Polypropylene/ethylene-*co*-propylene blends: influence of molecular structure and composition of EPR on melt rheology, morphology and impact properties of injection-moulded samples

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(*Received 7 April 1989; revised 8 February 1990; accepted 14 May 1990*)

Polypropylene (PP) based blends containing as second non-crystallizable component commercial ethylene–propylene copolymers (EPR) having different C_3 contents (wt/wt) and molecular-weight distributions (*MWD*), and, for fixed C_3 content and *MWD* almost constant, different average molecular mass, were investigated. The study was undertaken to establish the influence of EPR molecular structure and composition on the melt rheology, on the mode and state of dispersion of the minor component in the melt as well as in the solid state and on the impact properties of injection-moulded samples. An attempt to correlate the molecular structure of EPR with rheological behaviour, size of rubbery particles and impact resistance was also accomplished. It was found that the values of the blend zero-shear viscosity (η_0) and the α(blend) parameter, obtained by applying the Cross equation, decrease with increasing dispersion coarseness of the minor component according to the results already obtained while studying the different incompatible blend system made by polyamide-6 and ethylene–vinyl acetate copolymers. The size and size distribution of EPR domains are determined by the value of the phase viscosity ratio (μ) irrespective of C_3 content along the EPR chain. The trend of the number-average particle diameter ($\bar{D}_n$) *versus* log μ showed that $\bar{D}_n$ decreases with decreasing log μ, in agreement with expectation on the basis of Taylor–Tomotika theory. The range of particle size effective for PP toughening was dependent on test temperature; for a temperature higher than EPR T_g and close to PP T_g, such range is narrower than that effective at room temperature.

(Keywords: polypropylene; ethylene–propylene random copolymers; blends)

INTRODUCTION

Isotactic polypropylene (iPP) based blends have been extensively studied by many researchers throughout the past 10 years. Most of the systems studied contained as second component a rubber such as butyl rubber, ethylene–propylene copolymer (EPR), ethylene–propylene–diene terpolymer (EPDM), polyisobutylene and styrene–butadiene block copolymer. For the production of high-impact PP, as well as for the production of polyolefinic thermoplastic rubbers (TPO), EPR and EPDM rubbers were found to be the most suitable additives.

Many papers are reported in the scientific literature concerning the influence of blending process and crystallization conditions on morphology and on the relationships between overall morphology and final properties of iPP/rubber blend systems[1–25]. The studies on the morphology of the blends have dealt either with the changes in the crystalline phase, more exactly with the alteration of the supermolecular structure[2,5,6,13,21], or with the effect of the average particle size and particle size distribution of the dispersed phase on properties[3,7–12,14–16,18–23]. To sum up, despite the need for a rigorous understanding of the dominant structural parameters determining the overall morphology and properties of such materials, none of the cited papers contains a vertically integrated investigation of molecular parameters of the individual components, such as molecular weight, molecular-weight distribution, distribution of chemical defects, melt rheology, phase morphology and properties of PP-based systems.

In the present paper we investigated PP-based blends containing as second non-crystallizable component commercial ethylene–propylene copolymers (EPR) having different propylene (C_3) contents and molecular-weight distributions (*MWD*) and for fixed C_3 content and *MWD* almost constant, different average molecular mass.

The main goal of the work is to find how the molecular structure and composition of EPR may determine the

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0032-3861/91/071186-09

melt rheology behaviour of blends and the mode and state of dispersion of the minor component in the melt as well as in the solid state, that is after crystallization of iPP, in samples obtained by an injection-moulding process.

An attempt to correlate molecular structure of EPR with rheological behaviour, size of rubbery particles and impact resistance is also accomplished.

EXPERIMENTAL

Materials

The polymers used in this study were an isotactic polypropylene (PP) (Moplen S30G) made by Himont and three ethylene–propylene random copolymers (EPR) (Dutral C0038, Dutral D0034, Dutral C0059) kindly supplied by Dutral. The molecular characteristics of these polymers are summarized in *Table 1*.

Blending and sample preparation

The PP and EPR copolymers were mixed in a Werner mixer at 230°C with a blending time of 3 min. Blends with composition PP/EPR 80/20 (wt/wt) were prepared. After blending the materials were injection-moulded by means of an injection press (GBF 160/72) at 230°C and a mould temperature of 60°C.

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 homopolymers and blends, were determined at 200°C by means of a Rheometrics Mechanical Spectrometer in the plate–plate mode with a constant strain of 10% and an angular frequency ranging between 0.1 and 100 rad s^{-1}.

Mode and state of dispersion of the minor components

The mode and state of dispersion of the minor components were analysed by scanning electron microscopy (SEM) only in the core of injected bars in order to eliminate the probable effect of the mould walls on concentration and shape of the EPR particles. Thus the central parts of transverse sections of injection-moulded bars were placed in a Reichert-Jung 1150/Autocat microtome at room temperature. The smoothed surfaces so obtained were exposed to boiling xylene vapour for 1 s to extract the EPR phase and subsequently gold–palladium plated by sputtering (Polaron Equipment Ltd E5/50).

Testing

Notched Charpy impact strengths of the injection-moulded samples were measured by means of a Ceast pendulum AFSMK2 model 6547/000 in a temperature range from −60°C up to 30°C according to ASTM D256.

RESULTS AND DISCUSSION

Dynamic viscoelastic properties of single components and blends

The logarithm of the modulus of the complex viscosity $|\eta^*|$, dynamic storage modulus G' and loss modulus G'' values as functions of the logarithm of investigated frequencies for plain PP and EPR copolymers are reported in *Figures 1–3*. From the analysis of such curves it can be seen that in the whole range of explored frequencies:

(i) For both PP and EPR copolymers $|\eta^*|$ values decrease with increasing frequency, indicating that at the investigated frequencies PP and EPR melts are pseudoplastic.

(ii) For both PP and EPR copolymers G' and G'' values increase with frequency, suggesting that at the explored frequencies molecular entanglements have time to slip and relax out the stresses.

(iii) PP melt shows $|\eta^*|$, G' and G'' values lower than that of EPR copolymers. Since all the dynamic viscoelastic properties increase in value with molecular weight increase, at a given frequency[26], such results indicate that the PP studied could have an average molecular weight $\overline{M}_w$ or more likely some average molecular weight between $\overline{M}_w$ and $\overline{M}_z$ lower than EPR ones.

(iv) Among EPR copolymers lowest $|\eta^*|$, G' and G'' values are shown by Dutral C0034. In the first decade of investigated frequencies Dutral C0059 exhibits $|\eta^*|$, G' and G'' values higher than those shown by Dutral C0038. At increasing frequencies Dutral C0038 $|\eta^*|$, G' and G'' values tend to become comparable to that shown by Dutral C0059 copolymer. The above findings indicate that, between the EPR having almost the same propylene content (C_3) and molecular-weight distribution (*MWD*) (Dutral C0034 and Dutral C0038) (see *Table 1*), Dutral C0038 could have an average molecular weight between $\overline{M}_w$ and $\overline{M}_z$ higher than that of Dutral C0034. The highest average molecular weight could be ascribed to EPR

Table 1 Molecular characteristics, glass transition (T_g) and observed melting temperature (T'_m) of plain isotactic polypropylene (PP) and ethylene–propylene copolymers (EPR)

Materials	Trade name	Melt index (g/10 min)	Mooney viscosity $ML(1+4)$	C_3 content (% wt/wt)	$\overline{M}_w/\overline{M}_n$	T_g (°C)	T'_m (°C)
Isotactic polypropylene	Moplen S30G	1.7	–		7.4	−10	166
Ethylene–propylene random copolymer	Dutral C0038	–	67[a]	28	3.5	−40	45
	Dutral C0034	–	45[a]	27	3.5	−41	48
	Dutral C0059	–	85[a]	43	5.0	−45	-

[a] Measured at 100°C

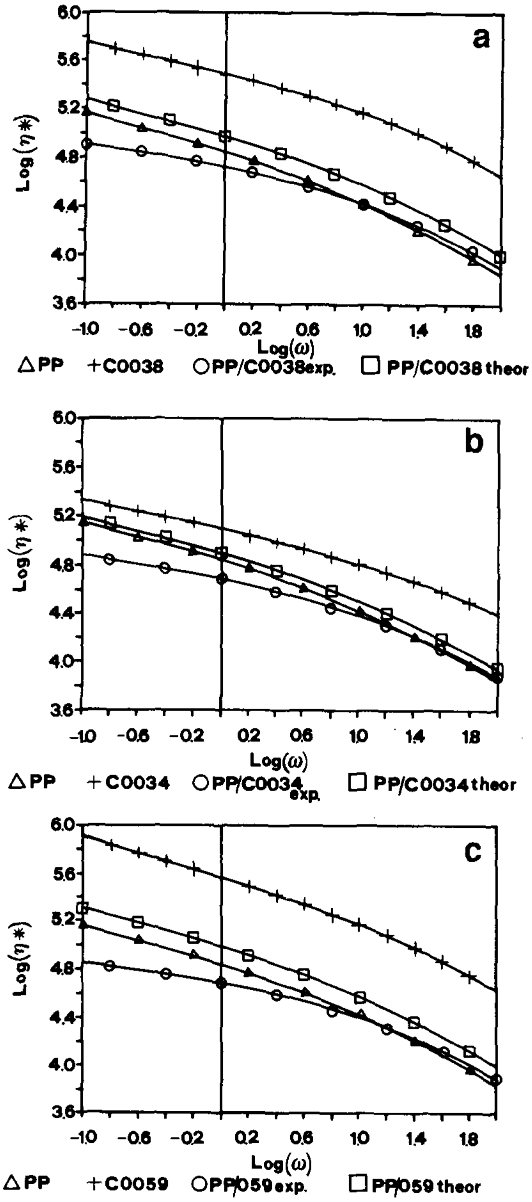

Figure 1 Log(|η*|) *versus* log(ω) for PP/EPR blends (experimental (○) and theoretical (□)), plain PP (Δ) and EPR copolymers (+): (a) PP/Dutral C0038; (b) PP/Dutral C0034; (c) PP/Dutral C0059

copolymer having highest C_3 content along its chain and broadest *MWD* (Dutral C0059) (see *Table 1*).

Figure 1 shows, moreover, the dependence of the logarithm of the modulus value of the complex viscosity ($|\eta^*|$) upon the logarithm of investigated frequencies for PP/EPR blends. For the sake of comparison in each plot the $|\eta^*|$ logarithm of single components are also reported. As shown in the whole range of explored frequency PP/EPR blends exhibit a decrease in viscosity value with increasing frequency, i.e. PP/EPR are pseudoplastic melts. It should be noted that mixing PP and EPR copolymers resulted in a decrease in viscosity below the mean value of the two pure components and that such a decrease is larger at low frequency. This effect is designated as a 'negative deviation'[29] from the following logarithm rule of mixtures that applies at constant temperature and shear rate[29–30]:

$$\log \eta = \phi_1 \log \eta_1 + \phi_2 \log \eta_2 \qquad (1)$$

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.

The finding that PP/EPR blends are negative deviation blends (NDB) agrees with results obtained by Danesi *et al.*[12] using a capillary rheometer.

Among the blends studied, larger and smaller deviations are respectively shown by PP/Dutral C0059 and PP/Dutral C0034 blends (compare *Figures 1a, 1b* and *1c*). Moreover, it should be pointed out that, irrespective of the molecular characteristics of EPR added to PP, the $|\eta^*|$ values of the three blends are very close to each other in the whole range of explored frequency, and that in the third frequency decade such values approach that of plain PP.

In *Figure 2* the dependence of the logarithm of the elastic modulus G' on the logarithm of the investigated frequencies of PP/EPR blends is compared with that of plain polymers. As shown, at low frequencies G' values of PP/EPR blends are lower than that of both single components; with increasing frequency such values tend

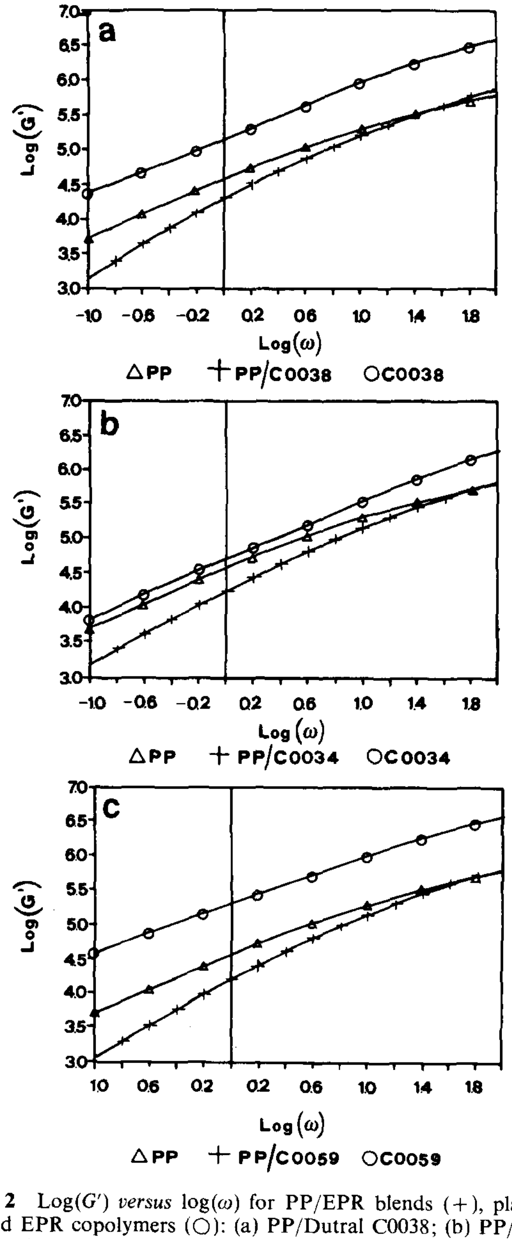

Figure 2 Log(G') *versus* log(ω) for PP/EPR blends (+), plain PP (Δ) and EPR copolymers (○): (a) PP/Dutral C0038; (b) PP/Dutral C0034; (c) PP/Dutral C0059

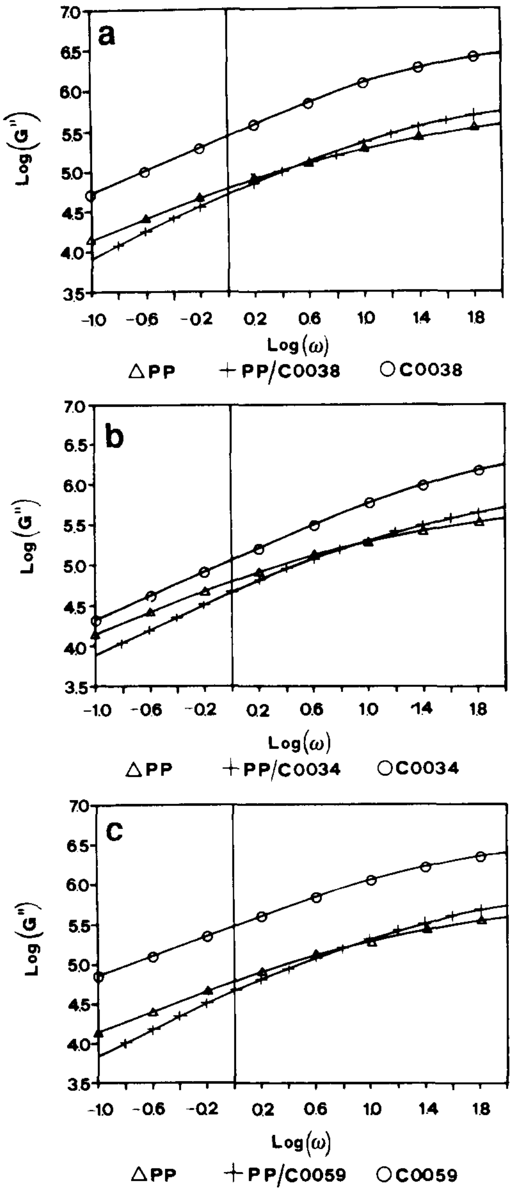

Figure 3 Log(G'') *versus* log(ω) for PP/EPR blends (+), plain PP (△) and EPR copolymers (○): (a) PP/Dutral C0038; (b) PP/Dutral C0034; (c) PP/Dutral C0059

to reach those of pure PP. Furthermore all PP/EPR blends show almost the same G' values in the whole range of explored frequencies.

Accepting that the dynamic storage modulus may be considered as the amount of energy stored, the above finding indicates that the PP/EPR melts investigated have almost the same elasticity and that such elasticity (at least in the two first frequency decades) is lower than that of both starting polymers. The dependence of the logarithm of loss modulus G'' on the logarithm of the investigated frequencies of PP/EPR blends and of starting polymers is shown in *Figure 3*. As shown, for all examined blends G'' values are lower than those of pure polymers at low frequency, approach that of pure PP at intermediate frequency and overcome that of pure PP at high frequency. It should be noted, moreover, that, as already observed for G' values of such blends, G'' assumes almost the same values irrespective of the EPR molecular characteristics.

Taking into account that the dynamic loss modulus G'' represents the amount of energy dissipated[27,28], such findings indicate that the energy dissipated by PP/EPR melt blends is lower than that dissipated by plain polymers at low frequency, comparable to that of neat PP at intermediate frequency and greater than that of neat PP at high frequency.

Determination of zero-shear viscosity of single components and of the blends

Taking into account that in oscillatory measurements on polymer melts the frequency (ω) becomes analogous to shear rate ($\dot\gamma$)[26,31] and assuming an approximate equivalence of η^* and apparent viscosity η_a[31–36], the zero-shear viscosity η_0 of both single components and blends was calculated by using the following modified Cross–Bueche equation[37]:

$$\eta_0\eta_a = 1 + (\alpha\dot\gamma)^m \tag{2}$$

where η_0 is the zero-shear viscosity, α is a parameter that according to Cross should correspond to the characteristic relaxation time related to molecular weight for the linear polymer solution and m gives a measure of the shear thinning of the melt, i.e. a measure of the decrease in viscosity with increasing rate of shear. According to Iwakura *et al.*[38] 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 $\eta_a = \eta_0/2$.

The m values found for single components to obtain linearity in plots of $1/\eta_a$ *versus* $\dot\gamma^m$ are reported in *Table 2*. As shown, for plain PP, m assumes the value usually obtained for polymer with a *MWD* ($m = 2/3$)[37]; for EPR copolymers, m values are lower, indicating a less severe shear thinning in the non-Newtonian region. Note that Dutral C0059 and Dutral C0038 show the same m value ($m = 4/7$); a slightly lower m ($m = 6/11$) is, on the other hand, shown by Dutral C0034.

From the lines $1/\eta_a$ *versus* $\dot\gamma^m$ the zero-shear viscosity η_0 and α are easily obtained from the reciprocal of the intercept and from the slope respectively.

The η_0 and α values of single components are also reported in *Table 2*. As shown, plain PP at 200°C has a zero-shear viscosity lower than those of pure EPR copolymers. More exactly PP η_0 value is 1.5, 4.5 and 7.5 times lower than that of Dutral C0034, Dutral C0038 and Dutral C0059 respectively. Among EPR copolymers lower η_0 value is shown by Dutral C0034. Dutral C0038 and Dutral C0059 exhibit η_0 values respectively three and five times as high as that of Dutral C0034.

As far as α values are concerned, PP shows a relaxation time slightly longer than that of Dutral C0038, about twice as long as that of Dutral C0034 and about three times as short as that of Dutral C0059. As the reciprocal of the parameter α corresponds to the shear rate at which

Table 2 Application of Cross–Bueche equation: values of zero-shear viscosity (η_0), m and characteristic relaxation time (α) for plain PP and EPR copolymers

Sample	m	η_0 (*P*)	C_3 content (% wt/wt)	α (s)
Moplen S30G	2/3	130 707	–	0.751
C0038	4/7	582 270	28	0.712
C0034	6/11	199 729	27	0.366
C0059	4/7	983 513	43	2.150

Table 3 Application of Cross–Bueche equation to PP/EPR blends: values of zero-shear viscosity (η_0), m and characteristic relaxation time (α); the shear viscosity values calculated assuming log additivity (η_0') for PP/EPR blends are also reported

Sample	m	α (s)	η_0 (P)	η_0' (P)
PP/Dutral C0038	2/3	0.212	72 850	176 198
PP/Dutral C0034	4/7	0.528	85 286	142 262
PP/Dutral C0059	2/3	0.193	65 143	195 684

η_a decreases to half of η_0, shorter α values mean that non-Newtonian flow starts at larger shear rate. Thus the range of Newtonian behaviour of plain PP is expected to be almost comparable to that of Dutral C0038, smaller than that of Dutral C0034 and larger than that of Dutral C0059.

The m, η_0 and α values calculated for PP/EPR blends are reported in *Table 3*; in the table, the zero-shear viscosity values for blends calculated assuming the additivity logarithm rule (η_0') are also reported. As shown for blends containing Dutral C0038 and Dutral C0059 the parameter m assumes the same value as shown by plain PP. For the blend containing Dutral C0034, m is lower, suggesting that for such a blend there is a less severe shear thinning in the non-Newtonian region.

As far as η_0 blend values are concerned, a very large negative deviation from the logarithm additivity rule is observed. It is interesting to underline the fact that, between blends containing EPR copolymers having almost the same C_3 content and *MWD*, a larger deviation is shown by the blend containing Dutral C0038; on the other hand the largest negative deviation is exhibited by the blend containing EPR with highest C_3 content and broadest *MWD*. It is to be noted, moreover, that, as indicated from the EPR Mooney viscosity values reported in *Table 1* and as expected on the basis of $|\eta^*|$, G' and G'' values shown for each copolymer, Dutral C0059 and Dutral C0039 could have respectively the highest and lowest average molecular weight.

From the above it may be concluded that the extent of the observed negative deviation increases with increasing EPR average molecular weight. Looking at PP/EPR α values, it is to be noted that PP/Dutral C0038 and PP/Dutral C0059 blends show characteristic relaxation times lower than those of both plain polymers, whereas PP/Dutral C0034 exhibits an α value almost intermediate between those of the starting polymers, the value being lower than that of PP and higher than that of Dutral C0034. Moreover, it should be underlined that the blend values decrease with increasing EPR molecular mass (see *Tables 1* and *2*). Taking into account that the reciprocal of the α parameter corresponds to the shear rate at which η_a decreases to half of η_0, from the analysis of α parameters of PP/EPR blends, it can be deduced that in the blend system the transition from Newtonian to pseudoplastic flow is able to start at a frequency higher than that of plain PP and the shift towards higher frequency tends to increase with increasing EPR molecular mass (see *Tables 1* and *3*).

Mode and state of dispersion of the minor components

The analysis of the EPR mode and state of dispersion, carried out by SEM in the core of transverse microtomed surfaces exposed to boiling xylene vapour to remove EPR, shows that the minor component segregates in spherically shaped domains (see *Figures 4–6*). Moreover no evidence of adhesion at the interface between PP and EPR copolymers is found. As shown by comparison of *Figures 4–6* the size and size distribution of EPR are dependent upon the molecular characteristics of EPR copolymers (molecular mass and C_3 content).

In the case of blends containing copolymers having almost the same C_3 content along their chain (Dutral C0038 and Dutral C0034), the SEM investigation shows that a finer dispersion is developed in blends containing Dutral C0034 (compare *Figure 4* with *Figure 5*). As a matter of fact in such a blend the EPR domains have a diameter ranging between 0.1 and 0.5 μm whereas in blends containing Dutral C0038 the range of particle size is wider (0.1–1.0 μm). The values of the number-average particle size ($\bar{D}_n$) found for Dutral C0034 and Dutral C0038 are 0.30 and 0.40 μm respectively. These morphological results indicate that the dispersion coarseness of such EPR copolymers tends to increase with increasing melt viscosity, i.e. with increasing phase viscosity ratio defined as $\mu = \eta_1/\eta_0$ where η_1 is the viscosity of the disperse phase and η_0 that of the matrix (see *Table 4*).

In the case of blends containing the copolymer having highest C_3 content and melt viscosity (Dutral C0059), the particle size of the dispersed phase is in the range 0.1–1.5 μm and $\bar{D}_n$ assumes a value of 0.50 μm. It should be pointed out that such range of particle size is wider

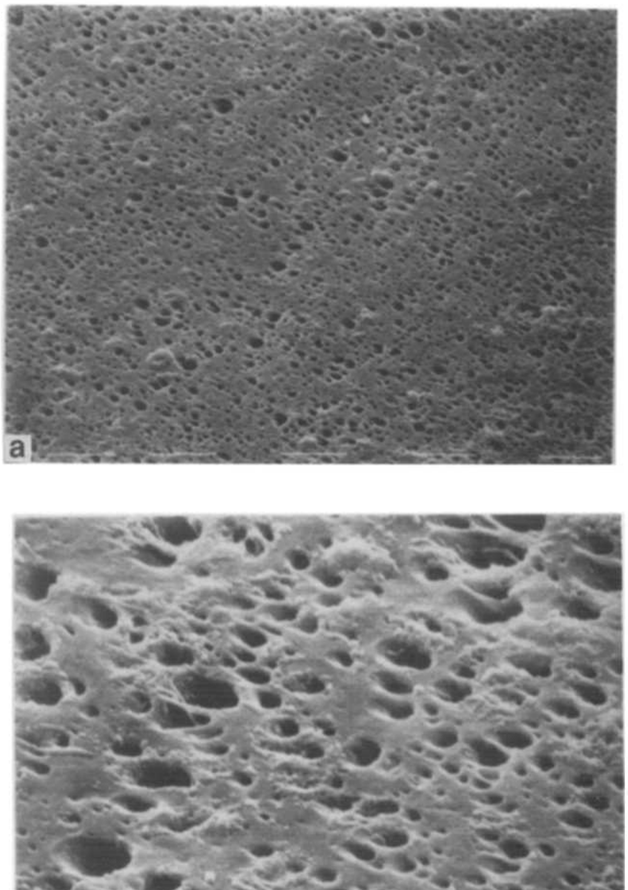

Figure 4 Scanning electron micrographs of smoothed and etched surfaces of PP/Dutral C0038: (a) ~780 ×, (b) ~3380 ×

than those shown by both Dutral C0038 and Dutral C0034 minor components and that for the blend containing Dutral C0059 the phase viscosity ratio assumes the highest value (see *Table 4*). This finding seems to support the idea that, irrespective of C_3 content along the EPR chain, the range of particle size and the average particle size of the disperse phase are mainly determined by the value of the phase viscosity ratio η_1/η_0. As a matter of fact, as shown by the data of *Table 4*, those quantities seem to increase monotonically with μ. Similar conclusions were reached by Karger *et al.* while studying PP/EPDM blends[7].

The trend of $\overline{D}_n$ *versus* log μ (see *Figure 7*) shows that $\overline{D}_n$ decreases with decreasing log μ. Such a trend agrees with expectation on the basis of the Rayleigh–Taylor–Tomotika theory[39–42], which gives the following function for the instability coefficient (q) of a cylindrical thread suspended in another viscous liquid:

$$q = \frac{\gamma}{2\eta_0 R}(1 - x^2)F(x, \mu)$$

$$= \frac{\gamma}{2\eta_0 R}\,\Omega(x, \mu) \qquad (3)$$

where γ is the interfacial surface tension, $x = 2\pi R/\lambda$, R is the diameter of the thread, λ is the varicosity of the thread and μ is the phase viscosity ratio.

It was found by Tomotika that, for a given value of μ, the maximum instability occurred at a certain definite value of λ, indicating that drops of definite size would be formed and that λ changed with μ. According to equation (3) the R *versus* log μ function should show a minimum in the vicinity of $\mu = 1$[41]. PP and EPR used in this study did not permit us to reach μ values far below

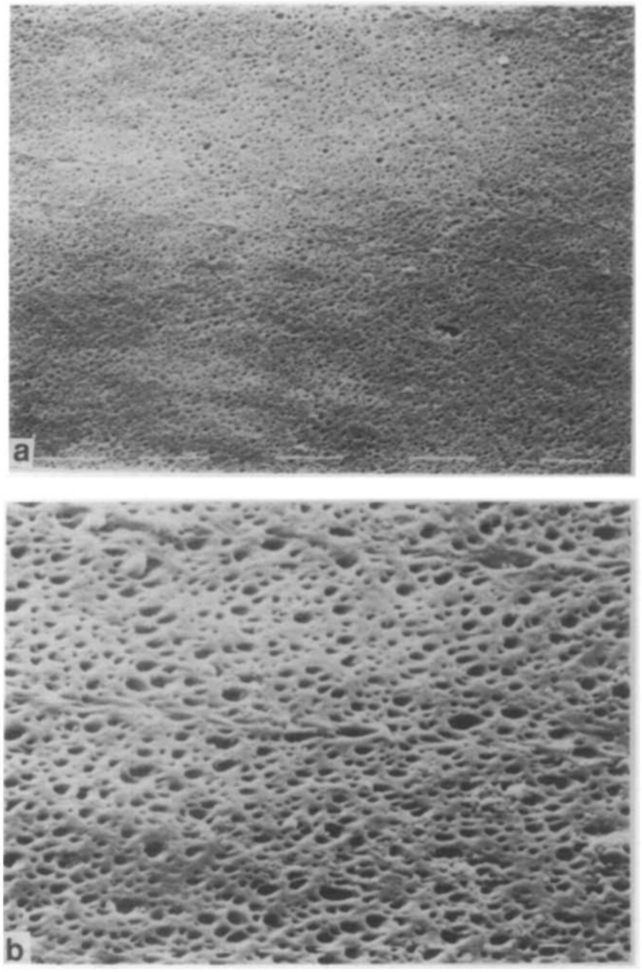

Figure 5 Scanning electron micrographs of smoothed and etched surfaces of PP/Dutral C0034 blend: (a) ~780×, (b) ~3380×

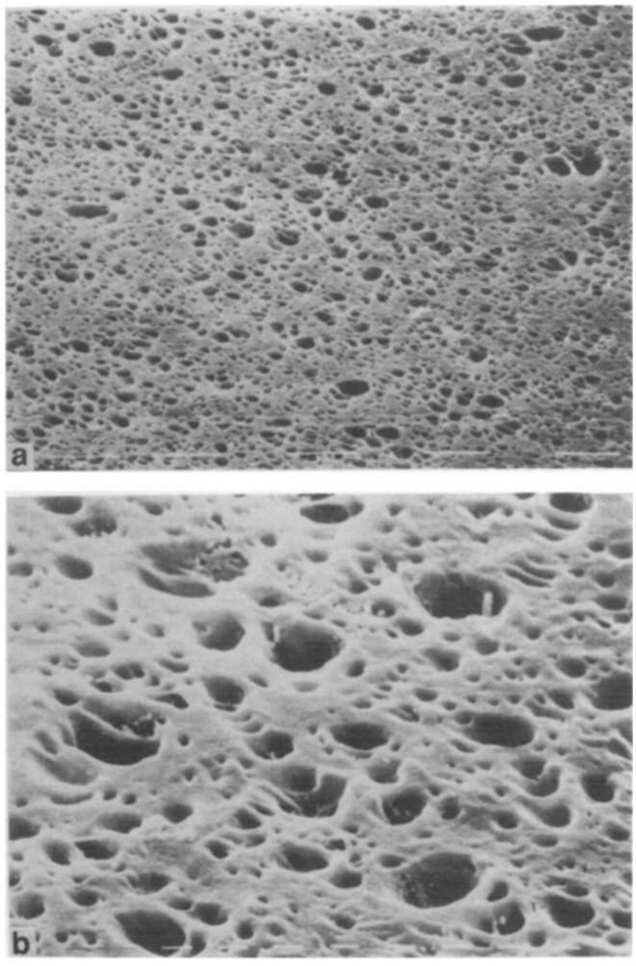

Figure 6 Scanning electron micrographs of smoothed and etched surfaces of PP/Dutral C0059 blend: (a) ~780×, (b) ~3380×

Table 4 Phase viscosity ratio (η_1/η_0), range of particle size (D), number-average particle size $\overline{D}_n$, zero-shear viscosity (η_0) and characteristic relaxation time (α) for PP/EPR blends; the EPR C_3 content and *MWD* are also reported

Sample	η_1/η_0	D (μm)	$\overline{D}_n$ (μm)	η_0(blend) (P)	α (s)	C_3 (% wt/wt)	*MWD*
PP/Dutral C0034	1.5	0.1–0.5	0.30	85 286	0.528	27	3.5
PP/Dutral C0038	4.5	0.1–1.0	0.40	72 850	0.212	28	3.5
PP/Dutral C0059	7.5	0.1–1.5	0.50	65 163	0.198	43	5

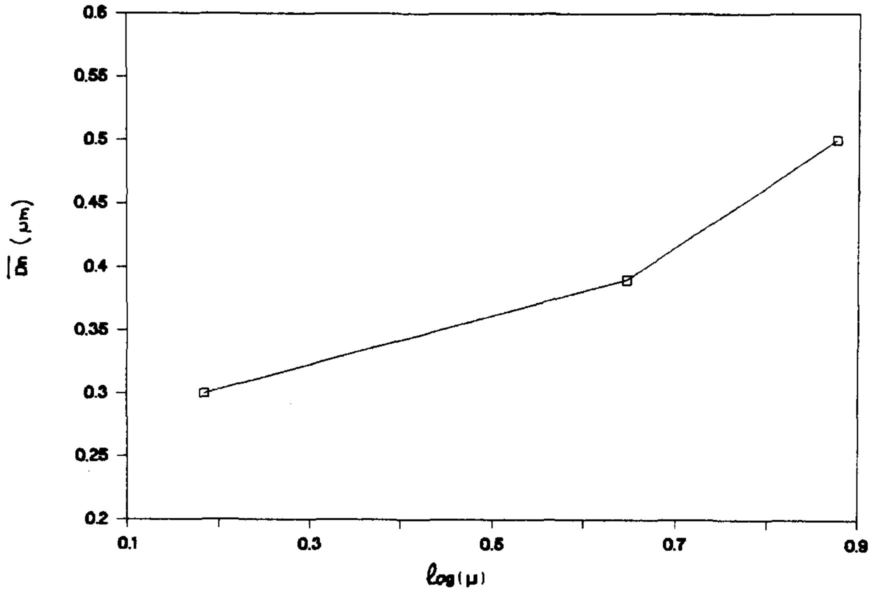

Figure 7 Number-average diameter ($\overline{D}_n$) of EPR particle size *versus* logarithm of phase viscosity ratio (μ)

1; thus it was impossible to determine the minimum in the $\overline{D}_n$ *versus* log μ function.

The rheological properties of PP/EPR blends can be related to the mode and state of dispersion of the minor component. It can be seen in fact that both η_0(blend) and α(blend) values decrease with increasing EPR dispersion coarseness (see *Table 4*). It is interesting to note that a decrease in η_0(blend) and α(blend) values with increasing dispersion coarseness of the minor components was already observed by Martuscelli and coworkers for a different melt-incompatible blend system made by polyamide-6 (PA6) and ethylene–vinyl acetate (EVA) copolymer[43].

These observations may suggest that, irrespective of rheological properties of the single component, the particle size of the suspended phase could be a critical parameter in affecting blend viscosity and $\dot{\gamma}$ value for which the transition from Newtonian to pseudoplastic behaviour starts.

Supposing that the addition of a second component in the form of more or less deformable droplets affects the mechanism of matrix flow, probably by changing molecular entanglement concentration and/or by allowing slippage to occur also at polymer–polymer interfaces, the observed decrease in η_0(blend) and α(blend) values with increasing particle size of dispersed phase could be ascribed to the fact that with increasing particle size the average end-to-end distance between PP molecules could tend to increase, reducing PP entanglement capability and consequently the viscosity of the blend system. The increased interface and the slippage between the two polymers with increasing particle size of the minor component must also be taken into account.

Note, moreover, that for PP-based blends the largest particle size and lowest η_0 and α values were shown by the blend containing the EPR copolymer having the highest molecular mass and C_3 content and broadest *MWD* (see *Tables 1* and *4*). On the other hand the smallest particle size and highest η_0 and α values were shown by the blend containing the EPR copolymer having the lowest molecular mass, a C_3 content of 27% (wt/wt) and a *MWD* of 3.5 (Dutral C0034) (see *Tables 1* and *4*).

With increasing EPR molecular mass, keeping almost constant C_3 content and *MWD* (look at the blend containing Dutral C0038), it can be observed that EPR particle size increases, whereas both η_0 and α values decrease.

Impact behaviour

The notched Charpy impact strength values for plain PP and the PP/EPR blends investigated are reported in *Figure 8* as a function of test temperatures. As expected, plain PP shows very poor impact properties in the whole range of explored temperatures and, for a test temperature below the glass transition temperature (T_g) of the EPR copolymers ($\leqslant 40$°C), no improvement in PP impact strength is obtained irrespective of EPR molecular characteristics (molecular mass and C_3 content).

For a test temperature higher than EPR T_g and close to PP T_g (-10 to 0°C), the enhancement in PP impact behaviour depends strongly on the molecular characteristics of the dispersed phase (see *Figure 8*). As a matter of fact, for EPR samples having C_3 content and *MWD* almost constant (look at blends containing Dutral C0038 and Dutral C0034) much better properties are shown by the blend containing Dutral C0038. As shown in *Figure 8*, at the temperature of 0°C, the impact value shown by such a blend is about 14 times as high as that shown by plain PP, whereas PP/Dutral C0034 blend exhibits an impact value just three times as high as that exhibited by plain PP. The very different behaviour of Dutral C0038 and Dutral C0034 copolymers as impact modifier could be ascribed to the fact that in blends with PP they give rise to domains with different degrees of dispersity (average particle size) (see *Table 4*). It is likely that EPR particles ranging in size between 0.1 and 1.0 μm with an average diameter of 0.4 μm are more effective for PP toughening than particles ranging between 0.1 and 0.5 μm and/or in the PP/Dutral C0038 blend a more effective interparticle distance is achieved.

Taking into account that the EPR dispersion coarse-

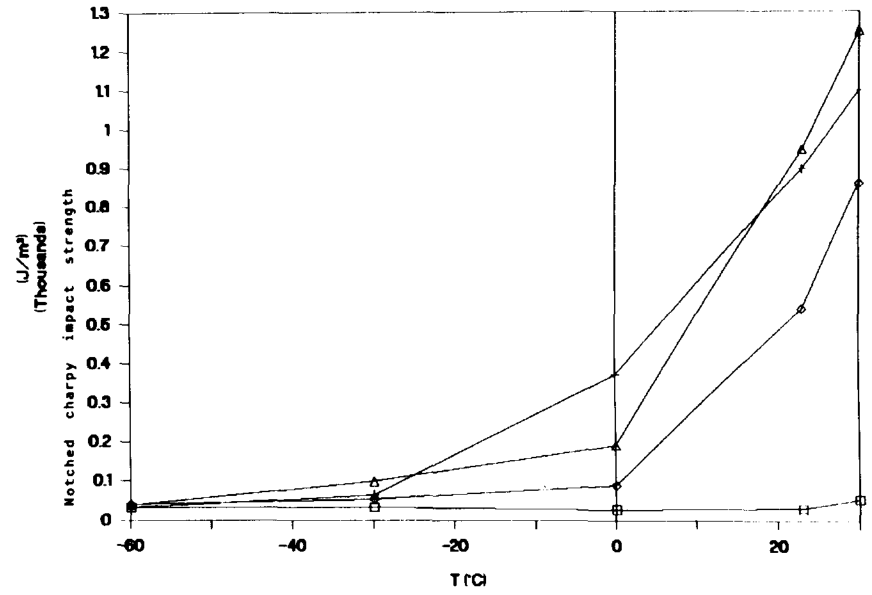

Figure 8 Notched Charpy impact strength as a function of temperature for plain PP and PP/EPR blends: (□) PP; (◇) PP/Dutral C0034; (+) PP/Dutral C0038; (Δ) PP/Dutral C0059

ness increases with increasing phase viscosity ratio (see *Table 4*) according to the Taylor–Tomotika theory, the parameter responsible for the different degree of dispersity of Dutral C0038 and Dutral C0034 copolymer turns out to be their different molecular mass.

With increasing EPR C_3 content and *MWD* (Dutral C0059 copolymer) the PP/Dutral C0059 blend exhibits in the same temperature range an impact behaviour respectively higher and lower than that shown by PP/Dutral C0034 and PP/Dutral C0038 blends.

The impact value shown by PP/Dutral C0059 at a temperature of 0°C is about seven times as high as that shown by plain PP, about twice as high as that shown by the blend containing Dutral C0034 and about twice as low as that shown by the blend containing Dutral C0038.

As shown in *Table 4* the PP/Dutral C0059 blend is characterized by the highest phase viscosity ratio (7.5) and widest range of particle sizes (0.1–1.5 μm). Such a finding suggests that, at relatively low temperature (around 0°C) at least, particle sizes wider than 0.1–1.0 μm and/or interparticle distances realized in the blend containing PP/Dutral C0059 are less effective in toughening PP.

For temperatures ranging between 20 and 30°C the impact strength of PP/Dutral C0034 blends is lower than that shown by both blends containing Dutral C0038 and Dutral C0059. It should be noted that with increasing test temperature the impact strength value shown by PP/Dutral C0059 blends tends to approach that shown by PP/Dutral C0038, overcoming it at a temperature of 30°C.

These results suggest that the range of particle sizes effective for PP toughening depends on test temperature. Such a range, effective for PP toughening at room temperature, is in fact, larger (0.1–1.0 μm) than that effective at 0°C (0.1–1.0 μm) (see *Figure 8* and *Table 4*).

The interparticle distance achieved between two nearest-neighbour dispersed particles also has to be taken into account according to the model proposed by Wu[44].

CONCLUDING REMARKS

A study concerning the influence of molecular structure and composition of EPR copolymers on the melt rheology behaviour of PP/EPR blends, on the mode and state of dispersion of the minor component in the melt as well as in the solid state and on the final properties of injection-moulded samples was reported. The following results are to be noted:

(i) All the PP/EPR blends studied exhibit in the whole range of explored frequencies (10^{-1} to 10^2 rad s^{-1}) $|\eta^*|$, G' and G'' values very close to each other irrespective of EPR molecular structure. Such blends are to be classified as negative deviation blends (NDB) according to the results obtained by Danesi *et al.*[12] by using a capillary rheometer. Furthermore the observed negative deviation increases with increasing EPR molecular mass.

It should be noted, moreover, that at low values of explored frequencies the blend system stores and dissipates a lower amount of energy than that respectively stored and dissipated by the single components. With increasing frequency the elasticity developed in the blend system reaches that developed by plain PP, whereas the amount of energy dissipated tends to overcome that dissipated by plain PP.

The application of the Cross–Bueche equation to PP/EPR blends reveals that for the blend system the transition from Newtonian to pseudoplastic flow starts at frequencies higher than that of plain PP and that the shift towards higher frequency tends to increase with increasing EPR molecular mass.

(ii) SEM analysis shows that PP/EPR blends are two-phase systems consisting of spherically shaped EPR particles distributed in the continuous PP matrix. The size and size distribution of EPR domains were found to be determined mainly by the value of the phase viscosity ratio (μ) irrespective of C_3 content along the EPR chain. Similar conclusions were reached by Karger *et al.* while studying PP/EPDM blends[7].

The trend of the $\overline{D}_n$ *versus* log μ shows that $\overline{D}_n$ decreases with decreasing log μ in agreement with expectation on the basis of the Rayleigh–Taylor–Tomotika theory.

Relating the rheological properties of PP/EPR blends to the mode and state of dispersion of the minor component, it emerges that both blend zero-shear viscosity (η_0) and α(blend) parameter values decrease with increasing EPR dispersion coarseness. It is interesting to underline that a decrease in η_0(blend) and α(blend) values with increasing dispersion coarseness of the minor components was already observed by Martuscelli and coworkers studying a different melt-incompatible blend system made by PA6 and EVA.

(iii) The notched Charpy impact strength values of PP/EPR blends for test temperature ranging between -10 and $+30$°C shows that the enhancement in PP impact behaviour depends strongly on the molecular characteristics of the dispersed phase. The very different behaviour of the EPR samples as impact modifiers was mainly ascribed to the fact that in a blend with PP they give rise to domains with different degree of dispersity (average particle size).

The range of particle size effective for PP toughening was found, moreover, to be dependent on test temperature. For a temperature higher than EPR T_g and close to PP T_g (-10 to 0°C) such a range is narrower (0.1–1.0 μm) than that effective at room temperature (0.1–1.5 μm).

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