Influence of Polymerization Conditions on the Structure and Properties of Polyethylene/Polypropylene In-Reactor Alloy Synthesized in the Gas Phase with a Spherical Ziegler–Natta Catalyst

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ABSTRACT: A spherical TiCl₄/MgCl₂-based catalyst was used in the synthesis of in-reactor polyethylene/polypropylene alloys by polyethylene homopolymerization and subsequent homopolymerization of propylene in the gas phase. Different conditions in the ethylene homopolymerization stage, such as monomer pressure and polymerization temperature, were investigated, and their influences on the structure and properties of in-reactor alloys were studied. Raising the polymerization temperature is the most effective way of speeding up polymerization and regulating the ethylene content of polyethylene (PE)/polypropylene (PP) alloys, but it will cause a greater increase in the PE-b-PP block copolymer fraction (named fraction D) than in the fraction of PP-block-PE in which the PP segments have low or medium isotacticity (named fraction A). Although changing ethylene monomer pressure could influence the ethylene

INTRODUCTION

There are many works on the modification of polypropylene (PP) aiming at improving impact strength.^{1–6} Among the ways to toughen PP, in-reactor blending of PP with other polyolefins (e.g., ethylene propylene random copolymer) by sequential multistage polymerization has been proved superior with respect to both polymer properties and production cost.^{7–9} Since the 1990s, use of a spherical Ziegler–Natta catalyst has been the main progress in the production of PP inreactor alloy.^{10,11} PP/EPR alloy synthesized by a spherical catalyst is in the form of regular spherical granules shows better mechanical properties compared to the conventional catalyst system. The polycontent of PE/PP alloys slightly, it is an effective way of regulating the structural distribution. Reducing the monomer pressure will evidently increase fractions A and D. The mechanical properties of the alloys, including impact strength and flexural modulus, can be regulated in a broad range with changes in polymerization conditions. These properties are highly dependent on the amount, distribution, and chain structure of fractions A and D. The impact strength is affected by both fraction A and fraction D in a complicated way, whereas the flexural modulus is mainly determined by the amount of fraction A. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2136–2143, 2006

Key words: polyethylene; polypropylene; alloys; structure; mechanical properties

merization process also benefits from the spherical shape of the polymer granules, as risks of scaling and blockage in the reactor can be lowered. However, because there is more than 10% random copolymer (EPR) with a low modulus in this PP/EPR in-reactor alloy, this kind of toughened PP suffers from a significant drop in flexural modulus in comparison with the PP homopolymer. A possible way of overcoming this drawback is to replace the EPR with polyethylene (PE) in the alloy, as PE is a crystalline polymer with moderate rigidity. On the other hand, ethylene polymerized with spherical Z-N catalyst would form spherical PE particles with high porosity for its high polymerization rate. This is propitious for in-reactor blending of PE with other olefins to gain high-performance polyolefin in-reactor alloy.

The structure of the alloy strongly influences the alloy's mechanical properties. But the composition and chain structure of the alloy is controlled by polymerization conditions. In a multistage process for synthesizing in-reactor PE/PP alloys, a direct way to regulate the composition and chain structure of the rubber phase is to change the conditions of polymerization. Up to now there is no literature concerning the

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Figure 1 Appearance of PE particles and PE/PP alloy particles.

influences of polymerization conditions on the structure and properties of in-reactor PE/PP blends. In this study, a spherical, high-yield TiCl₄/MgCl₂-based catalyst was used in the synthesis of in-reactor PE/PP alloys by a two-stage gas phase polymerization process. Different conditions in the ethylene homopolymerization stage, such as monomer pressure and polymerization temperature, were investigated, and their influences on the structure and properties of in-reactor alloys are reported.

EXPERIMENTAL

Polymerization

Prepolymerized catalyst was made by homopolymerization of propylene in a well-stirred glass bottle containing 40 mL petroleum ether (60–90 °C) at 50 °C and atmospheric pressure for 30 min. A high-yield, spherical TiCl₄/MgCl₂ · ID (ID = internal donor) catalyst (DQ00–189, kindly donated by the Beijing Research Institute of Chemical Industry) was used in polymerization, with Al(C₂H₅)₃-Ph₂Si(OCH₃)₂ as a cocatalyst.

In the first stage, polyethylene was prepared after prepolymerized catalyst was transferred to a 0.5-L jacketed Büchiglasuster reactor with a helical stirrer. The reaction rate is calculated from the feed rate required to keep the pressure constant and measured by a mass flow controller. A special helical stirrer was used to enforce good mixing inside the reactor. Moreover, 50 mL petroleum ether was used for every experiment to prevent prepolymerized catalyst particles from sticking to each other and to the reactor wall. We still call the polymerization gas phase processing, because there was so little solution that after 20 min of polymerization it was absorbed thoroughly by the polymer produced in the reactor. Most of the processing was in the gas phase. In this stage, spherical PE granules 0.45–2 mm in diameter were produced and residual ethylene in the particles was completely removed before propylene was added to the same reactor. In the second stage, propylene at a constant pressure of 0.8 MPa was continuously supplied to the gas phase reactor and polymerized for 2 h. In this work the pressure of ethylene feed gas was regulated in the rage of 0.35–0.65 MPa (named PEP 35-PEP 65) and the temperature of the experiments was changed in the range of 50-75 °C (named PET 50-PET 75). As a result, spherical in-reactor alloys granules of 0.45-2.5 mm diameter were produced.

Fraction of the alloy

A modified Kumagawa extractor was used to carry out a temperature-gradient extraction fractionation of

 TABLE I

 Size Distribution of PE Prepared at Different Temperature (wt %)

Sample	Temperature (°C)	D (wt %)	≥2 mm	2–1.45 mm	1.45–1 mm	1–0.45 mm	≤0.45 mm
PET50	50	92.42	0	5.64	25.96	60.82	7.58
PET60	60	87.33	0	8.96	24.52	53.85	12.67
PET70 PET75	70 75	92.45 95.79	0.39 2.28	12.65 26.28	29.79 28.47	49.61 38.76	7.55 4.21

Al/Ti = 60, Al/Si = 25; the pressure of ethylene is 0.6 MPa, polymerized for 60 min. \overline{D} , weight percentage of the polymer particle whose size is in the field of 0.45–2.0 mm.

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Sample	Pressure	D̄ (wt %)	≥2 mm	2–1.45 mm	1.45–1 mm	1–0.45 mm	≤0.45 mm
PEP65	0.65 MPa	90.8	0	9.4	26.1	55.3	9.2
PEP60	0.6 MPa	87.3		8.9	24.5	53.9	12.7
PEP50	0.5 MPa	88.86	0	4.8	21.7	62.3	11.2
PEP35	0.35 MPa	87.34	0	0	1.1	86.3	12.6

 TABLE II

 Size Distribution of PE Prepared at Different Pressure (wt %)

Al/Ti = 60, Al/Si = 25, 60 °C, polymerized for 60 min.

the polymer.¹² *n*-Octane was used as the solvent to successively extract the sample at different controlled temperatures (25, 90, 110, and 120°C). Five fractions were collected by extracting 2 g of every sample at 25, 90, 110, 120, and >120°C, and they were named fractions A, B, C, D, and E, respectively. Purified fractions were obtained after the extract solutions were concentrated, the polymer was precipitated, and the fractions were washed and dried in a vacuum.

Measurement of the ethylene content

Fourier transform infrared (FTIR) spectra of the alloy samples and the fractions were recorded on a Bruker Vector 22 FTIR spectrometer. A thin film of the samples was prepared through hot pressing. An empirical equation⁸ was used for estimation of the ethylene content based on the infrared spectrum,

$$\ln A_{1150} / A_{720} = 2.98 - 0.060 \times C_2,$$

where C_2 is the molar percentage of ethylene in the polymer.

Measurement of the particle porosity

The measurement of the particle porosity was carried out in a density bottle whose weight was W_0 . The volume of the density bottle weighted (*V*) was calibrated by *n*-butanol. The density bottle was filled with polymer particle, W_1 , and then filled with *n*-butanol. The density bottle was put into a thermostatic bath for 4 h. It was then dried and weighed, W_t . The following equation was used to calculate the bulk density of polymer particles (ρ_b):

$$V = \frac{W_{\rm polymer}}{\rho_{\rm b}} + \frac{W_{\rm t} - W_{\rm l}}{\rho_{\rm n-butanol}},$$

where $W_{polymer}$ refers to the weight of polymer particles, and $\rho_{n-butanol}$ refers to the density of *n*-butanol.

The apparent density of polymer particles ρ_{app} can be measured by substituting mercury for *n*-butanol. The porosity of polymer particles (*P*) can be calculated by the equation

$$P = 1 - \frac{\rho_{\rm app}}{\rho_{\rm b}}$$

Measurement of the mechanical and physical properties

The notched Izod impact strength of alloy samples was measured on a Ceast impact strength tester according to ASTMD 256. The flexural modulus and flexural strength were measured following ASTMD 709 on a REGER-2000 electronic tester. The sample strips were prepared by injection molding using a mini-injector.

The intrinsic viscosity of polymer fractions was measured using an Ubbelohde viscometer at 135°C with decahydronaphthalene as solvent.

 TABLE III

 Size Distribution of PE/PP Alloys Prepared at Different Temperature (wt %)

Sample	Temperature (° C)	Catalytic efficiency (kg polymer/g Ti)	<i>D</i> (wt %)	≥2 mm	2–1.45 mm	45–1 mm	1–0.45 mm	≤0.45 mm
PET75	75	38.2	97.8	0.3	9.2	28.1	60.5	1.9
PET70	70	74.4	95.7	0.2	17.6	36.6	41.5	4.1
PET60	60	133.2	93.4	2.6	38.2	28.6	26.6	4.1
PET50	50	91.7	84.3	0.5	8.7	16.6	58.9	15.3

Al/Ti = 60, Al/Si = 25; the pressure of ethylene is 0.6 MPa, polymerized for 60 min; the pressure of propylene is 0.8 MPa, polymerized for 2 h.

Sample	Pressure (MPa)	Catalytic efficiency (kg polymer/g Ti)	<i>D</i> (wt %)	≥2 mm	2–1.45 mm	1.45–1 mm	1–0.45 mm	≤0.45 mm
PEP65	0.65	86.2	87.38	5.25	23.69	27.49	36.21	7.37
PEP60	0.6	133.2	93.37	2.57	38.15	28.58	26.60	4.09
PEP50	0.5	81.4	92.55	0.20	13.40	32.16	46.99	7.25
PEP35	0.35	50.7	93.29	0.33	3.24	23.45	66.60	6.38

 TABLE IV

 Size Distribution of PE/PP Alloys Prepared at Different Pressure (wt %)

Al/Ti = 60, Al/Si = 25; the reaction temperature is 60 °C, time for polyethylene polymerization is 60 min; the pressure of propylene is 0.8 MPa, polymerized for 2 h.

RESULTS AND DISCUSSION

Influence of polymerization conditions on alloy compositions

In the first stage of polymerization, the gas phase polymerization of ethylene was conducted in a glass autoclave under different conditions. Figure 1 shows the appearance of PE particles and PE/PP in-reactor alloy particles. Spherical PE particles 0.45-2.5 mm in diameter were produced. About 90 wt % of PE particles fell within a diameter range of 0.45-2.0 mm. Tables I and II show the size and its distribution of PE particles under different temperature or pressure, where D represents the weight percentage of particles in the range of 0.45–2.0 mm. PE particles produced under different conditions are slightly different in size and distribution, which is mainly determined by the size and distribution of the catalyst used. The size and distribution of PE/PP alloys are listed in Tables III and IV. The size of the PE/PP alloy is similar to that of PE particles. We conjecture that the polymer produced in the second stage mostly exists in tiny holes inside the PE particles. Figure 2 shows the internal morphology of PE particles and PE/PP in-reactor particles. PE/PP in-reactor alloy particles are more compact than PE particles. The average porosity of PE particles and PE/PP alloy particles is listed in Tables V and VI. Under appropriate conditions we could obtain PE particles with porosity as great as 64 vol %. After being blending with PP, we still obtained PE/PP alloys with porosity of 50 vol %. That is very fit for further blending with other polymers or modifying by polar monomer. This makes it possible to make more and more new materials. The catalyst efficiency of the whole polymerization (two stages) was about 1.13×10^5 g polymer/g Ti.

The kinetics of the whole polymerization was determined by monitoring the flow rate of monomer entering the reactor. A typical rate profile of polymerization is shown in Figure 3. It is interesting to find two maxims of activity profiles. There are two accepted theories in titanium-based Ziegler–Natta catalyst:^{13–15} (1) the oxidation state of titanium undergoes a stepwise reduction after it is contacted with aluminum alkyl (e.g., TEA); (2) Ti³⁺ is reactive for both ethylene and α -olefin polymerization and Ti²⁺ is only active for ethylene.

Chien et al.¹⁶ reported that the distribution of oxidation states of various active Ti does not change with



(a)

(b)

Figure 2 SEM micrographs of internal morphology of PE particles and PE/PP alloy particles.

at Different Temperature					
Conditions (°C)	Porosity (vol %)				
75	26				
70	28				
60	64				
50	38				
	at Different Tempera Conditions (°C) 75 70 60 50				

TABLE V

Porosity of PE Particles Prepared

time after 30 min of polymerization. As shown in Figure 3, the second peaks begin to appear at 20 min (less than 30 min). Hence, we can propose that changes in the titanium oxidation state aren't responsible for the second peak. Dispersion limit is the key

factor influencing the form of the kinetic profile. After the second peak there was a rapid decay of polymerization rate during the reaction. Such a rate decay seems not to have resulted from the activity decay of active centers, as the catalyst should have reached its stationary stage after about 2 h of homopolymerization. Therefore, it is more likely that the rate decay was caused by diffusion limitation in the polymer particles. As polymerization of propylene proceeded, the tiny holes in the PE particles were gradually filled with polymer, and the monomers had to diffuse through the solid polymer layer before reaching the active sites. This possibly resulted in diffusioncontrolled kinetics of polymerization. If there were diffusion limitation in the reaction, it influenced the relations between the reaction conditions and polymerization behaviors.

In our previous work,¹⁷ we proved that the *n*-octane-soluble part at 25°C in PE/PP in-reactor alloy is made up of PP-block-PE in which the PP segments have low or medium isotacticity. Figure 4 shows the effects of polymerization temperature on the content of the 25°C fraction (fraction A) and ethylene in the alloys. The content of fraction A is very low. Changing the temperature from 50 to 75°C exerted only a limited influence on the content of fraction A. But the ethylene content dropped sharply as the reaction temperature was reduced. By carefully analyzing the relationship between the content of fraction A and the content of propylene, we found that the content of fraction A was roughly proportional to the content of propylene. When the reaction temperature is high, the initial polymerization rate is high too. This results in the com-

 TABLE VI

 Porosity of PE Particles Prepared at Different Pressure

Sample	Conditions (MPa)	Porosity (vol %)
PEP65	0.65	41
PEP60	0.6	64
PEP50	0.5	47



Figure 3 Rate profile of polymerization at 60°C and 0.6 MPa of ethylene monomer pressure.

pact PE shell produced in the first stage that limits propylene monomer entrance into the PE particle. In the polymer particles the concentration of propylene is very low and it is hard to form fraction A. If the reaction temperature is too low, the whole polymerization activity is low. This also leads to low fraction A content. Only at an appropriate temperature will the fraction A content be high.All in all there are limits in regulating fraction A content with changes in reaction temperature.

As shown in Figure 5, rising ethylene pressure had a much stronger effect on fraction A content. Fraction A content was inversely proportional to ethylene pressure because when pressure is high the initial poly-



Figure 4 Effect of polymerization temperature on the composition of PE/PP in-reactor alloys. Ethylene pressure = 0.6 MPa, time = 1 h; propylene pressure = 0.8 MPa, time = 2 h.



Figure 5 Effect of ethylene pressure on the composition of PE/PP in-reactor alloys. Reaction temperature = 60° C. Other conditions are as in Figure 4.

merization rate is high too. There is a great deal of heat release during polymerization and the temperature rises ($\Delta T \ge 10^{\circ}$ C). There was agglomeration of polymer particles in the reactor that prevented propylene from penetrating the polymer particles. As ethylene pressure decreased, the ethylene concentration in the reactor decreased too and the polymerization rate dropped gradually. Therefore, the ethylene particles produced under low ethylene pressure loosened. In the second stage propylene was able to enter the ethylene particles more easily, which could be due to the rising propylene content in the alloys as ethylene pressure decreased.

Influence of polymerization conditions on polymer structural distribution

In our previous work,¹⁷ we proved that PE/PP inreactor alloy is made up of five portions: PP-block-PE in which the PP segments have low or medium isotacticity (fraction at 25°C), ethylene propylene segmented copolymer (fraction at 90°C), polyethylene (fraction at 110 °C), PE-*b*-PP block copolymer (fraction at 120°C), and polypropylene (fraction at \geq 120°C). The ethylene-propylene block copolymer plays an important role in improving the mechanical properties of the alloy, especially impact strength. Thus, controlling the structural distribution is an effective way of finetuning the properties of the final product. To study the structural distribution of the alloy samples, we separated each sample into five fractions by TGEF. The fraction distributions of samples prepared at different reaction temperature are shown in Figure 6. In every

sample, the content of the 25°C fraction is very low (≤ 0.29 wt %). The content of the 25°C fraction in PE/PP in-reactor alloy is much lower than that in the PP/EPR alloy. But the content of PE-b-PP block copolymer (120°C fraction) in PE/PP in-reactor alloy is high $(\geq 25.4 \text{ wt }\%)$, whereas that in PP/EPR alloy is less than 28.2 wt %.8 The large difference in structural distribution between PE/PP in-reactor alloy and PP/ EPR alloy should create different properties. The amount of 25°C fraction increased slightly when the reaction temperature decreased, but the amount of PE-b-PP block copolymer decreased. To understand this phenomenon, we should consider the PE-b-PP block copolymer formed at the very beginning of the homopolymerization of propylene after ethylene homopolymerization. At the beginning of propylene homopolymerization, many of the active centers still have chemically bonded PE propagation chains that are formed in the ethylene homopolymerization stage. When these active centers meet propylene monomer in the second stage, copolymerization will occur on these living PE chains, forming block copolymers with long PE segments. After a chain-transfer reaction, such block copolymer chains will leave the active centers, and the later formed chains will be mainly random copolymer chains. This fact implies that the amount of PE-b-PP block copolymer formed at the switching point from the ethylene homopolymerization stage to the propylene homopolymerization stage should only depend on the number of active centers. A high reaction temperature is propitious to overcome its activation energy. Hence, raising the polymerization temperature will accelerate the reduction of the catalyst's oxidation state to produce active centers. The higher the polymerization temperature, the more active centers are produced during a certain period of reaction.



Figure 6 Fraction distributions of PE/PP in-reactor alloys prepared under different reaction temperatures. Polymerization conditions are given in Figure 4.



Figure 7 Fraction distributions of PE/PP in-reactor alloys prepared under different ethylene monomer pressure. Polymerization conditions are given in Figure 5.

Then more block copolymer is formed. Raising the reaction temperature will slightly influence the amount of random copolymer, but will favor the formation of block copolymer.

Changing the ethylene monomer pressure can also obtain PE/PP in-reactor alloys with very low content of 25 °C fraction (\leq 1.67 wt %), but a high content of PE-*b*-PP block copolymer (\geq 38.3 wt %). Changing the ethylene monomer pressure exerted a slight influence on the content of the 25 °C fraction. But the content of PE-*b*-PP block copolymer is much different. As shown in Figure 7, the content of the 25°C fraction increased slightly when ethylene monomer pressure decreased from 0.65 to 0.35 Mpa. But the content of PE-b-PP block copolymer decreased as the pressure was reduced. Because for these alloys the synthesis conditions are the same except for ethylene monomer pressure, this result should not relate to the amount of active centers. As stated above, the dispersion limit controlled the polymerization process. We observed that the lower the ethylene monomer pressure is, the looser the PE particles formed in the first stage are. That is, the lower the ethylene monomer pressure is,

the more active centers can meet propylene monomer. At the very beginning of the second stage (propylene homopolymerization), there are two competitive polymerizations in the reactor. One is the copolymerization of living PE chain and propylene. The other is propylene homopolymerization. At high ethylene monomer pressure, the polymerization rate is high and it is possible for PE to form a tight shell around the active center. Thus, propylene monomer can't meet the living PE chain. Then there is no random copolymer and multiblock copolymer in the product. Under this condition propylene just meets the active center, which never reacts with ethylene to form homopropylene, so the content of fraction E (polypropylene) in these alloys increases as ethylene monomer pressure is reduced from 0.65 to 0.35 MPa.

Mechanical and physical properties of the inreactor alloys

Some important mechanical properties such as impact strength and flexural modulus were measured, and the results are summarized in Table VII. The content of PE-*b*-PP block copolymer was the most important parameter determining impact strength. At PE-*b*-PP block copolymer contents of 25.4 wt %, impact strength was as high as 67.3 kJ/m². As a reference, the impact strength of iPP at room temperature is only about 7.74 kJ/m². Therefore, in-reactor blending based on a spherical Ziegler–Natta catalyst is a very effective way of improving the impact properties of iPP.

As shown in Table VII, there is a limit in improving the impact strength by simply introducing more PP*block*-PE in which the PP segments have low or medium isotacticity (25°C fraction) in the alloy. The sample prepared at 0.35 MPa and 60°C contained more 25°C fraction than the sample prepared at 0.5 MPa and 60°C (1.67 versus 0.71 wt %), but the former showed lower impact strength than the latter. This means that the 25°C fraction is not the only factor in improving the impact strength. In previous work, we reported that there was a synergistic effect between random copolymer fractions and block copolymer fractions in

 TABLE VII

 Influence of Polymerization Conditions on the Mechanical and Physical Properties of In-Reactor Alloys

	Ethylene pressure (MPa) ^b		
Polymerization conditions	0.5	0.35	
Content of 25°C fraction (wt %)	0.71	1.67	
Content of 120°C fraction (wt %)	43.2	38.3	
Impact strength (kJ/m^2)	143.9	131.5	
Flexual module (MPa) $[\eta] (1/g \cdot ml)$	1614.5 12 1043.1 (233.6 619.1	
$[\eta] (1/g \cdot ml)$	161	4.5 12 3.1 (

^a Pressure of the ethylene monomer, 0.6 MPa; time of polyethylene, 60 min.

^b Polymerization temperature, 60°C; time of polyethylene, 60 min.

relation to impact properties. The coexistence of both portions in a suitable ratio is the key to high impact strength.

However, the flexural modulus of the alloy was strongly affected by the content of the 25°C fraction. This is easy to understand because the 25°C fraction is a kind of elastomeric material with very low strength and modulus. Therefore, simply increasing the 25°C fraction portion is an effective way of lowering the flexural modulus, as the sample prepared at 0.6 MPa and 60°C showed much higher flexural modulus than the sample prepared at 0.35 MPa and 60°C, although both had similar ethylene contents (26.12 versus 33.06 wt %). In this way, in-reactor alloys may be made that can be applied in cases where both high toughness and high flexibility are required. They can substitute for some engineering plastics.

The intrinsic viscosity of the in-reactor alloys also depended on polymerization conditions. Ass shown in Table VII, the intrinsic viscosity of the alloy decreased as the 25°C and 120°C fraction contents of the alloy increased. This was likely caused by the molecular weights of the copolymers (both 25°C and 120°C fractions) being low.

CONCLUSIONS

The conditions of gas phase ethylene polymerization strongly influence the composition and structural distribution of in-reactor PE/PP alloys based on a spherical, high-yield Ziegler–Natta catalyst. Raising the polymerization temperature is the most effective way of speeding up polymerization and regulating the ethylene content of PE/PP alloys, but it will cause a greater increase in PE-*b*-PP block copolymer fraction than in the fraction of PP-*block*-PE in which the PP segments have low or medium isotacticity. Although changing ethylene monomer pressure could influence the ethylene content of PE/PP alloys slightly, it is an effective way of regulating structural distribution. Reducing the monomer pressure will increase the content of PP-block-PE in which the PP segments have low or medium isotacticity and PE-b-PP block copolymer. The mechanical properties of the alloys, including impact strength and flexural modulus, can be regulated in a broad range with changes in polymerization conditions. These properties are highly dependent on the amount, distribution, and chain structure of the PPblock-PE in which the PP segments have low or medium isotacticity and PE-*b*-PP block copolymer. The impact strength is affected by both PP-block-PE, in which the PP segments have low or medium isotacticity, and PE-b-PP block copolymer portions in a complicated way, whereas flexural modulus is mainly determined by the amount of PP-block-PE in which the PP segments have low or medium isotacticity.

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