 110 µg per gram of PP. This metallocene supported PP particles were then applied for ethylene and propylene slurry copolymerization to produce *i*PP/m-EPR reactor alloys.

The effects of MAO/Zr ratio on the copolymerization activity and property of the obtained polymer was investigated. As shown in Table 2, the reaction activity rapidly increased from 1.29 to 12.28 g of EPR/(mol Zr h Pa) when increasing MAO/Zr ratio from 1000 to 3000 (run 1–3), since more potential active sites of metallocene anchoring on PP particles were activated by more amount of MAO. As a result, the amount of m-EPR in alloy increased from 9.55% to 49.93%. Figure 3 showed that the melting peak attributing to EPR component gradually became stronger as MAO/Zr ratio increased. Furthermore, T_m of EPR gradually shifted to higher temperature with increasing MAO/Zr ratio.

Table 2. Copolymerization of ethylene and propylene with metallocene supported PP particles^a

Run	Pressure (MPa)	Ethylene in feed (mol%)	Al/Zr	Time (min)	EPR content (wt%)	Activity (g of EPR/ (mol Zr h Pa))	M_n of EPR ($\times 10^4$)
1	0.101	50	1000	40	9.55	1.29	—
2	0.101	50	2000	40	36.68	7.13	—
3	0.101	50	3000	40	49.93	12.28	—
4	0.101	30	3000	40	7.82	1.09	—
5	0.101	40	3000	90	53.03	6.04	—
6	0.101	65	3000	40	56.76	16.14	—
7	0.606	30	3000	20	65.71	7.82	—
8	0.606	50	3000	20	88.29	28.61	9.9
9	0.606	65	3000	20	94.19	40.40	—
10 ^b	0.606	50	1000	7	—	62.48	2.1

^a Conditions: T = 45°C, metallocene supported PP particles = 2 g, solvent = 100 mL of toluene; ^b Copolymerization of ethylene and propylene with homogeneous *rac*-Et(Ind)₂ZrCl₂ catalyst: [Zr] = 10 µmol, solvent = 100 mL of toluene

The copolymerization activity was also greatly influenced by the monomers composition in feed (run 3–6 performed at 0.101 MPa) as shown in Table 2. The activity increased greatly from 1.09 to 16.14 g of EPR/(mol Zr h Pa) as ethylene content in feed increased from 30% to 65%, which resulted from the higher reactivity of ethylene compared with propylene in copolymerization catalyzed by metallocene catalyst. The content of EPR in alloy also increased with increasing ethylene content in feed. The situation was analogous for run 7–9 which were performed with different feed composition at 0.606 MPa. Figures 4 and 5 showed the DSC profiles of PP/m-EPR alloys produced with variable monomer composition at 0.101 MPa and 0.606 MPa respectively. The melting peak of m-EPR prepared by the metallocene catalyst shifted to higher temperature with increasing ethylene content in monomer feed due to the increasing content of ethylene in EPR. Therefore, high ethylene content in feed was propitious to the production of blocky EPR, while low ethylene content in feed was propitious to the production of EPR with random microstructure.

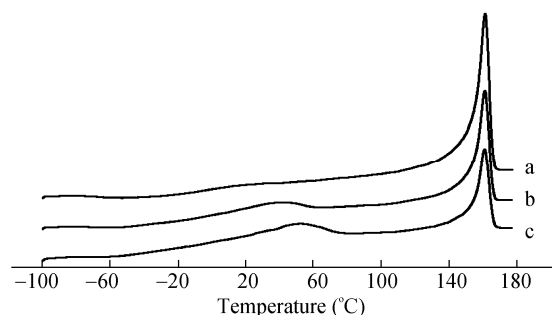


Fig. 3 DSC curves of PP/m-EPR alloys prepared at different MAO/Zr
a) 1000 (run 1); b) 2000 (run 2); c) 3000 (run 3)

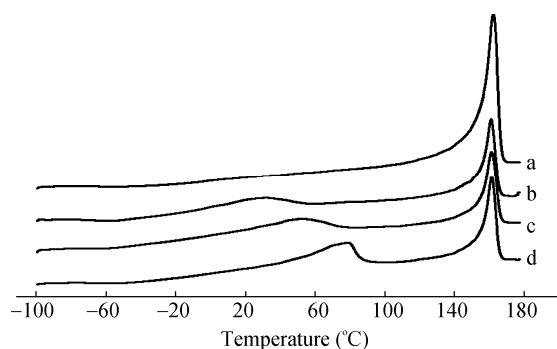


Fig. 4 DSC curves of PP/m-EPR alloys prepared at different feed composition at 0.101 MPa
Ethylene content in feed: a) 30% (run 4); b) 40% (run 5); c) 50% (run 3); d) 65% (run 6)

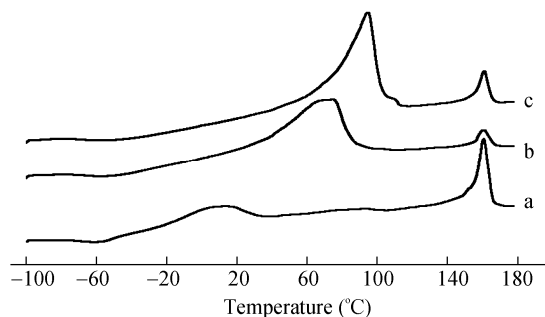


Fig. 5 DSC curves of PP/m-EPR alloys prepared at different feed composition at 0.606 MPa
Ethylene content in feed: a) 30% (run 7); b) 50% (run 8); c) 65% (run 9)

The m-EPR in reactor alloy prepared by metallocene supported on PP particles was compared with that prepared by the homogeneous metallocene catalyst. As shown in Table 2, the molecular weight of m-EPR produced by metallocene supported on PP particles (run 8) was much higher than that produced by homogeneous metallocene (run 10) due to the steric hindrance in catalyst supporting. As shown in Fig. 6, m-EPR in the reactor alloy presented more intensive and broader melting peak comparing with the neat m-EPR prepared with homogeneous metallocene catalyst. The intensive melting peak (*i.e.* high value of melting enthalpy) of run 8 indicated that the copolymer prepared with the supported metallocene was less random than that prepared with homogeneous one. The broad melting peak of m-EPR in the reactor alloy was believed to be related to the broad distribution of monomer composition from the surface to inner of PP particle, which resulted from monomer diffusion limitations.

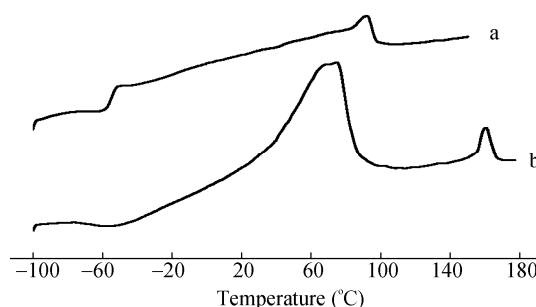


Fig. 6 DSC curves of PP/EPR alloys prepared by (a) homogeneous metallocene catalyst (run 10) and (b) PP-supported metallocene catalyst (run 8)

Figure 7 showed the DSC curves of PP/EPR alloy prepared by sole Z-N catalyst and PP/m-EPR alloy prepared from metallocene supported PP particles. Comparing with the PP/EPR, m-EPR in PP/m-EPR alloy showed much lower melting temperature, indicating that ethylene-propylene copolymers synthesized from metallocene supported PP particles had much more random features in microstructure. Therefore, it is possible to optimize the structure of EPR in reactor alloy by integrating the advantage of metallocene catalyst in copolymerization of ethylene and α -olefin.

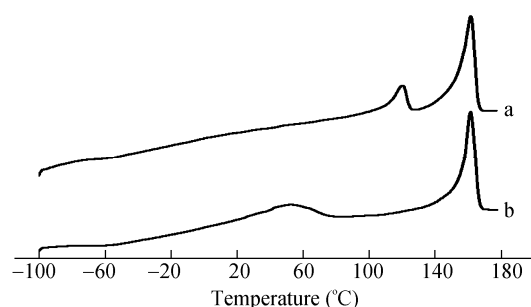


Fig. 7 DSC curves of PP/EPR alloys prepared by (a) Z-N catalyst (EPR = 19 wt%) and (b) metallocene supported PP particles (run 2 in Table 2)

Morphology

With the aid in morphological replication of Z-N catalyst particles under mild polymerization, the functional PP particles were spherical and porous with diameter of 300–500 μm as observed in Fig. 8. PP/m-EPR reactor alloy with 37 wt% copolymer prepared from metallocene supported PP particles maintained the spherical shape of PP particles and were well scattered. However, the pores of original PP particles were filled with copolymer phase resulting in smooth surface of alloy. The active sites of metallocene catalyst, which were immobilized on the surface of pores or in the amorphous phase, conducted copolymerization of ethylene with propylene, and the produced copolymer phase would fill gradually in the pores.

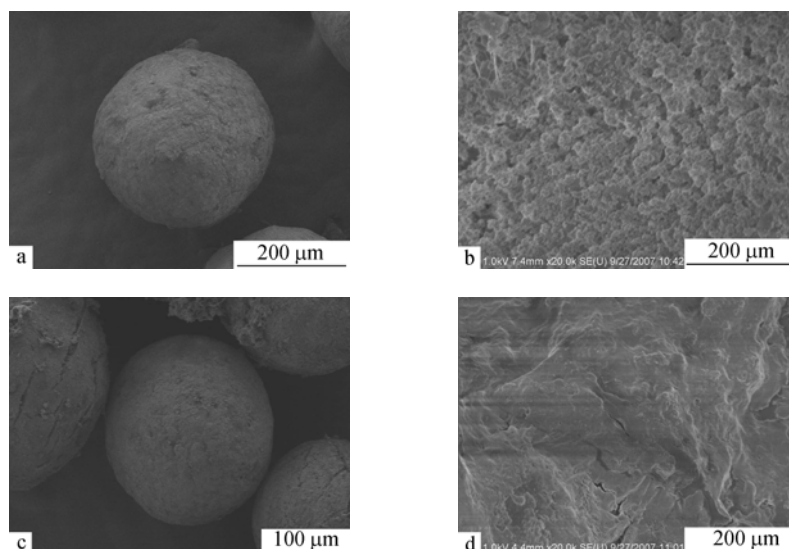


Fig. 8 Surface morphologies of particles
a, b) Functional polypropylene particles; c, d) PP/m-EPR alloy containing 37 wt% copolymer (run 2 in Table 2)

To investigate the m-EPR phase distribution in PP matrix, the obtained *i*PP/EPR reactor alloy with 37 wt% m-EPR was melt-blended in a mixer, and then heat-molded into sheet which was subsequently extracted by boiling heptane for 24 h. Finally, the m-EPR on the surface of sheet was removed away by the solvent. Figure 9 showed that the m-EPR separated phases were finely and uniformly dispersed in PP matrix, and the domains of m-EPR micro phase were mostly less than 2 μm in size.

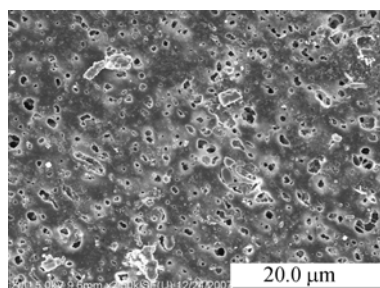


Fig. 9 Distribution of m-EPR phase in PP matrix after melt blending of *i*PP/EPR reactor alloy

CONCLUSIONS

Spherical isotactic polypropylene porous particles containing a certain amount of hydroxyl groups were prepared with the copolymerization of propylene and triethylaluminum treated dihydromyrcene alcohol by Ziegler-Natta catalyst. These particles were efficient in supporting *rac*-Et(Ind)₂ZrCl₂ by chemical anchoring and were applied to ethylene and propylene slurry copolymerization to produce PP/m-EPR reactor alloys. It was found that the copolymerization activity of metallocene supported PP particles increased with the increase of MAO/Zr ratios and ethylene content in feed, and the composition of m-EPR formed could be adjusted by monomer composition in feed. Ethylene-propylene copolymers in reactor alloys obtained from metallocene supported PP particles showed much more random features than that prepared with conventional Z-N catalyst. Under appropriate reaction conditions, well scattered spherical particles of *i*PP/m-EPR reactor alloy containing

up to about 40 wt% m-EPR were obtained. SEM analysis result showed that m-EPR microphases less than 2 μm in size were uniformly distributed in PP matrix after melt blending the *i*PP/m-EPR reactor alloy.

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