

Polyolefin blends: 1. Effect of EPR composition on structure, morphology and mechanical properties of HDPE/EPR alloys

R. Greco, C. Mancarella, E. Martuscelli and G. Ragosta

Istituto di Ricerche su Tecnologia dei Polimeri e Reologia del CNR, Arco Felice, 80072 Naples, Italy

and Yin Jinghua

Changchun Institute of Applied Chemistry, Academia Sinica, China

(Received 13 October 1986; revised 4 March 1987; accepted 21 April 1987)

Differential scanning calorimetry, wide-angle X-ray diffraction, morphology, and mechanical and impact properties of a high-density polyethylene (HDPE)/ethylene-propylene copolymer (EPR) blend (80/20 weight ratio), with the EPR copolymer having various compositions, have been investigated. The results show no evidence of cocrystallization between HDPE and the EPR copolymers even at the highest C_2 content. During blend mixing, the copolymers are able to dissolve HDPE low-molecular-weight chains, giving rise to a system with lower crystallinity and higher HDPE crystallite perfection. The observed behaviour is very similar to that of an isotactic polypropylene/ethylene-propylene copolymer studied in a parallel work.

(Keywords: high density polyethylene; ethylene-propylene copolymers; blends; morphology; mechanical properties)

INTRODUCTION

In recent years, the properties of semicrystalline polyolefins, such as low-density polyethylene (LDPE), linear high-density polyethylene (HDPE) and isotactic polypropylene (iPP), blended with ethylene-propylene-diene terpolymer (EPDR) or with ethylene-propylene copolymer (EPR) have been investigated by several authors¹⁻¹⁰. Generally the above-mentioned copolymer or terpolymer has been used as a toughening agent for polypropylene matrices, especially if coupled with linear polyethylene (HDPE)³⁻⁵. Therefore a number of investigations have been carried out on the influence of such rubbery polymers on the crystallization behaviour, the morphology and the mechanical properties of iPP^{1,4,9-11}.

LDPE- or HDPE-based blends, containing EPR or EPDR, have received less attention in the literature, probably because of the minor technological need to toughen them. Therefore fundamental knowledge of these systems in the area of structure-properties relationships is still rather limited. A few EPDR terpolymers were mixed with LDPE and HDPE and the blend properties analysed. Cocrystallization effects were invoked between LDPE and the EPDR having the highest ethylene (C_2) content in order to explain the data, whereas a limited mixing for all the EPDRs was observed with HDPE. On lowering the C_2 content in the EPDR, the interactions between matrix and rubber were reduced in both cases. Some results on HDPE/EPR⁷ and HDPE/EPDR⁸ blends have been presented. The whole composition range was investigated using an EPR with a high C_2 content in the first work⁷ and an EPDR with a lower C_2 content in the second one⁸. Mainly morphological

influences and limited mixing interactions were found in both cases.

In the present paper a rather systematic study of the influence of EPR composition on the properties of an HDPE/EPR system at a fixed blend ratio (80/20 weight ratio) has been made. The aim is also to compare these results with those relative to a parallel analysis carried out using analogous conditions for iPP/EPR blends¹².

EXPERIMENTAL

Material

Ethylene-propylene copolymers were synthesized by using the Ziegler-Natta catalyst, $TiCl_3, Al(C_2H_5)_2Cl$ ($Al/Ti=4/1$). The concentration of the catalyst was 6 mmol l^{-1} (n-heptane solvent). The temperature for the polymerization was 50°C and the polymerization time was an hour. No purification was made thereafter. Copolymers contained long C_2 (ethylene) (or C_3 (propylene)) sequences along the molecular chain. The characterization of the copolymers is given in Table 1: from left to right, the code (letters are an abbreviation of ethylene-propylene (EP) and digits represent the percentage of ethylene in moles), the percentage of ethylene in weight, the feed ratio of monomers to the polymerization reactor, the intrinsic viscosity, the crystallinity X_c , the melting temperature T_m and the glass transition temperature T_g .

High-density polyethylene, kindly supplied by RAPRA (Rubber and Plastics Research Association of Great Britain), has the following characteristics: $M_w = 1.1 \times 10^5$, $M_n = 1.1 \times 10^4$, $M_w/M_n = 10$ and $MFI = 3.7$.

Table 1 Compositions and properties of EPR copolymers

Code	C ₂ content (wt %)	Feed ratio of monomers (C ₂ /C ₃)	$[\eta]$ (dl g ⁻¹) in decahydronaphthalene at 135°C	X _c (%) (d.s.c.)	T _m (°C)	T _g (°C)
EP-84	78	75/25	3.73	27	125	-50
EP-69	60	64/36	2.36	14	126	-50
EP-59	49	55/45	2.08	12	125	-44
EP-45	35	44/56	1.65	2	123	-36
EP-12	8	4/96	1.66	42	143	0 to -6

Blend preparation

Blends of HDPE and EPR (the weight ratio is HDPE/EPR = 80/20) were prepared by melt mixing in a Brabender-like apparatus (Haake Rheocord instrument). Blending temperature was 200°C and blending time was 15 min. The rate of the rotor was 32 rpm.

Specimen preparation

Specimens for mechanical tensile tests. The material obtained by blending was hot-pressed in a hydraulic press (Wabash) at 170°C and about 240 kg cm⁻². The thickness of the sheets obtained was about 1 mm. Dumbbell specimens were cut from the sheets obtained and used for the mechanical investigations.

Specimens for d.s.c. experiments. The following standard procedures were used to prepare specimens for d.s.c. experiments. The specimens were obtained as follows: first the blended samples were heated to 170°C and kept at this temperature for 15 min; then they were quenched at room temperature in water. Fibre specimens were cut from the middle of stretched sample fibres having the same draw ratio of 1200%.

Specimens for morphology observations. The thin sections used for optical microscopy were cut cryogenically with an LKB ultramicrotome. Those to be utilized for electron microscopy were cut by using a Reichert-Sung microtome. Some SEM specimens were etched using n-heptane vapour to remove the copolymers. The other SEM specimens were etched with CrO₃/H₂SO₄ saturated solution at room temperature for 50 min to destroy the amorphous phase of the blends. The procedure to prepare this kind of solution was as follows: first the concentrated sulphuric acid was diluted with water (the ratio of H₂SO₄ to water was 1:4); then it was heated to 80°C and the CrO₃ added to form the saturated solution.

Specimens for fracture tests. First the blended materials with different HDPE/EPR weight ratios were hot-pressed in the same hydraulic press at 200°C and at a pressure of 240 kg cm⁻². The moulded sheets obtained were 3.0 mm thick. Then Charpy-type specimens 6.0 mm wide and 6.0 mm long were cut by a mill. Finally all the specimens were notched at the middle of their length as follows: a blunt notch was made by a slotter and then a very sharp notch 0.2 mm deep was produced by a razor blade fixed on a micrometer apparatus. The final value of the notch depth was measured after fracture by using an optical microscope. For the impact studies the following blends were prepared: HDPE/EP-84 and HDPE/EP-45 with 100/0, 90/10, 85/15 and 80/20 (w/w) compositions.

Techniques

Mechanical tensile tests. Dumbbell specimens were

elongated by using an Instron testing machine (at room temperature and at a constant crosshead speed of 10 mm min⁻¹). The draw ratio for HDPE and HDPE/EPR blends was about 1200%. Three parameters were calculated from the stress-strain curves: (1) Young's modulus E from the initial slope $(d\sigma/d\varepsilon)_{\varepsilon=0}$; (2) yield strength σ_y ; and (3) constant stress σ_c at cold-drawing.

Fibres were cut from stretched specimens between the two necks at a length of 5 cm and were redrawn by the same testing machine (at room temperature and at constant crosshead speed of 10 mm min⁻¹). From stress-strain curves were calculated the following: (1) Young's modulus E ; (2) tensile strength σ_b ; and (3) elongation at break ε_b .

D.s.c. measurements. Crystallinity X_c , melting temperature T_m , crystallization temperature T_c and widths at half height of the melting and crystallization peaks for the d.s.c. specimens mentioned earlier were determined by using a Mettler TA 3000 system apparatus. The rate of increasing and decreasing the temperature was 20 K min⁻¹. For the determination of T_c the samples were kept for 10 min at 200°C. The weight of the specimens was about 7 mg.

Morphology observations. Optical micrographs were taken by using a Wild M420 microscope. The surfaces of the specimens observed by SEM were coated with Au-Pd and observed by a Philips 501 B scanning electron microscope.

WAXD measurements. Wide-angle X-ray diffraction measurements were performed by means of a Philips PW 1060/71 diffractometer with Ni-filtered Cu K α radiation. The high voltage was 50 kV and the tube current was 30 mA.

Impact fracture measurements. Charpy impact tests were carried out at an impact speed of 1 m s⁻¹ by using a Ceast fracture pendulum. Samples with a notch depth-to-width ratio of 0.3 and a span test of 48 mm were fractured at different temperatures ranging from -100 up to 20°C. The temperature was changed by means of a home-made liquid-nitrogen apparatus. Curves of the impact strength as a function of the test temperature were obtained for all the HDPE/EP-84 and HDPE/EP-45 blends.

RESULTS AND DISCUSSION

Unoriented specimens

Morphology. Optical micrographs with crossed polars of thin films of HDPE, HDPE/EP-84 and HDPE/EP-12 blends are reported in Figure 1. The nucleating influence of the EP-84 and EP-12 copolymers on HDPE is clearly demonstrated by comparing the micrographs, since a heterogeneous nucleation effect due to inclusions or added nucleants can be excluded by indirect evidence.

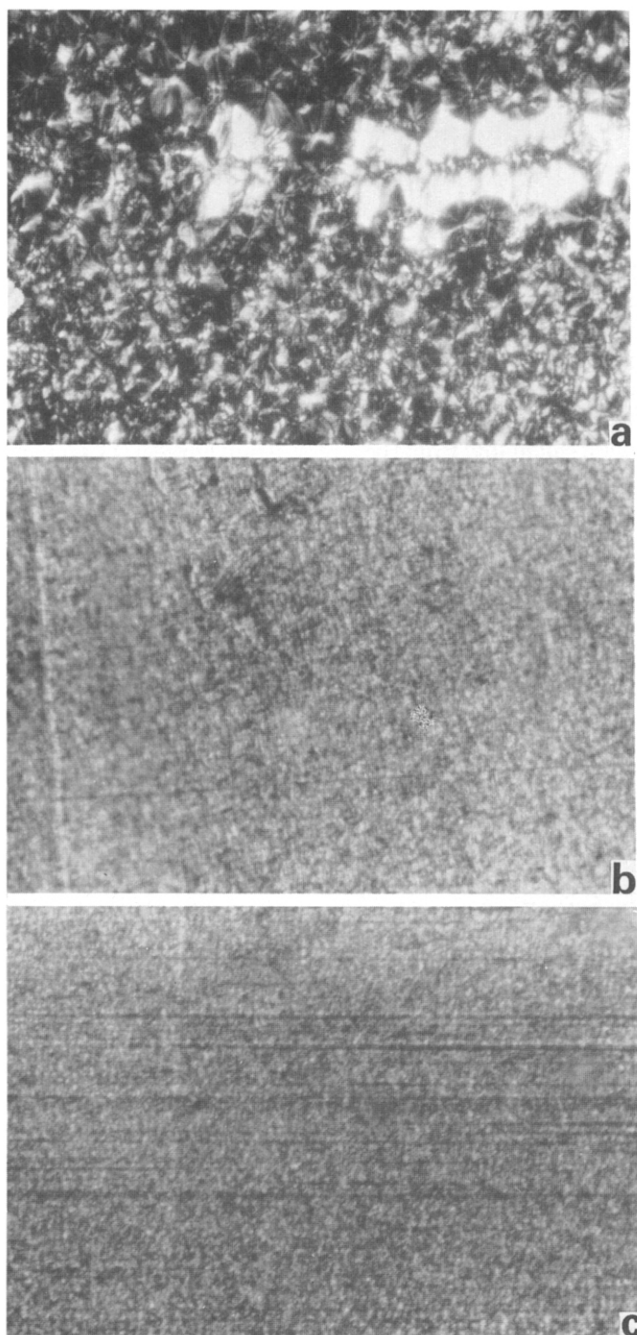


Figure 1 Optimal micrographs (150 \times) at crossed polars of thin sections: (a) HDPE; (b) HDPE/EP-80; (c) HDPE/EP-12

In the third paper of this series¹³, for blends crystallized at a low undercooling, this effect on the iPP matrix did not always occur. It depended, instead, only on the C₂ content of the copolymers. This result tends therefore to indicate that, even though the copolymers were not purified after synthesis, the eventual impurities have a negligible influence on iPP nucleation. If this holds for iPP matrices^{12,13}, in HDPE ones also the nucleation will depend only on the rubber's action.

Electron micrographs of smoothed surfaces, etched with n-heptane, are shown in Figures 2–7. Going from the pure HDPE (Figure 2) and progressively decreasing the C₂ content in the added copolymers (from Figure 3 to Figure 7) it was possible to extract more and more amorphous material from the surface by dissolving in boiling n-heptane. In fact the holes increase in size more and more, indicating a diminution of compatibility in the

amorphous regions between the HDPE matrix and the copolymers.

A different etch with strong oxidants (CrO₃/H₂SO₄) revealed the spherulitic structure and some details of the

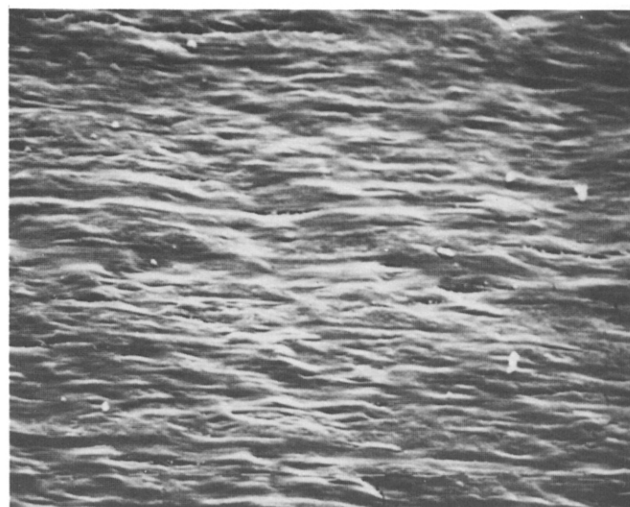


Figure 2 Electron micrographs (3600 \times) of a smoothed HDPE sample surface etched for 15 min with boiling n-heptane vapour

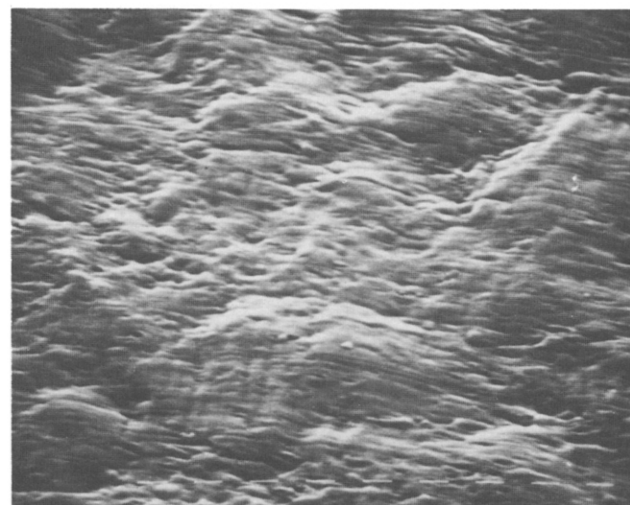


Figure 3 Scanning electron micrograph (3600 \times) of a smoothed HDPE/EP-84 sample surface etched for 20 min with boiling n-heptane vapour

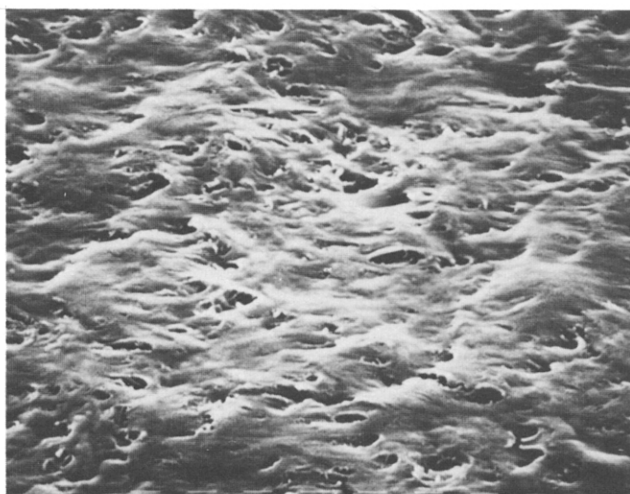


Figure 4 Scanning electron micrograph (3600 \times) of a smoothed HDPE/EP-69 sample surface etched for 10 min with boiling n-heptane vapour

lamellar structure by attack of all the amorphous regions of both HDPE and the copolymers. This is shown in *Figure 8* for HDPE, in *Figure 9* for EP-84 and in *Figure 10* for EP-69. For HDPE/EP-84 and HDPE/EP-69 blends the spherulites looked more open since there was more

amorphous content to be destroyed among spherulites and lamellae.

Thermal properties. The parameters calculated from the differential scanning thermograms are reported for

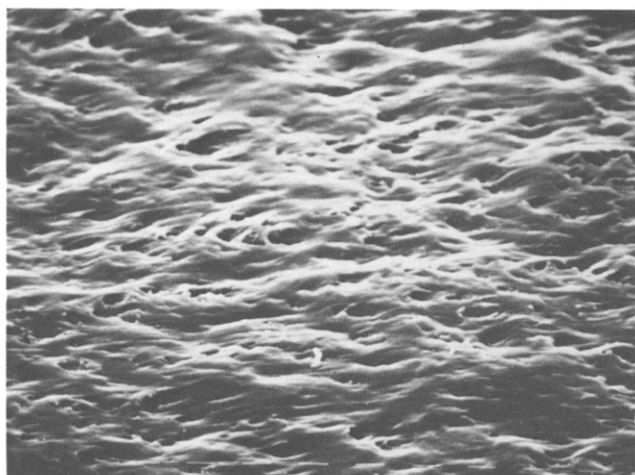


Figure 5 Scanning electron micrograph (3600 \times) of a smoothed HDPE/EP-59 sample surface etched for 10 min with boiling n-heptane vapour



Figure 6 Scanning electron micrograph (3600 \times) of a smoothed HDPE/EP-45 sample surface etched for 1.5 min with boiling n-heptane vapour



Figure 7 Scanning electron micrograph (3600 \times) of a smoothed HDPE/EP-12 sample surface etched for 3 min with boiling n-heptane vapour

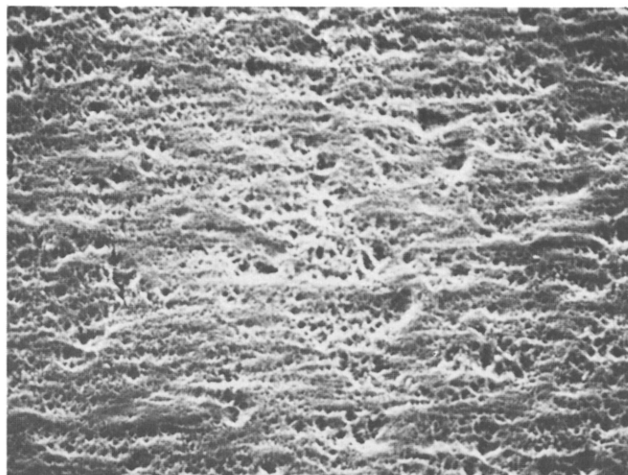


Figure 8 Scanning electron micrograph (3600 \times) of a smoothed HDPE sample surface etched by a strong oxidant mixture (for details see text) for 90 min

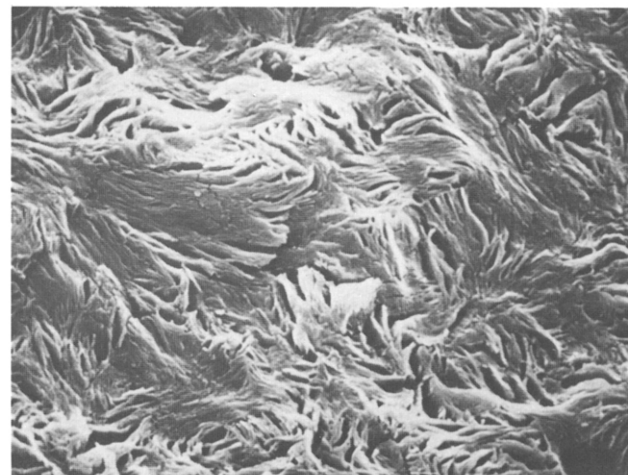


Figure 9 Scanning electron micrograph (3600 \times) of a smoothed HDPE/EP-84 sample surface etched by an oxidant mixture (for details see text) for 150 min

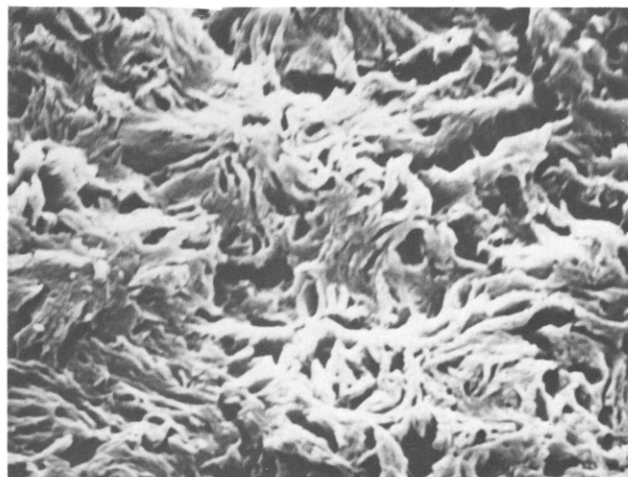


Figure 10 Scanning electron micrograph (3600 \times) of a smoothed HDPE/EP-69 sample surface etched by an oxidant mixture (for details see text) for 150 min

Table 2 Crystallinity, melting temperature T_m , crystallization temperature T_c and width at half height of T_m and T_c peaks for HDPE/EPR blends

Sample	Crystallinity (%)		Melting temperature (°C)	Crystallization temperature (°C)	Width at half height of peak (K)	
	X_c	X_c^p			T_m peak	T_c peak
HDPE	79	79	137	111	19	20
HDPE/EP-84	60	68	142	114	17	17
HDPE/EP-69	55	66	141	114	17	17
HDPE/EP-59	52	65	141	115	18	17
HDPE/EP-45	50	64	141	114	18	17
HDPE/EP-12	59	71	148	114	19	18

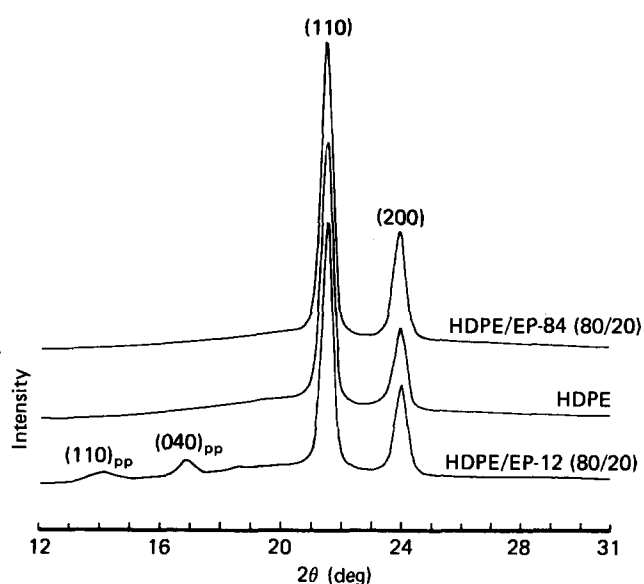
pure HDPE and for all the HDPE/EPR (80/20) blends in Table 2: from left to right, the type of blend, the measured overall crystallinity X_c , the crystallinity X_c^p (calculated assuming no HDPE-EPR interaction from the equation $X_c^p = W_{HDPE}X_{HDPE} + W_{EP}X_{EP}$ where W and X are the relative weight ratios and crystallinities, between the polyolefin and the copolymer), the melting and crystallization temperatures T_m and T_c and the width at half height of the melting and crystallization peaks are shown.

The overall crystallinity X_c decreases for all the blends with respect to the pure HDPE. This can be due partly to the substitution of 20% HDPE with less crystalline copolymers. But X_c is lower than X_c^p , indicating that there is a certain amount of interaction between HDPE and EPR during crystallization.

This effect is also confirmed by the fact that the melting and crystallization temperatures T_m and T_c are higher for the blends than for the homopolymer. A further complementary observation is the width at half height of the T_m and T_c peaks, which are narrower for the blends than for the HDPE.

All these features could be tentatively explained as follows. During the melt-mixing in the Brabender-like apparatus the copolymers were able to dissolve HDPE defective molecules (i.e. of lower molecular weight). Therefore during pressure moulding and the successive rapid crystallization this segregation between high-molecular-weight HDPE and the new HDPE/copolymer phase containing defective HDPE chains was still retained. Hence more perfect crystals (high T_m and T_c) and a narrower distribution of lamellae or crystallite dimensions (lower width at half height of T_m and T_c peaks) for the blends than for pure HDPE were obtained. The behaviour of the last blend (HDPE/EP-12) should be analysed more carefully since it contains two crystalline phases, the HDPE one and the C_3 crystallites, as will be shown later also by wide-angle X-ray scattering measurements. In fact the melting and crystallization peaks of HDPE also contain the C_3 crystallite contribution, which cannot be evaluated. This effect can, at least partially, explain the even higher T_m and the broader peak in comparison to that of all other blends.

X-ray diffraction. Wide-angle X-ray scattering (WAXS) patterns are shown in Figure 11, where the intensities in arbitrary units are plotted against the diffraction angle 2θ . As shown the blend HDPE/EP-84 reveals the same pattern as pure HDPE, whereas the HDPE/EP-12 blend also contains C_3 crystallites, indicating that its X_c (Table 2) has been overestimated. This finding confirms the substantial incompatibility in the solid EP-12 copolymer and the better compatibility of the other ones with the

**Figure 11** Wide-angle X-ray diffraction intensity as a function of diffraction angle 2θ for HDPE and blends

HDPE matrix, evidenced by the morphology of the etched specimens (Figures 2–7).

Mechanical properties. The Young's modulus E , the yield stress σ_y and also the stress at cold-drawing σ_c are reported in Table 3 for all the investigated blends. All of them exhibit the same trend with a minimum at C_2 of about 50%. There is no σ_c value for the HDPE/EP-12 blend since its specimens broke before cold-drawing due to the gross morphology of the EP-12 dispersed phase (see Figure 7).

The analogous trends of E and σ_y can be explained as follows. In the range of C_2 from 40 to 100% in the copolymers up to pure HDPE there is an increase of crystallinity from 50 to 79% (see Table 2). Moreover, the glass transition temperature of HDPE and also of the copolymers is far below room temperature (see Table 1), at which the mechanical tensile tests have been performed. Therefore E and σ_y follow an increasing trend with enhancing C_2 content of the EPR copolymers.

If one considers now the HDPE/EP-12 blend one can see, from the above-mentioned tables, that its crystallinity content is a little higher with respect to all the other blends. But what is more significant is that its glass transition temperature (0–6°C) is lower than the test temperature (20°C). This tends to increase the E and σ_y values, which become comparable to that of pure HDPE. A further consideration is that for this last blend there is a strong segregation of the copolymer from the matrix in semicrystalline glassy particles.

Table 3 Young's modulus E , tensile yield stress σ_y and cold-drawing constant stress σ_c of HDPE and HDPE/EPR blends

Sample	Composition (HDPE/EPR in weight)	C ₂ content of EPR (wt %)	$E \times 10^{-3}$ (kg cm ⁻²)	$\sigma_y \times 10^{-2}$ (kg cm ⁻²)	$\sigma_c \times 10^{-2}$ (kg cm ⁻²)
HDPE	100/0	—	11.3	3.2	2.0
HDPE/EP-84	80/20	78	8.5	2.5	1.7
HDPE/EP-69	80/20	60	7.5	2.2	1.4
HDPE/EP-59	80/20	49	7.4	2.0	1.4
HDPE/EP-45	80/20	35	7.2	2.0	1.3
HDPE/EP-12	80/20	8	11.0	3.1	—

There are in fact long C₃ sequences in chains which are rejected by the growing fronts of the HDPE spherulites. These large dispersed hard domains strongly hamper matrix cold-drawing and cause premature rupture before fibre formation. This effect is evidenced by the morphology observations already mentioned above.

Impact properties. The impact strength (R) obtained by Charpy tests as a function of temperature is reported in Figure 12 for HDPE homopolymer and for all the HDPE/EP-45 and HDPE/EP-69 blends. As can be seen, at low temperatures up to about -40°C , the impact data of pure HDPE remain constant at low values and the corresponding fracture surfaces exhibit features characteristic of a brittle material. As the temperature rises the impact strength begins to increase and the appearance of a stress-whitening zone near the base of the notch, which increases in extent with enhancing temperature, can be observed.

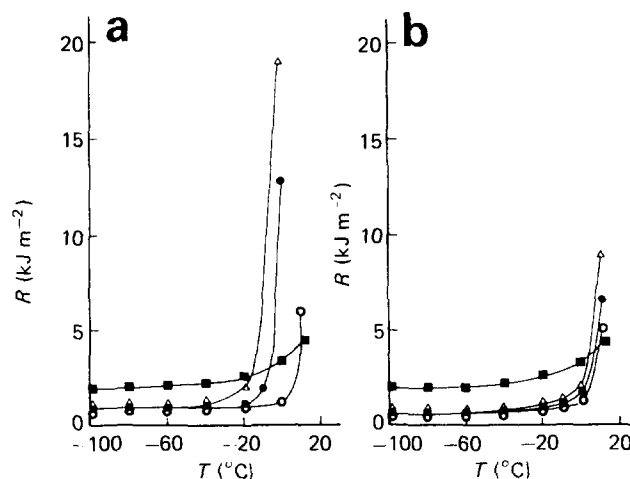
The addition of a copolymer (EP-45 or EP-69) produces in the region of low temperatures a lowering of the impact strength due essentially to the fact that the rubber particles behave as hard fillers and their adhesion to the surrounding matrix is very poor. Thereafter at test temperatures beyond -20°C for PE/EP-45 blends and 0°C for PE/EP-69 blends a sharp rise in the R values is detected, being higher for greater amounts of copolymer. This enhancement, which is larger in the case of PE/EP-45 alloys, is accompanied by a diffuse stress-whitening phenomenon over the entire fracture surface.

The lower toughening action observed for EP-69 with respect to the EP-45 copolymer can probably be ascribed to its higher crystallinity content, which renders the EP-69 domains more rigid and therefore less effective in controlling the craze propagation process in the HDPE matrix.

Fibres

Thermal properties. The parameters of fibres, i.e. overall crystallinity X_c , melting temperature T_m and width at half height of T_m peak, are reported in Table 4. Comparison of Table 4 with Table 3 shows that the crystallinity of HDPE fibres has remained unchanged with respect to the initial unoriented material, whereas the melting point is increased. This indicates that some local melting and recrystallization under stress has improved crystal perfection and probably also that they are less polydispersed in size (the width at half height of the melting peak is lower for fibres).

Instead for the blends the T_m of fibres is slightly lower, whereas the crystallinity content X_c is considerably higher with respect to the unoriented samples. This seems to suggest that here also some local melt mixing and recrystallization has occurred during cold-drawing into

**Figure 12** Resilience R as a function of testing temperature: (a) curves for HDPE/EP-45 blends at various EP-45 contents: ■, 0%; ○, 10%; ●, 15%; △, 20%; (b) curves for HDPE/EP-69 blend at various EP-69 contents: ■, 0%; ○, 10%; ●, 15%; △, 20%**Table 4** Crystallinity, melting temperature and width at half height of melting peak for fibres of HDPE and HDPE/EPR blends

Sample	Crystallinity (%)	Melting temperature ($^\circ\text{C}$)	Width at half height of melting peak (K)
HDPE	79	140	13
HDPE/EP-84	68	140	13
HDPE/EP-69	65	139	13
HDPE/EP-59	64	139	14
HDPE/EP-45	63	139	14

the neck. Therefore the segregation effect between the HDPE and the copolymers is not so sharp as before. Of course the HDPE blend matrix improves its crystal perfection as well as pure HDPE.

Tensile properties. The Young's modulus E , the tensile strength σ_b and the elongation at break ϵ_b are reported in Table 5. For E and σ_b there is a sharp increase with C₂ increase, probably due to the enhanced crystallinity content (see Table 5). During the morphological transformation, in fact, from the microspherulitic structure to the fibrillar one, X_c is higher the larger the number of taut tie molecules that bridge the fibrils formed during cold-drawing. Hence E and σ_b increase with increasing C₂ content. The elongation at break ϵ_b , in contrast, decreases, showing a minimum value for pure HDPE. This is still due to the more rigid structure built on a material structured on a higher crystallinity content.

Table 5 Young's modulus E , tensile strength σ_b and elongation at break ϵ_b of HDPE and HDPE/EPR fibres

Sample	Composition (HDPE/EPR in weight)	C ₂ content of EPR (wt %)	$E \times 10^{-3}$ (kg cm ⁻²)	$\sigma_b \times 10^{-2}$ (kg cm ⁻²)	ϵ_b (%)
HDPE	100/0	—	42.4	26.1	31
HDPE/EP-84	80/20	78	20.2	17.0	39
HDPE/EP-69	80/20	60	19.2	16.8	44
HDPE/EP-59	80/20	49	20.2	16.9	45
HDPE/EP-45	80/20	35	12.1	12.2	45

CONCLUSIONS

The influence of copolymer composition on the properties of HDPE/EPR blends having a fixed composition (80/20 weight ratio) have been extensively analysed. In particular the following conclusions can be drawn:

(1) The nucleating effect of the copolymers on the HDPE matrix has been observed by optical microscopy.

(2) The compatibility between HDPE and the copolymer increases with increasing C₂ copolymer content.

(3) Higher melting points and lower crystallinity content are obtained for the blends with respect to pure HDPE.

(4) The mechanical properties (E , σ_y and σ_c) of unoriented specimens decrease with decreasing C₂ content in the blends. An exception must be made for the HDPE/EP-12 blend due to the presence of C₃ crystallites (as shown by WAXS), which act as reinforcing elements. For fibres E and σ_b decrease and ϵ_b increases with decreasing C₂.

(5) The impact properties improve slightly for the blends and are better in the case of lower compatibility between HDPE and the copolymer used.

The above results are very similar to those found in a parallel work for iPP-based blends with EPR at different C₃ contents.

ACKNOWLEDGEMENTS

The authors wish to thank Mr L. Serio, Mr V. D. Liello and Mr M. Viola for their help in carrying out the experimental work.

REFERENCES

- 1 Karger-Kocsis, J., Kallo', A., Szafner, A., Boder, G. and Sényei, Z. *Polymer* 1979, **20**, 37
- 2 Starkweather, H. W. Jr, J. *Appl. Polym. Sci.* 1980, **25**, 139
- 3 Stehling, F. C., Huff, T., Speed, C. S. and Wissler, G. J. *Appl. Polym. Sci.* 1981, **26**, 2695
- 4 Martuscelli, E., Silvestre, C. and Abate, G. *Polymer* 1982, **23**, 229
- 5 D'Orazio, L., Greco, R., Mancarella, C., Martuscelli, E., Ragosta, G. and Silvestre, C. *Polym. Eng. Sci.* 1982, **22**, 536
- 6 D'Orazio, L., Greco, R., Martuscelli, E. and Ragosta, G. *Polym. Eng. Sci.* 1982, **23**, 489
- 7 Kalfoglou, N. K. J. *Macromol. Sci.* 1983, **B22**, 343
- 8 Kalfoglou, N. K. J. *Macromol. Sci.* 1983, **B22**, 363
- 9 Karger-Kocsis, J., Kiss, L. and Kuleznev, V. N. *Polym. Commun.* 1984, **25**, 122
- 10 Karger-Kocsis, J., Kallo', A. and Kuleznev, V. N. *Polymer* 1984, **25**, 279
- 11 Barkczak, Z., Galeski, A. and Martuscelli, E. *Polym. Eng. Sci.* 1984, **24**, 1155
- 12 Greco, R., Mancarella, C., Martuscelli, E., Ragosta, G. and Jinghua, Y. *Polymer* 1987, **28**, 1929
- 13 Greco, R., Martuscelli, E., Ragosta, G. and Jinghua, Y. *Polymer* submitted for publication