Isotactic Polypropylene/Ethylene-*co*-Propylene Blends: Influence of the Copolymer Microstructure on Rheology, Morphology, and Properties of Injection-Molded Samples

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ABSTRACT: Melt rheological behavior, phase morphology, and impact properties of isotactic-polypropylene (iPP)-based blends containing ethylene-propylene copolymer (EPR) synthesized by means of a titanium-based catalyst with very high stereospecific activity (EPR_{Ti}) were compared to those of iPP/EPR blends containing EPR copolymers synthesized by using a traditional vanadium-based catalyst (EPR_v) . The samples of EPR copolymers were synthesized ad hoc. They were characterized by comparable propylene content, average molecular masses, and molecular mass distribution in order to assess the effects of distribution of composition and sequence lengths of the structural units on the structure-properties correlations established in the melt and in the solid state while studying different iPP/EPR pairs.¹⁻⁵ Differential scanning calorimetry, (DSC), wide-angle X-ray spectroscopy (WAXS), small-angle X-ray (SAXS), and scanning electron microscopy (SEM) investigations showed that the EPR_{Ti} chain is characterized by the presence of long ethylenic sequences with constitutional and configurational regularity required for crystallization of the polyethylene (PE) phase occurring, whereas a microstructure typical of a random ethylene–propylene copolymer was exhibited by the EPR_v copolymer. The different intra- and intermolecular homogeneity shown by such EPR phases was found to affect their melt rheological behavior at the temperatures of 200 and 250°C; all the EPR_{Ti} dynamic-viscoelastic properties resulting were lower than that shown by the EPR_V copolymer. As far as the melt rheological behavior of the iPP/EPR_v and iPP/EPR_{r_i} blends was concerned, both the iPP/EPR pairs are to be classified as "negative deviation blends" with G' and G" values higher than that shown by the plain components. The extent of the observed deviation in the viscosity values and of the increase in the amounts of stored and dissipated energy shown by such iPP/EPR pairs was found to be dependent on copolymer microstructure, being larger for the melts containing the EPR_{Ti} copolymer. The application of the Cross-Bueche equation also confirmed that, in absence of shear, the melt phase viscosity ratio is the main factor in determining the viscosity of iPP/EPR blends and their viscoelastic parameters. The general correlation established between EPR dispersion degree (range of particle size and number-average particle size), as determined in injection-molded samples, and melt phase viscosity ratio (μ) was ratified; the type of dependence of EPR size upon μ value was in qualitative agreement with the prediction of the Taylor–Tomotika theory. Contrary to expectation,^{1–5} for test temperature close to iPP T_g , EPR_V particles ranging in size between 0.75 and 1.25 μ m resulted and were

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more effective than EPR_{Ti} particles, ranging in size between 0.25 and 0.75 μ m, in promoting multiple craze formation. Also taking into account the SAXS results, revealed that the molecular superstructure (i.e., crystalline lamellar thickness and amorphous interlayer) of the iPP matrix is unaffected by both the presence of EPR_{Ti} and EPR_{v} phase. The above finding was related to the ethylenic crystallinity degree shown by the EPR_{Ti} copolymer. In particular, such a degree of crystallinity was supposed to deteriorate toughening by decreasing the tie molecules density in the EPR_{T_i} domains, notwithstanding the beneficial effect of the ethylenic lamellar buildup. For test temperature close to room temperature, the ductile behavior exhibited by the iPP/EPR_{Ti} blends was accounted for by a predominant shear yielding fracture mechanism probably promoted by a high concentration of interlamellar tie molecules among iPP crystallites in agreement with DSC results. Nonisothermal crystallization experiments showed, in fact, that the crystallization peak of the iPP phase from iPP/EPR_{Ti} melt is shifted to higher temperatures noticeably, thus indicating a material characterized by a comparatively higher number of spherulites per unit value grown at lower apparent undercooling values. Accordingly, WAXS analysis revealed comparatively higher iPP crystal growth in the directions perpendicular to the crystallographic planes (110) and (040) of the iPP. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 701–719, 1999

Key words: polypropylene; ethylene–propylene copolymers; blends; melt rheology; phase structure; impact properties

INTRODUCTION

The results of investigations concerned with the influence of the molecular structure (molecular mass, molecular mass distribution, and chain constitution) of random ethylene-propylene copolymers (EPR) on melt rheology, phase morphology, and impact properties of isotactic-polypropylene (iPP)-based blends have been reported in previous articles.^{1–5} It has been demonstrated that, for a given iPP/EPR pair, the molecular mass and molecular mass distribution of both components are the dominant structural factors. together with the crystallization conditions, in determining the phase structure in the melt and in the condensed state, on which mainly the final properties of iPP/EPR materials depend. A general correlation can be established between the mode and state of dispersion of the EPR domains, in the melt and in the condensed state, and the melt rheological properties of the single components. Such a correlation is between the EPR dispersion degree (range of the EPR particle size and EPR number-average particle size), as determined in crystallized samples, and the melt phase viscosity ratio. The type of dependence of the size of the EPR dispersed particles upon the melt phase viscosity ratio has been found to agree qualitatively with the prediction of the Taylor-Tomotika theory. It has been demonstrated, moreover, that a general correlation can also be established between the toughening of iPP/EPR blends and the dispersion degree of the EPR co-

polymers. Such a correlation is between the impact strength values of iPP/EPR blends and the number-average particle size of the EPR copolymers (D_n) . Taking into account that the D_n value increases with an increasing logarithm of the melt phase viscosity ratio (μ), showing a minimum in the vicinity of $\mu = 1$, the toughening of iPP/EPR blends can be directly related to the melt phase viscosity ratio, that is, for a given iPP sample to the molecular mass and molecular mass distribution (MMD) of the EPR copolymer. The prediction of Taylor-Tomotika was found, in fact, to fail for EPR high MMD values (\overline{M}_{w} larger than $10 \cdot M_n$). In addition, it has been shown that, for a given crystallization process, the properties of iPP/EPR blends depend also upon the crystalline texture, as at the end of the crystallization process, the iPP/EPR material is characterized by the presence of iPP spherulites (larger or smaller according to the nucleation density and undercooling) that have occluded mainly in intraspherulitic regions of the EPR domains. Moreover, the EPR phase can modify the inner structure of the iPP spherulites (crystalline lamellar thickness and amorphous interlayer thickness) and the physical structure of the interspherulitic boundary regions and amorphous interlamellar regions.^{2,3} In order to achieve a deeper and more rigorous understanding of the influence of the EPR molecular structure and, particularly, of the effects of distribution of composition and sequence lengths of the structural units on the

Sample	$ar{M}_n\cdot 10^3$	$ar{M}_w\cdot 10^3$	$ar{M}_w/ar{M}_n$	C_3 Content (% wt/wt)	T_g (°C)	T'_m (°C)
iPP	78.7	509	6.5	_	7	165
$\mathrm{EPR}_{\mathrm{Ti}}$	34.8	213	6.1	38.5	-41	122
EPR_v	30.8	199	6.5	38.5	-43	

Table I Number-Average Molecular Mass (\overline{M}_n) , Weight-Average Molecular Mass (\overline{M}_w) , Molecular Mass Distribution $(\overline{M}_w/\overline{M}_n)$, Glass Transition Temperature (T_g) , and Apparent Melting Temperature (T'_m) for Plain iPP and EPR Copolymers, Together with EPR Propylene Content (C_3)

structure-properties correlations of iPP/EPR blends, EPR copolymers of comparable propylene content, average molecular mass, and molecular mass distribution were synthesized ad hoc using catalysts with very different stereospecific activity. The synthesized EPR copolymers were meltblended with the same iPP sample used in the previous works. The melt rheological behavior, phase morphology, and impact properties of iPP/ EPR blends containing EPR phase synthesized by means of a titanium-based catalyst with very high stereospecific activity have been compared to that shown by iPP/EPR blends containing EPR phase synthesized by means of a so-called traditional vanadium-based catalysts. In the present article, results of studies dealing with injectionmolded samples of this type of iPP/EPR blends are reported. The final target of the research is to impart desired properties to EPR-modified iPP materials by suitably selecting iPP and EPR components according to their molecular masses, molecular mass distribution, constitution, and tacticity and by optimizing crystallization conditions.

EXPERIMENTAL

Materials

The materials used in this study were an iPP (HS005) made by Himont and two EPR copolymers synthesized in the Himont–"Giulio Natta" Research Center following the following two different procedures: the first was a synthesis process in gas phase with a titanium-based catalytic system; the second one was a suspension polymerization with a vanadium-based catalytic system. The EPR copolymers so obtained have been referred to as EPR_{Ti} and EPR_V , respectively. The average molecular masses and molecular mass distributions of the starting polymers, deter-

mined by means of gel permeation chromatography (GPC) in ortho-dichlorobenzene at the temperature of 135°C, are reported in Table I.

Blending and Sample Preparation

The iPP and EPR copolymers were adiabatically mixed in a Werner mixer with a blending time of 3.5 min. Blends with composition 80/20 (wt/wt) were prepared. After blending, the materials were injection-molded by means of an injection press at 260°C with a mold temperature of 60°C.

Techniques

Oscillatory Shearing Flow Properties

The oscillatory shearing flow properties, namely, the complex viscosity η^* (defined by $\eta^* = \eta' - i \eta''$, where η' is the dynamic viscosity or the real part of the viscosity, and η'' is the imaginary part of the viscosity), the storage modulus G' (defined by $G' = \omega \eta''$, where ω is the frequency of the oscillations in radians per second) and the loss modulus G'' (defined by $G'' = \omega \eta'$) of the plain components and blends, were determined at 200 and 250°C by means of a Rheometrics Mechanical Spectrometer in the plate-plate mode with a constant strain and an angular frequency ranging between 0.01 and 100 rad s⁻¹.

Differential Scanning Calorimetry

The thermal behavior of the single components and blends was analyzed by means of a differential scanning calorimeter Mettler TA 3000 equipped with a control and programming unit (microprocessor T_c 10). The apparent melting temperatures (T'_m) and the crystallinity indices (X_c) of the single components and blends were determined following this procedure: the samples were heated from room temperature up to 200°C with a rate of 10°C min, and the heat evolved













during the scanning process (dH/dt) was recorded as a function of temperature. The T'_m values and the apparent enthalpies of melting (ΔH^*) were obtained from the peak temperature and the area of the $dH/dt - T'_m$, respectively. The crystallinity indices were calculated from the ratio between ΔH^* value and the enthalpy of melting of 100% crystalline phase (ΔH^o) .

The effect of nucleating ability of the EPR phase on the crystallization process of iPP was investigated following this procedure: the samples were heated from room temperature up to 200° C with a rate of 10° C min, kept at this temperature for 10 min, and cooled with a rate of 10° C min.

Dynamic Mechanical Thermal Analysis

The tangent δ and storage modulus of samples of single components and blends were measured by means of dynamic mechanical thermal analysis (DMTA; Rheometric Scientific MK III). Test data were collected in tensile mode from -100 to 100 C° using a scanning rate of 1.5 C°/min and a frequency of 1 Hz.

Scanning Electron Microscopy

The mode and state of dispersion of the minor component were investigated by means of a scanning electron microscope (Philips 501) on iPP/ EPR cryogenically fractured surfaces and etched smoothed surfaces after coating with gold-palladium.

Wide-Angle X-ray Scattering

Wide-angle X-ray scattering (WAXS) studies were carried out on samples of single components and blends by means of a PW 1060/71 Philips diffractometer (Cu K α Ni-filtered radiation) equipped with sample spinning; the high voltage was 40 KV, and the tube current was 30 mA. The crystallinity indices were obtained from the ratio between the areas under the crystalline peaks and the total area of the diffractograms.

Small-Angle X-ray Scattering

Small–angle X-ray scattering (SAXS) studies were carried out on samples of single components

and blends by means of a compact Kratky camera equipped with a Braun one-dimensional positional sensitive detector. Ni-filtered Cu (K α) radiation generated from a Philips X-ray generator (PW 1730/10) operating at 40 KV and 30 mA was used. The raw scattering data were corrected for parasitic scattering, absorption, and slit smearing by using Vonk's method.⁶ The desmeared intensities were then Lorentz-factor-corrected by multiplying by s^2 ($s = 2 \sin\theta/\lambda$).⁷

Impact Strength

Notched Izod impact strengths of injectionmolded samples were measured by means of a Ceast pendulum in a temperature range from -60 up to 23°C according to ASTM D256. The fractographic analysis of fractured surfaces was carried out by scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Melt Rheology of Single Components and Blends

Dynamic Viscoelastic Properties of Single Components and Blends

The dependence of the logarithm of the modulus value of the complex viscosity $(|\eta^*|)$, dynamic storage modulus (G'), and loss modulus (G'') upon the logarithm of the investigated frequencies for the plain EPR_{Ti} copolymer at the temperatures of 200 and 250°C is compared to that shown by the plain EPR_v copolymer in Figure1; in each plot, for the sake of comparison, the $|\eta^*|$, G' and G' logarithms of the plain iPP are also reported. As shown, and as expected on the basis of results already obtained by studying different iPP and EPR copolymers, for both iPP and EPR copolymers used in this work, $|\eta^*|$ values decrease; whereas G' and G'' values increase with increasing frequency. It is to be noted that, in the two first decades at least, the EPR samples show different rheological behavior. All the EPR_{Ti} dynamic properties results, in fact, are lower than that shown by the EPR_{V} sample (see Fig. 1); in particular, higher decreases are observed in the $|\eta^*|$ and G' values, contrary to the expectation on

Figure 1 Logarithm of the modulus value of the complex viscosity $(|\eta^*|)$, storage modulus G', and loss modulus G'' as a function of logarithm of the frequency (ω) for plain EPR and iPP at the temperatures of 200 and 250°C.

the basis of the average molecular masses of such copolymers (see Table I). Such results seem to suggest that the EPR_{Ti} melt is characterized by comparatively lower entanglements concentration and/or that the EPR_{Ti} entanglements have time to slip and relax out the stresses. Taking into account that the average molecular mass M_w dominates the viscosity at low frequency,⁸⁻¹¹ the different rheological behavior shown by such EPR melts could be ascribed to different intra- and intermolecular homogeneity of such copolymers (distribution of composition and length of the sequences of the structural units) that affect the flow mechanism in agreement with the principle that the system tends to reduce its dissipation of energy to a minimum. The different MMD of such investigated EPR copolymers also has to be taken into account (see Table I); results obtained by previous study on different EPR melts having, for the same \overline{M}_{w} and/or \overline{M}_{n} , different MMD, showed, in fact, that the sensitivity of the EPR melts to frequency increases with increasing the M_w/M_n $ratio.^3$

Figure 2 shows the dependence of the logarithm of the modulus value of the complex viscosity $|\eta^*|$ upon the logarithm of the investigated frequencies at the temperatures of 200 and 250°C for $iPP\!/EPR_{Ti}$ and $iPP\!/EPR_V$ blends. As shown, and as expected, such iPP/EPR melts are pseudoplastic: $|\eta^*|$ values decrease with increasing frequency, moreover, mixing results in a decrease in viscosity below the mean value of the plain components, such a decrease being larger at low frequency. Note that a comparatively higher extent of such a deviation is shown by the blends containing the EPR_{Ti} copolymer. This effect is designated as a negative deviation from the following logarithm rule of mixture that applies at constant temperature and shear rate,^{12,13} as follows:

$$\log \eta = \phi_1 \log \eta_1 + \phi_2 \log \eta_2$$

where η is the viscosity of the mixture, η_1 and η_2 are the viscosities of the two components measured at the same temperature, and ϕ_1 and ϕ_2 are their volume fractions. Such results agree with those obtained previously by studying different iPP/EPR blends.¹

Figures 3 and 4 show for the iPP/EPR blends the dependence of the logarithm of G' and G''values upon the logarithm of the investigated frequencies at the temperatures of 200 and 250°C, respectively; in each plot, the modulus logarithm of the single components for the sake of comparison is also reported. As shown by the comparison between such figures, both the amount of energy stored and dissipated by the blend systems decrease with increasing temperature. Note that, for a given temperature in the two first decades of the investigated frequency, such iPP/EPR melts show G' and G'' values higher than that of the plain components, with the extent of such an increase being larger for the blend containing EPR_{Ti} copolymer.

Determination of Zero-Shear Viscosity of Single Components and Blends

Taking into account that, in oscillatory measurements on polymer melts, the frequency (ω) becomes analogous to shear rate (γ);^{14–17} and, assuming an approximate equivalence of η^* and apparent viscosity (η_a),^{17–22} the zero-shear viscosity (η_o) of both single components and blends has been calculated by using the following modified Cross–Bueche equation²³:

$$\frac{\eta_o}{\eta_a} = 1 + (\alpha \ \gamma)^m$$

where η_o is the zero-shear viscosity, α is a parameter that, according to Cross, should correspond to the characteristic relaxation time related to molecular mass for the linear polymer solution, and m gives a measure of the shear-thinning of the melt, that is, a measure of decrease in viscosity with increasing rate of shear. According to Iwakura et al.,²⁴ for polymer melts, α is related to the size of the apparent flow unit; the reciprocal of α corresponds to the shear rate at which η_a $= \eta_o/2$. From $1/\eta_a$ versus γ^m curve, the zeroshear viscosity η_o and α values are easily obtained from the intercept and slope, respectively.

The m, η_o , and α values of the single components and blends at the temperatures of 200 and 250°C are reported in Tables II and III, respectively. For the blends, the zero shear viscosity values were calculated assuming the additivity logarithm rule (η'_o) according to the following equation:

$$\log \eta'_{o} = \phi_{1} \log \eta_{0(1)} + \phi_{2} \log \eta_{0(2)}$$

where η'_o is the zero-shear viscosity of the blend, $\eta_{0(1)}$ and $\eta_{0(2)}$ are the zero-shear viscosities of the two components measured at the same tempera-



(|_{*}m|) gol







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Sample	η_o (Pa)		α	(s)	m	
	200°C	250°C	200°C	250°C	200°C	250°C
iPP	18791	8200	0.886	0.804	2/3	4/7
EPR_{Ti}	12489	4271	0.138	0.078	2/3	4/7
EPR _v	17383	7298	0.488	0.233	4/7	6/11

Table II Application of Cross Equation: Values of η_0 , α , and *m* for Plain iPP and EPR Copolymers at the Temperatures of 200 and 250°C

ture, and ϕ_1 and ϕ_2 are their volume fractions. These are also reported in Table III. As shown in Table II, for a given temperature, the zero-shear viscosity and α values calculated for EPR_{Ti} copolymer results are considerably lower than that obtained for the EPR_v copolymer, indicating that the transition from Newtonian to pseudoplastic flow of EPR_{Ti} starts at a frequency higher than that of the EPR_{v} copolymer. On the other hand, the EPR_{v} melt undergoes comparatively less severe shear thinning in the non-Newtonian region. From the above, it could be supposed that, in the absence of shear, the EPR_{Ti} melt may be described in terms of a discontinuous two-phase model, where the physical entrapping among the macromolecules results is hindered by the presence of macromolecules with comparatively lower viscosity.

The application of the Cross equation to iPP/ EPR blends reveals that, for a given temperature, higher η_o and α values are obtained for the blend containing the EPR_{Ti} copolymer; whereas the same value is found for the *m* parameter (2/3) and (4/7) (see Table III). Moreover, the η_o values of all the blends show a negative deviation from the logarithm additivity rule; the extent of such a deviation decreases strongly on increasing the temperature. The activation energies for the viscous flow values (ΔE^*) for the single components and blends were obtained by applying the following exponential relation accounting for the temperature dependence of the viscosity at temperatures far above the T_g or the melting point²⁵:

$$\eta_o = A \, \exp(\Delta E^*/RT)$$

where A is a constant characteristic of the polymer and its molecular mass, ΔE^* is the activation energy for the viscous flow, R is the gas constant, and T is the temperature in Kelvin degrees. There are reported in Table IV. As shown, both the EPR copolymers exhibit ΔE^* values higher than that shown by the plain iPP, indicating a comparatively higher volume of the flow elements; the highest ΔE^* value shown by the EPR_{Ti} phase could suggest a more rigid chain of such copolymer. Note, moreover, that for the iPP/EPR blends, the activation energy values depend on the EPR molecular structure. For the blends containing EPR_v copolymer, the ΔE^* value results are quite comparable to that of the plain iPP; whereas a ΔE^* value lower than that of the plain iPP is obtained for the blends containing the EPR_{Ti} copolymer. Such findings indicate that for the iPP/EPR_{Ti} blends, a volume reduction of the flow element occurs.

Thermal Behavior and Crystallinity

The differential scanning calorimetry (DSC) thermograms of samples of the neat EPR_{Ti} copolymer

Table III Application of Cross Equation: Values of η_o , α , and *m* for iPP/EPR Blends, Together with the Zero-Shear Viscosity Values Calculated Assuming Log Additivity (η'_o) and the Melt Flow Viscosity Ratio (μ) at the Temperatures of 200 and 250°C

	η_o	(Pa)	α	(s)	<i>n</i>	n	η_o'	(Pa)		ı
Sample	200°C	250°C	200°C	250°C	200°C	$250^{\circ}\mathrm{C}$	200°C	250°C	200°C	250°C
iPP/EPR _{Ti} iPP/EPR _V	18315 17778	9599 7730	$0.690 \\ 0.665$	$\begin{array}{c} 0.805\\ 0.611\end{array}$	2/3 2/3	4/7 4/7	$\frac{415405}{455332}$	$207874 \\ 247340$	0.66 0.92	$0.57 \\ 0.89$

Table IV Activation Energy for the Viscuous Flow (ΔE^*) for Plain iPP and EPR Copolymers and for iPP/EPR Blends

Sample	ΔE^* (J mol ⁻¹)
iPP EPR _{Ti} EPR _V iPP/EPR _{Ti} iPP/EPR _V	$14,823 \\19,178 \\15,514 \\11,548 \\14,888$

show a single endothermic peak when heated from -100 to 215° C (see Fig. 5); the temperature position of the observed peak (T'_m) is reported in Table I and seems to indicate the presence of polyethylene (PE) phase.²⁶ As a matter of fact, the WAXS diffractogram of the plain EPR_{Ti} copolymer reported in Figure 6 shows, in addition to the broad diffraction noncrystalline halo typical of a random EPR copolymer, two peaks whose diffraction angles are characteristic for the orthorhombic crystal structure of linear polyethylene in the (110) and (200) crystallographic planes, respectively.²⁷ The above results show that by using the Ti-based catalyst, the EPR chain is characterized by the presence of long ethylenic sequences with constitutional and configurational regularity required for crystallization of the PE phase. The WAXS crystallinity index (X_c) of the EPR_{Ti} copolymer obtained from the ratio between the areas under the crystalline peaks and the total area result is equal to 0.11; on the other hand, the X_c value calculated from the ratio between the apparent enthalpy of melting and the enthalpy of melting of 100% crystalline polyethylene²⁶ is 0.06.

DMTA analysis performed on injection-molded samples of the iPP/EPR blends shows that such systems exhibit two distinct glass transition temperatures to be ascribed to EPR and iPP component, respectively. The T_g values shown by such iPP/EPR blends are reported in Table V, together with the values of the apparent melting temperatures (T'_m) of the iPP phase crystallized in presence of EPR phase. The DSC thermograms of samples of the iPP/EPR blends show, in fact, a single endothermic peak whose temperature position is characteristic of the melting of the α -form of iPP. From such thermal behavior, iPP and EPR are confirmed to be immiscible both in the amorphous condensed and in the melted state, in

agreement with results obtained by studying different iPP/EPR pairs.^{1–5}

The WAXS crystallinity index of the iPP/EPR blends $[X_{c(\text{blend})}]$ and of the iPP phase $[X_{c(\text{iPP})}]$ are also reported in Table V, together with the DSC crystallinity indices of the iPP/EPR_V blend. Because of the crystallization of EPR_{Ti} ethylenic sequences, it has been impossible to determine correctly the DSC crystallinity indices of the iPP/EPR_{Ti} blends.

The DSC nonisothermal crystallization curves of the plain iPP and EPR_{Ti} copolymer and of iPP/ EPR blends are shown in Figures 7 and 8. As shown, the plain iPP crystallizes between 121 and 92°C, with the temperature position of the maximum of the peak being at 110°C; whereas the EPR_{Ti} crystallizable ethylenic sequences crystallize between 111 and 88°C, with the temperature position of the maximum of the peak being at 102°C. As shown in Figure 8, when the iPP crystallizes in the presence of EPR phase, the crystallization peak shifts to higher temperature, indicating that both the EPR copolymers used in this work contain heterogeneous nuclei that migrate toward the iPP phase. It is to be noted that from the EPR_{Ti} phase, such a migration phenomenon is much higher than that occurring from the EPR_v phase.

Phase Structure

Mode and State of Dispersion of the Minor Component

The analysis by SEM of the mode and state of dispersion of the EPR copolymers realized in injection-molded samples shows that a layered structure parallel to the mold-filling direction, according to the schematic model reported in Figure 9, is developed. Moving from the border toward the core of the samples, the following three different layers are found:



Figure 5 DSC thermogram of the plain EPR_{Ti} co-polymer.



Figure 6 WAXS diffractogram of the plain EPR_{Ti} copolymer.

- 1. A skin surface (*S*) where no dispersed EPR domains can be observed probably due to the preferential wetting of the mold wall with iPP, as proposed by Southern and Ballman^{8,9};
- 2. an intermediate transition layer (I) where the EPR segregates into ellipsoidal-shaped domains with their major axis oriented along the mold-filling direction according to the flow pattern proposed by Tadmor²⁸ on the observation of Rose²⁹;
- 3. a core showing EPR droplet-like morphology to be ascribed presumably to relaxation and/or breaking up of the previously formed domains.

The layered distribution generated in such iPP/ EPR blends by the injection-molding process with reference to Figure 9, together with the stereological parameters of the EPR domains, are summarized in Table VI. As shown for the iPP/EPR_{Ti} blend, the thickness of the *S* layer is almost three times as high as that shown by the iPP/EPR_V blend; whereas comparatively lower thickness for both intermediate layer and core are found. Note

that a much finer dispersion is achieved in blends containing EPR_{Ti} copolymer. The values of the number-average particle size (D_n) found for EPR_{V} and EPR_{Ti} are 1.0 and 0.5 μ m, respectively. Therefore, the dispersion coarseness of such EPR copolymers increases with increasing their melt viscosity, that is, with an increasing phase viscosity ratio defined as $\mu = \eta_1/\eta_2$, where η_1 is the viscosity of the dispersed phase, and η_2 is that of the matrix in agreement with previous results by studies on different iPP/EPR blends.^{1–5} The type of dependence of the size of the dispersed particles upon the phase viscosity ratio observed for all the iPP/EPR systems investigated so far agrees qualitatively with the prediction of the Taylor-Tomotika theory.^{30–32} According to this theory, the plot of average particle diameter (\overline{D}_n) versus log μ should show a minimum in the vicinity of μ = 1 (see Fig. 10). Referring to Figure 10, the different dispersion degree shown by the EPR copolymers investigated in this work is accounted for by assuming that the data points of iPP/EPR blends containing such EPR phases lie on the left-hand branch of the curve; the data points of the iPP/EPR_v blends tend to approach the mini-

Table V Glass Transition Temperatures (T_g) , Apparent Melting Temperatures (T'_m) , and Crystallinity Indices (X_c) for Plain iPP and iPP Crystallized in the Presence of EPR_{Ti} and EPR_V Copolymers

Sample	T_g (°C)	T_m' (°C)	$\begin{array}{c} X_c \; (\text{Blend}) \\ \text{DSC} \end{array}$	$\begin{array}{c} X_c \ (\text{Blend}) \\ \text{WAXS} \end{array}$	$\begin{array}{c} X_c \ (\mathrm{iPP}) \\ \mathrm{DSC} \end{array}$	$egin{array}{c} X_c \ { m (iPP)} \ { m WAXS} \end{array}$
iPP	16	167	0.41	0.64	0.41	0.64
iPP/EPR _{Ti}	14; -42	167	_	0.50	_	0.63
iPP/EPR_v	15; -47	166	0.32	0.52	0.40	0.65



Figure 7 DSC nonisothermal crystallization curve of the plain EPR_{Ti} copolymer.

mum predicted by the theory. On the contrary, all the data points of the iPP/EPR pairs previously investigated lie on the right-hand of such a curve.^{1–5}

To get a deeper understanding of the EPR phase structure, an etching technique, based on selective dissolution of the copolymers by means of boiling xylene vapors, has been developed. It was shown in previous work that the iPP remains unaffected by such vapors also for a long exposure time (15 min).^{1,3} SEM micrographs of smoothed and etched surfaces of iPP/EPR_V and iPP/EPR_{Ti} blends are reported in Figure 11. As shown after an exposure time of 3 min, the EPR_V copolymer is apparently dissolved completely. In contrast, no apparently complete dissolution of the EPR_{Ti} domains is seen even for a longer exposure time (7 min), the EPR_{Ti} domains appearing to be swelled



Figure 9 Schematic model of the layered structure generated in injection-molded samples of iPP/EPR blends.

by the xylene boiling vapors. Such a morphological result indicates that only the amorphous phase of the EPR_{Ti} copolymer can be etched by xylene vapors, with the crystalline core of the EPR_{Ti} particles remaining unaffected.

Wide-Angle X-ray Scattering Analysis

The apparent crystal size (D) of polyethylene phase of the EPR_{Ti} copolymer, in the direction perpendicular to the (110) and (200) crystallographic planes, of the plain iPP and iPP phase crystallized in presence of EPR copolymers in the direction perpendicular to the (110), (040), and



Figure 8 DSC nonisothermal crystallization curve of (a) the plain iPP, (b) iPP/EPR_{Ti}, and (c) iPP/EPR_v.

	Layer Thickness (μm)		Shape of E	PR Domains	Size of EPR Domains (μm)		
Layer Code	iPP/EPR(V)	iPP/EPR(Ti)	iPP/EPR(V)	iPP/EPR(Ti)	iPP/EPR(V)	iPP/EPR(Ti)	
S	500	190	_	_	 major axis	 major axis	
Ι	1040	1230	ellipsoidal	ellipsoidal	$1.0 \div 4.2$	$0.75 \div 2.5$	
С	125	180	spherical	spherical	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{r} 0.25 \ \div \ 1.0 \\ 0.25 \ \div \ 0.75 \end{array}$	

Table VI Layered Distribution in Injection-Molded Samples of iPP/EPR Blends

(130) crystallographic planes, has been calculated by the Sherrer equation,⁷ as follows:

$$D_{hkl} = \frac{K\lambda}{\beta_o \cos(\theta_{hkl})}$$

where β_o is the half-width in radians of the reflection corrected for instrumental broadening; λ is the wavelength of the radiation used (1.5418 Å). The shape factor *K* is set equal to unity, and so the size data have to be considered as relative data.

The apparent crystal size of polyethylene phase of the EPR_{Ti} copolymer is found to be equal to 112 and 106 Å in the directions perpendicular to the (110) and (200) crystallographic planes,



Figure 10 Average diameters (\overline{D}_n) of dispersed particles as function of the logarithm of phase viscosity ratio (μ) , with the trend as predicted by Taylor–Tomotika.

respectively. The D values calculated for plain iPP and iPP/EPR blends are reported in Table VII, together with the ratio between the $D_{(110)}$ values and $D_{(040)}$ values. As shown for injectionmolded samples of both plain iPP and iPP/EPR blends, the $D_{(040)}$ values are considerably higher than the $D_{(110)}$ and $D_{(130)}$ values. Moreover, the crystal size of iPP phase crystallized in presence of EPR phase results are quite comparable in the direction perpendicular to the (130) crystallographic plane or larger than that shown by the plain iPP. These findings suggest that for the blends, a higher growth of the iPP crystals in the directions perpendicular to the (110) and (040)planes occurs. Such a higher growth can be accounted for by considering the DSC results. In the blends, the nonisothermal crystallization peak of the iPP phase is shifted to higher temperatures (see Fig. 8), indicating that crystal formation occurs at comparatively lower apparent undercooling. Note, moreover, that the $D_{(110)}/D_{(040)}$ ratios of the plain iPP and iPP/EPR blends are found to be almost constant (~ 0.6) within experimental error, indicating that when the iPP phase crystallizes in presence of EPR phase, the lamellar crystals grown in the directions perpendicular to the (110) and (040) crystallographic planes have size whose ratio is the same as that of the plain iPP.

Small-Angle X-ray Scattering Analysis

Typical Lorentz-corrected desmeared patterns for the plain EPR_{Ti} and EPR_V samples are compared in Figure 12. As shown, only the desmeared SAXS profile of the EPR_{Ti} copolymer exhibits a defined maximum. By applying the Bragg's law, the long period (*L*) calculated from the peak position has been obtained. Taking into account that the EPR_{Ti} crystallizable ethylenic sequences crystallize in a microspherulitic superstructure, as



(a)



(c)





(b)

(d)

Figure 11 SEM micrographs of smoothed surfaces of iPP/EPR blends etched with boiling xylene vapors: (a) iPP/EPR_v blend (5000×); (b) iPP/EPR_v blend (10,000×); (c) iPP/EPR_{Ti} blend (5000×); (d) iPP/EPR_{Ti} blend (10,000×).

shown by the morphological analysis carried out by optical microscopy at crossed and parallel polarizers on thin films of plain EPR_{Ti} copolymer, a two-phase model for the PE spherulite fibrillae

Table VII	Apparent Crystal Size (D) of Plain
iPP and iP	P/EPR Blends, Together with the
$D_{(100)}$ and $D_{(100)}$	$D_{(040)}$ Ratios

	$D_{(110)}$	$D_{(130)}$	$D_{(040)}$	D(110)/
Sample	(Å)	(Å)	(Å)	<i>D</i> ₍₀₄₀₎
iPP	94	94	149	0.63
iPP/EPR _{Ti}	105	94	162	0.64
iPP/EPR _v	99	97	162	0.61

with alternating parallel crystalline lamellae and a morphous layer have been assumed. Therefore, from the L value, the crystalline lamellar thickness (L_c) has been calculated by using the following relation:

$$L_c = \frac{X_c \cdot L}{(\rho_c/\rho_a)(1-X_c) + X_c}$$

where X_c is the crystallinity index, and ρ_c and ρ_a are the densities of the crystalline and amorphous PE phase, respectively. Subtracting the obtained L_c value from the L value, the average thickness of the amorphous interlamellar layer (L_a) has been obtained.



Figure 12 Desmeared SAXS patterns for EPR_{Ti} and EPR_{V} copolymers.

Typical Lorentz-corrected desmeared patterns for the iPP/EPR blends are shown in Figure 13; note that for both the blends, defined maxima are exhibited by the desmeared SAXS profiles. The L values calculated by applying the Bragg's law, and the L_c and L_a values determined by applying the L values to the above relation and introducing the Xc_{iPP} values by DSC and WAXS, are reported in Table VIII, together with those of the plain iPP. As shown, the L_{iPP} and $L_{iPP/EPR}$ values are considered to be within the experimental error $(\pm 5 \text{ Å})$, in agreement with results of different iPP/EPR blends.2-5 It is observed that when iPP crystallizes in presence of the EPR copolymers, the lamellar thickness and amorphous interlamellar layer of blends are comparable to that of the plain iPP. A different iPP phase structure, with L_c and L_a values lower and higher than that respectively shown by the plain iPP, was found to be generated in both injection-molded and isothermallycrystallized samples of different iPP/EPR pairs.^{2–5} In order to explain these results, it was assumed that EPR molecules with lower molecular mass, owing to their higher mobility, diffuse into the iPP interlamellar amorphous layer, forming domains more or less interconnected with the amorphous iPP phase, thus increasing its thickness and hindering the iPP crystal growth. The finding that the inner structure of the iPP spherulites is unaffected by the EPR phase used in this work can be accounted for the different molecular mass and molecular mass distribution of such copolymers, supporting the results of previous work that such structural factors determine the phase structure of iPP/ EPR blends both in the melt and after crystallization process.

Impact Behavior

The notched Izod impact strength values for the plain iPP and iPP/EPR $_{Ti}$ and iPP/EPR $_{V}$ are re-

ported in Figure 14 as a function of the test temperature. As shown, for a test temperature below the EPR T_g (-40°C), very poor improvement in the iPP impact strength is obtained, irrespective of the EPR molecular structure, and the corresponding fracture surfaces show the typical appearance of brittle materials. For a test temperature higher than the EPR T_g and closer to the iPP T_{σ} (0°C), higher impact strength is achieved by the blends containing the EPR_V copolymer (see Fig. 14). The fracture surfaces of such blends broken at 0°C show a stress-whitening phenomenon involving the whole volume of the induction area; whereas for the blends containing the EPR_{Ti} copolymer, only the central part of the fracture induction area is stress-whitened slightly. Taking into account that higher impact values are shown by the blend samples that undergo stress whitening with higher intensity, a multicraze formation rather than cavitation process is to be associated with the observed whitening. Note that EPR particle sizes ranging between 0.75 and 1.25 μ m result in more effective iPP toughening than particles ranging between 0.25 and 0.75 μ m. From previous studies on different iPP/EPR blends, it has been demonstrated that the EPR particle size, to optimize iPP toughening, ranges between 0.35 and 0.40 μm^{1-5} ; moreover, the results of SAXS investigation revealed that the molecular superstructure of the iPP matrix is unaffected by the presence of both EPR_{Ti} and EPR_{V} copolymers. Therefore, the different behavior of such EPR phases is to be related to their different microstructure rather then their dispersion coarseness. The ethylenic crystallinity shown by the EPR phase, synthesized by using the titanium-based catalyst, could induce toughening deterioration by a decrease of tie molecules density in the EPR_{Ti} domains, notwithstanding the beneficial



Figure 13 Desmeared SAXS patterns for iPP/EPR $_{Ti}$ and iPP/EPR $_{V}$ blends.

	L	$L_c(\text{DSC})$	La(DSC)	Lc(WAXS)	$L_{a}(\text{WAXS})$
Sample	(Å)	(Å)	(Å)	(Å)	(Å)
EPR _{Ti} 216	11	205	21	196	
iPP	135	52	83	83	52
iPP/EPR _{Ti}	135	_	_	82	53
iPP/EPR _v	142	54	88	89	53

Table VIII Long Period (L), Lamella Thickness (L_c), and Interlamellar Amorphous Thickness (L_a) for Plain EPR_{Ti} Copolymers and iPP and iPP/EPR Blends

effect of the ethylenic lamellar buildup.³³ For test temperatures close to room temperature, it seems that the impact strength of the iPP/EPR_{Ti} blends is slightly lower than that of the iPP/EPR_{v} blends. With increasing test temperature, the intensity of the stress-whitening phenomenon and the volume of material involved increases strongly for the iPP/EPR_{v} blends as the whole sample appears stress-whitened. On the other hand, for iPP/EPR_{Ti} blends, the stress whitening remains localized to the fracture induction area, suggesting that, on increasing test temperature, shear yielding also occurs. Therefore, the fracture mechanisms, active for test temperatures close to room temperature, result in a combination of shear yielding and multiple craze formation. The relative amounts of the two fracture mechanisms could depend on both the average size of the EPR dispersed phase and on the level of interaction throughout the material. The ductile behavior



Figure 14 Notched Izod impact strength as function of temperature for plain iPP and iPP/EPR blends.

shown by the iPP/EPR_{Ti} blend seems to be related to the noticeable concentration of interlamellar tie molecules among iPP crystallites according to DSC results.

CONCLUDING REMARKS

A study aimed at going deeper into the influence of the molecular structure of EPR copolymers (in particular, distribution of composition and length of the sequences of the structural units) on the structure-properties correlations already established in the melt and solid state for iPP/EPR blend systems¹⁻⁵ has been carried out.

The following results are to be remarked. The iPP/EPR blends investigated in this work are to be classified as negative deviation blends; a larger extent of such a deviation is shown by the blends containing the copolymer, showing comparatively less intra- and intermolecular homogeneity (EPR_{Ti}). Therefore, the apparent viscosity of such iPP/EPR pairs cannot be expected to conform to the logarithm additivity rule that applies at constant temperature and shear rate. This result agrees with results obtained in our first work concerning iPP/EPR blends¹ and by Danesi et al.³⁴ and disagrees with results recently found for iPP/EPR blends constituted of components having melt viscosity values very close to each other.³ Taking into account that the EPR copolymers used in this work have the lowest melt viscosity among the EPR phase investigated so far, and that such values are relatively close to the iPP melt viscosity, the conflict among the results shows that the iPP/EPR blends can exhibit very different rheological behavior, depending on the EPR molecular mass and molecular mass distribution, that is, depending on the melt phase viscosity ratio, defined as the ratio between the zero shear viscosity of the dispersed phase and the zero shear viscosity of the iPP matrix. The application of the Cross-Bueche equation also confirms that in the absence of shear, the melt phase viscosity ratio is the main factor in determining the viscosity of iPP/EPR pairs and their viscoelastic parameters. The EPR molecular homogeneity also affects the activation energy for the viscous flow (ΔE^*) of the iPP/EPR blends. As a matter of fact, the blends containing the EPR_V phase show ΔE^* values quite comparable to that shown by the plain iPP; whereas for the blends containing the EPR_{Ti} phase, a volume reduction of the flow element has been found.

A general correlation is confirmed to be established between mode and state of dispersion of EPR domains, in the melt and in the solid state, and melt rheological parameters of the blend components. Such a correlation is between the EPR dispersion degree (range of particle size and number-average particle size), as determined in the injection-molded samples and melt phase viscosity ratio. A finer EPR dispersion is achieved in blends containing the EPR_{Ti} copolymer as the values of the number-average particle size found for EPR_{Ti} and EPR_v were 0.5 and 1.0 μ m, respectively. The type of dependence of the EPR size upon μ value agrees qualitatively with the prediction of the Taylor-Tomotika theory in agreement with previous results;¹⁻⁵ that is, the EPR dispersion coarseness increases with increasing μ value showing a minimum in the vicinity of μ equal to 1.

When the iPP crystallizes, in the presence of the EPR copolymers investigated in this work, its nonisothermal crystallization peak shifts to higher temperature, indicating that a migration of heterogeneous nuclei from both the EPR phase toward the iPP phase occurs. Note that from the EPR_{Ti} phase that such a migration is noticeably higher than that occurring from the EPR_V phase, giving a material characterized by a comparatively higher number of spherulites per unit volume.

WAXS analysis shows that the EPR_{Ti} copolymer is characterized by the presence of PE crystalline phase along its chains. As far as the structure of iPP/EPR blends is concerned, the apparent crystal size (D) of the iPP, crystallized in the presence of the EPR phase, is larger in the directions perpendicular to the (110) and (040) crystallographic planes than that exhibited by the plain iPP, with no relevant dependence on the EPR molecular microstructure. Such a higher growth of the iPP crystals has been related to the DSC results, showing that the nonisothermal crystallization process of the iPP phase from the iPP/ EPR melts investigated in this work occurs at an apparent undercooling level lower than that of the plain iPP. It has been found, moreover, that $D_{(110)}/D_{(040)}$ ratios are almost constant for the plain iPP and iPP/EPR blends, indicating that the iPP lamellar crystals grown in the presence of EPR, in the directions perpendicular to the (110) and (040) crystallographic planes, have a size whose ratio is the same of the plain iPP.

SAXS investigations revealed that the EPR_{Ti} phase possesses a long-range order with a periodic distance between two adjacent PE crystalline lamellae. Assuming for the iPP spherulites fibrillae a two-phase model consisting of alternating parallel crystalline lamellae and amorphous layers, it has been shown, moreover, that when the iPP crystallizes in presence of both the EPR_{Ti} and EPR_v copolymers, the phase structure developed in their blends is characterized by lamellar thickness and amorphous interlamellar layer thickness comparable to that shown by the plain iPP. This morphological result indicates that, irrespective of the copolymer microstructure, no diffusion of EPR amorphous phase into the iPP interlamellar amorphous layer (L_a) occurs. Diffusion of EPR molecules with lower molecular masses, accounted for by higher mobility, into iPP L_a have been found, on the other hand, while studying different iPP/EPR pairs, with such an effect being composition-dependent.¹⁻⁵

For test temperatures higher than the EPR T_g and close to the iPP T_g , better impact properties are shown by the blends containing the EPR_V copolymer. The different behavior of EPR_{Ti} and EPR_v copolymers has been related to their different microstructure rather than to their different dispersion degree. From previous studies on different iPP/EPR blends, it has been demonstrated that the particle size, to optimize iPP toughening, ranges between 0.35 and 0.40 μ m.^{1–5} Therefore, the finding that for a test temperature closer to iPP T_g , larger particles (1.0 μ m in number-average diameter) are more effective than smaller particles (0.5 μ m in number-average diameter) in promoting multiple craze formation, has been ascribed to the ethylenic crystallinity degree shown by the EPR_{Ti} copolymer, that is, to a decrease of tie molecules density in the $\ensuremath{\text{EPR}}_{Ti}$ domains. The ductile behavior exhibited by the iPP/EPR_{Ti} blends for test temperature close to room temperature has been accounted for by a predominant shear yielding fracture mechanism, probably promoted by high concentration of interlamellar tie

molecules among iPP crystallites according to the DSC results.

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