



Preparation and Characterization of High Fluidity Polypropylene/Poly (ethylene-co-propylene) In-reactor Alloys

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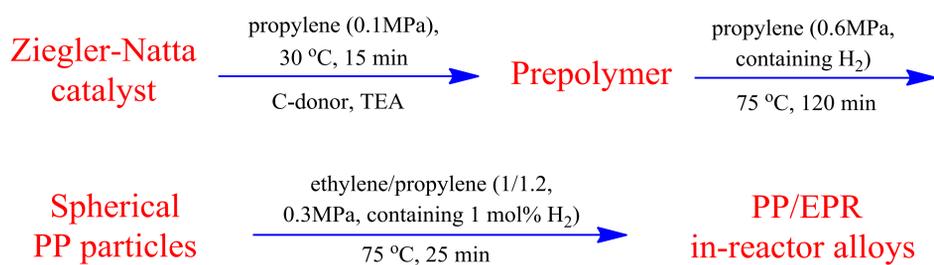
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Background and purpose of the work

• With the improvement of production technology and introduction of high efficiency catalyst, high fluidity IPC (MFR ≥ 20 g/10min), has been well developed and successfully applied in electric appliances, auto parts, packaging, and so on. The application of high fluidity PP polymers can make the products easy for processing, and thus improve product yield by shortening molding cycle. Besides, it can be made into thin wall products, reducing raw materials requirement. At present, high fluidity PP/EPR of good performance can not keep up with the demand and needs to be imported. Hydrogen, as an effective chain transfer agent, is always used to adjust the molecular weight of polymers, and then control their MFR. In this work, spherical Ziegler-Natta catalysts (cat. G and cat. Y) were used to prepare PP and PP/EPR in-reactor alloys with MFR of ~ 30 g/10min. The properties of four polymers were respectively studied, and two catalysts were also compared.

Experimental



Scheme 1 Preparation process of high fluidity PP and PP/EPR in-reactor alloys

Results and discussion

Table 1 Preparation and fractionation results of four polymers^a

Entry ^b	Activity (kg/g cat·h)	H ₂ (mol%)	MFR (g/10min)	C8-sol. ^c (wt%)	C7-sol. ^d (wt%)	C7-insol. ^e (wt%)
Polymer-1	1.0	1.4	30.8	1.5	2.8	95.7
Polymer-2	1.1	1.9	31.2	1.5	3.4	95.1
Polymer-3	1.2	2.1	30.1	11.7	7.2	81.1
Polymer-4	1.2	2.2	29.5	17.2	7.0	75.8

a) Al/Ti = 100; Si / Ti = 5.

b) Polymer-1 and Polymer-2 are PP prepared by cat. G and cat. Y, respectively;

Polymer-3 and Polymer-4 are PP/EPR in-reactor alloys prepared by cat. G and cat. Y, respectively.

c) The soluble part of polymers in *n*-octane at room temperature.

d) The soluble part of polymers in boiling *n*-heptane.

e) The insoluble part of polymers in boiling *n*-heptane.

Table 2 GPC results of different fractions in four polymers

Entry	$M_w \times 10^{-3}$ (C8-sol.)		$M_w \times 10^{-3}$ (C7-sol.)		$M_w \times 10^{-3}$ (C7-insol.)	
	Low MW	High MW	Low MW	High MW	Low MW	High MW
Polymer-1	1.4	70.9	--	15.4	--	207.0
Polymer-2	1.0	60.0	--	17.2	--	192.9
Polymer-3	0.9	184.8	7.9	194.8	--	178.6
Polymer-4	0.9	151.1	5.4	139.0	--	174.7

Table 3 Results of ¹³C-NMR analysis on C7-soluble fraction of PP/EPR in-reactor alloys

GPC-NMR conversion	Entry	E	P	EEE	EEP+ PEE	PEP	EPE	PPE+ EPP	PPP	$r_E' \cdot r_P'$	n_E'	n_P'
before	Polymer-3	47.68	52.32	39.82	7.87	0.00	4.12	3.16	45.04	88.0	9.9	10.9
	Polymer-4	53.56	46.44	46.15	7.41	0.00	3.75	6.86	35.83	66.0	9.8	8.5
after	Polymer-3	83.05	16.95	68.09	13.46	0.00	7.04	5.40	6.01	9.6	10.1	2.1
	Polymer-4	82.99	17.01	69.27	11.12	0.00	5.63	10.30	3.68	9.9	10.1	2.1

• The true sequence distribution of s-EP is corrected based on the data of relative percentage of mi-PP and s-EP estimated from the GPC curve. As shown in Table 3, both samples have $r_E' \cdot r_P'$ value of nearly 10, indicating high blockiness of their s-EP chains. The proportion of alternating triads (PEP+EPE) is pretty low, which also shows a strong block tendency. The n_E' is almost 5 fold higher than n_P' , meaning that long polyethylene segments are liable to be formed in the s-EP copolymer, which will make it highly compatible with r-EP.

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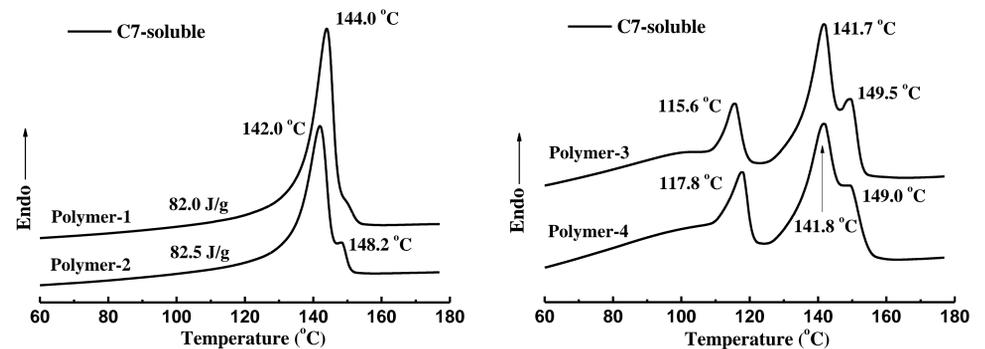


Figure 1 DSC melting traces of C7-soluble fraction of the polymers

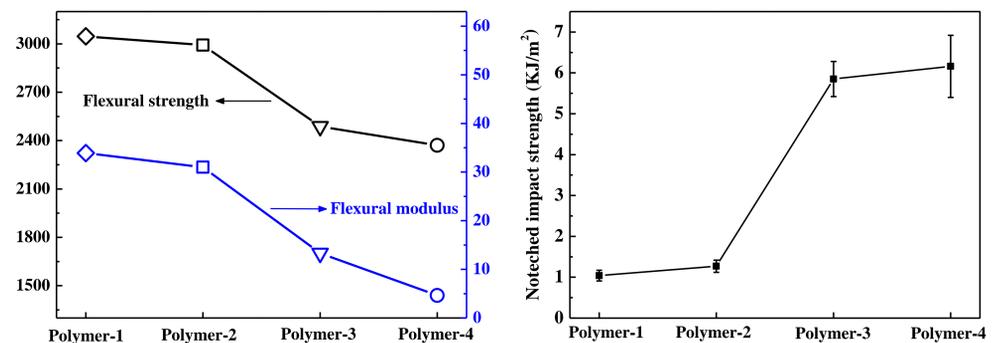


Figure 2 Mechanical properties of the polymers

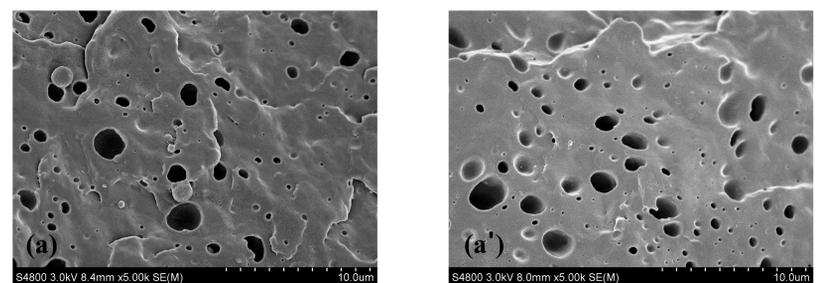


Figure 3 SEM micrographs for cryo-fractured surfaces etched by xylene of the PP/EPR in-reactor alloys: (a) Polymer-3; (a') Polymer-4

Table 4 Statistical result of the disperse phase morphology

Entry	Minimum surface area (μm^2)	Maximum surface area (μm^2)	Number of cavities	Fraction of cavity area (%)	Density ^a (Num./ μm^2)	A_n^b (μm^2)	PDI ^c
Polymer-3	7.38×10^{-3}	3.68	674	6.31	0.24	0.26	4.01
Polymer-4	7.38×10^{-3}	4.76	753	8.69	0.27	0.33	4.51

a) Number of cavities per square micrometer counted in the SEM photo.

b) Number average cavity area calculated according to the equation: $A_n = \sum(N_i A_i) / \sum N_i$, where N_i and A_i are number and area of cavities of a certain size, respectively.

c) Polydispersity of the cavity area, $PDI = A_w / A_n$, where A_w is area average cavity area calculated according to the equation: $A_w = \sum(N_i A_i^2) / \sum(N_i A_i)$.

• By comparison, it seems that cavities in Polymer-3 are more circular, and their size and quantity are smaller than those of Polymer-4 (see Figure 3). From the statistical results, area distribution of the cavities in Polymer-3 ranges from $7.38 \times 10^{-3} \mu\text{m}^2$ to $3.68 \mu\text{m}^2$, but much wider for Polymer-4. Cavity ratio of the latter is a little higher, which means higher EPR content, in consistent with the fractionation result. For Polymer-3, the number of cavities (density) and average size (A_n) are both lower than those of Polymer-4. In addition, a larger polydispersity (A_w/A_n) of the latter occurs, which shows a larger heterogeneity of size distribution, and this may be due to the existence of more large EPR domains.

Conclusions

- Cat. G and cat. Y exhibits similar polymerization activity. However, whether for PP homopolymer or alloy, the hydrogen sensitivity of cat. G is a little higher than cat. Y.
- PP/EPR alloys prepared by cat. Y (Polymer-4) contains much more random E-P copolymer than those prepared by cat. G (Polymer-3).
- The sequence distributions of two alloys are basically the same. The s-EP fraction of Polymer-3 has higher [PPP] content than that of Polymer-4, implying that the former may have better compatibility with PP matrix than the latter.
- Two PP polymers exhibited similar mechanical properties. However, for alloys, Polymer-3 showed higher Flexural modulus (E) and Flexural strength (δ) but lower toughness.
- Owing to uneven distribution of EPR domains in Polymer-4, even if it contains much more EPR content than Polymer-3, the toughening effect only exhibits a little higher.