Multiple morphology in polypropylene/ethylene–propylene–diene terpolymer blends

B. Pukánszky and F. Tüdös*
Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525 Budapest, PO Box 17, Hungary

A. Kalló and G. Bodor
Research Institute for the Plastics Industry, H-1950 Budapest, Hungary

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The morphology of polypropylene/ethylene–propylene–diene terpolymer (PP/EPDM) blends was investigated in the entire composition range by differential scanning calorimetry (d.s.c.), small angle and wide angle X-ray scattering (SAXS, WAXS) and transmission and scanning electron microscopy (TEM, SEM). Only slight changes were observed in the crystalline morphology of PP blends quickly cooled from the melt. On melting and recrystallization at a lower rate, elastomers show β nucleation effect on PP. Above 80 vol% elastomer content crystallization of PP is hindered. Dispersed morphology of the blends shows structural changes as a function of composition: PP is the continuous phase at low and elastomer at high EPDM content; in between a transitional morphology is observed. At high EPDM content, PP is finely dispersed in the statistical copolymer, while it forms large islands in block EPDM.

(Keywords: polypropylene; EPDM rubber; blends; morphology; electron microscopy; crystallization; d.s.c.)

INTRODUCTION

Polypropylene (PP) is often blended with elastomers to improve its otherwise poor low temperature impact strength. Various elastomers are used as impact modifiers, including polyisobutylene[1], styrene–butadiene block copolymers[2–6], polyisoprene[4] and natural rubber[7], but ethylene–propylene copolymers (EPR)[2,4,8–10] and ethylene–propylene–diene terpolymers (EPDM)[2,4,9,11–14] have proved to be the most effective in this application. To improve impact strength, the blends usually contain <25–30 vol% elastomer. The morphology and properties of such blends have been widely investigated[9–16]. Less research has been done on PP/EPDM blends in the entire composition range[17–19], although such investigations could give valuable information on the interaction of the components and on the effect of component properties. Moreover, blends of high EPDM content also find practical application as thermoplastic elastomers.

The main purpose of morphological studies is generally to determine the correlations between the structure and properties of such polymer systems. In PP/EPDM blends numerous structural levels have to be taken into consideration. PP has a complicated morphology in itself. Being a semicrystalline polymer, it contains amorphous and crystalline phases and the latter has a complex structural hierarchy: crystal lattice, lamellar structure and spherulitic morphology[20]. Since PP is immiscible with EPDM, besides changing crystalline morphology, blending of the two components results in a two-phase dispersed morphology of a different level. The characteristics of this level change with composition and opinions concerning the structure are especially contradictory in the intermediate composition range. The structure of the blends may be influenced by the properties of the elastomer too. It was proved that the relative viscosity of the elastomer influences the size of the dispersed rubber particles[18,21,22], and EPDM – especially the block copolymer – may possess a multiphase morphology in itself[23,24]. It is widely accepted that close correlation exists between the structure and properties of polymer blends, but there are still questions concerning the role of the different morphological levels on the final blend properties.

The aim of this work was to study the changes in the multiple morphology of PP as an effect of blending with EPDM, to determine the influence of elastomer properties on these changes and to establish correlations between structure and properties of the blends. In this paper our results on the morphology will be reported. The relation of the structure to blend properties will be discussed in a subsequent publication.

EXPERIMENTAL

Throughout the experiments Tipplen H501 (TVK, Hungary) isotactic polypropylene was used as matrix polymer ($M_n = 3.1 \times 10^4$, $M_w = 51.6 \times 10^4$), which was blended with seven EPDM elastomers. The most important characteristics of the elastomers are listed in *Table 1*. All the elastomers were produced by Hüls (FRG). Two of the elastomers were block copolymers and the others were statistical copolymers. The elastomer content

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* To whom correspondence should be addressed

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Table 1 Characteristics of the EPDM elastomers studied

Type	Copolymer type	Ethylene content (mol%)	Density ($g cm^{-3}$)	Mooney viscosity	Molecular weight × 10^{-4}	
					M_n	M_w
Buna AP 147	Block	75	0.835	30	0.85	12.5
Buna AP 447	Block	72	0.862	85	4.88	19.5
Buna AP 251	Statistical	55	0.854	42	1.08	15.7
Buna AP 331	Statistical	61	0.858	70		1.62[a]
Buna AP 341	Statistical	64	0.855	70	5.33	18.7
Buna AP 451	Statistical	60	0.857	90	2.23	22.3
Buna AP 541	Statistical	60	0.859	110	2.02	22.0

[a] Intrinsic viscosity ($dl g^{-1}$), in toluene, at 25°C

of the blends changed from 0 to 1 volume fraction in ten steps. The blends also contained 0.2 wt% Irganox 1010 (Ciba-Geigy, Switzerland) antioxidant.

The blends were prepared in a Brabender W 50 EH mixing chamber attached to a HAAKE Rheocord EU-10V Plasti Corder. Mixing conditions were 190°C set temperature, 40 rev min^{-1}, 45 cm^3 charge volume and 15 min mixing time. After mixing, the blends were dumped and compression moulded into 1 or 4 mm thick plates at 190°C.

Wide angle X-ray scattering (WAXS) measurements were carried out on Phillips Micro Müller 111 equipment (40 kV, 20 mA) using Ni filtered CuK_α radiation. To perform small angle X-ray scattering (SAXS) measurements, a Rigaku-Denki small angle chamber was attached to the Phillips Micro Müller 111 generator. SAXS patterns were recorded at a scanning rate of 0.5′/100 s using Ni filtered radiation.

Scanning electron microscope (SEM) studies were carried out on a Cambridge Stereoscan S-410 electron microscope. Micrographs were taken on fracture surfaces, which after fracture were etched for 20 s in n-heptane. Transmission electron microscopy (TEM) was performed on a Zeiss Elmi D-2 type apparatus. Ultra-thin sections were prepared on a Reichert Om U-2 ultramicrotom at −50°C. Before investigation, the sections were treated in a 1 wt% aqueous solution of OsO_4 for 3 d.

Melting and crystallization of the blends were studied in a Mettler DSC 30 apparatus at 10°C min^{-1} heating and cooling rate. 10 mg samples were investigated, and in some cases a second run was carried out to study the thermal behaviour of blends with controlled thermal history.

RESULTS AND DISCUSSION

Crystalline structure of the components

The modulus and strength of PP are determined by its crystalline structure. Any changes in this structure will result in a change of the properties, so it is essential to determine the effect of elastomer blending on the crystalline structure as well as on the melting and crystallization behaviour of PP. According to the WAXS diffractograms, there is no change in the crystal structure of PP with increasing elastomer content (*Figure 1*). The dominating α monoclinic modification is maintained at all compositions and no differences could be detected between the effect of the statistical and block copolymers.

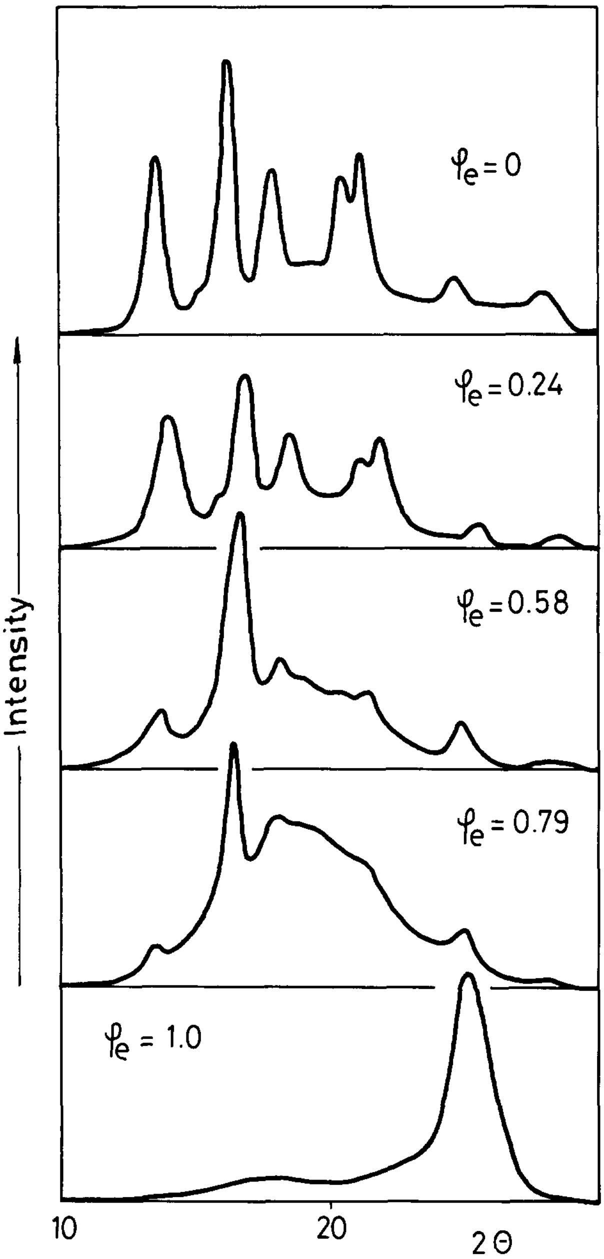

Figure 1 WAXS diffractograms of PP/EPDM (Buna AP 147) blends with different elastomer content

These results are corroborated by the differential scanning calorimetry (d.s.c.) thermograms recorded during the melting of the blends (*Figure 2*). A single peak, characteristic of the melting of α PP can be observed at

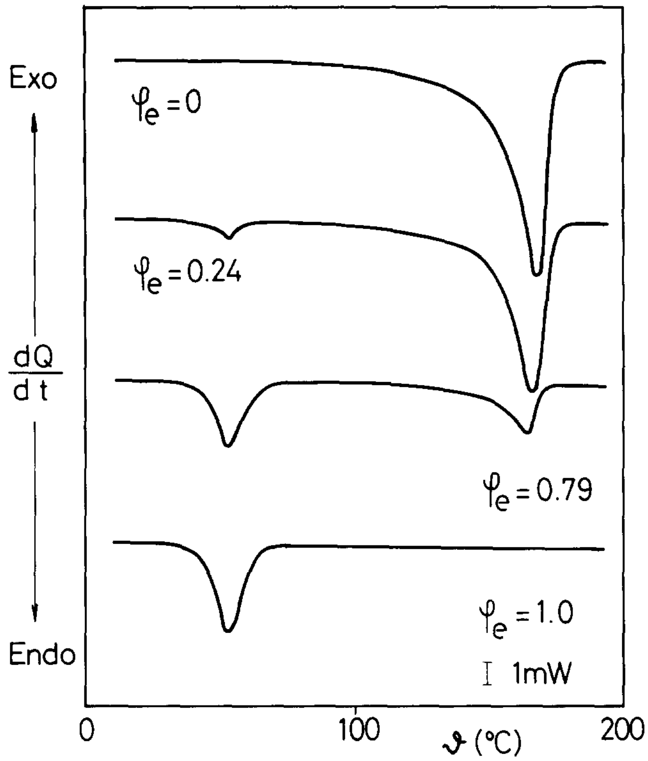

Figure 2 Melting endotherms of PP/EPDM (Buna AP 447) blends of different composition

about 165°C. No melting peak was detected at a lower temperature, which would prove the existence of the hexagonal β modification of PP in the blends. A melting peak can be observed, however, at a much lower temperature ($\approx$52°C). This peak suggests some kind of structural organization of EPDM block-copolymer, most probably an imperfect crystallization of PE blocks. Such a peak was completely absent for the statistical copolymers, i.e. the inherent structure of the two kinds of copolymer is sigificantly different.

Although no hexagonal β modification could be detected with either WAXS or d.s.c., the blends show very interesting behaviour during a second melting run after being crystallized at 10°C min^{-1} cooling rate. Thermograms of the blends containing between 5 and 50 vol% elastomer show a distinct melting peak at a lower temperature (*Figure 3*). The temperature of this peak exactly corresponds to the melting temperature of β PP[25] (148°C). Both block and statistical EPDM induce the formation of β modification, but only in the above mentioned composition range. Above 60 vol% elastomer content, the formation of β PP, as can be seen in *Figure 3*, was not observed. The maximum amount of β PP seems to form at about 0.25 volume fraction of elastomer. Up to now, no unambiguous explanation has been found for this phenomenon. Moreover, some references in the literature indicate, contrary to our results, that with increasing elastomer content the amount of β PP decreases in PP/elastomer blends[4,26]. Only further investigations can give enough information to explain the observed β nucleation effect of EPDM elastomers.

Melting temperatures of crystalline polymers can be related to the size and perfection of their crystal units[27]. *Figure 4* shows only slight changes in the melting peak temperature of the components in the second melting process. The melting peak temperature of the α PP

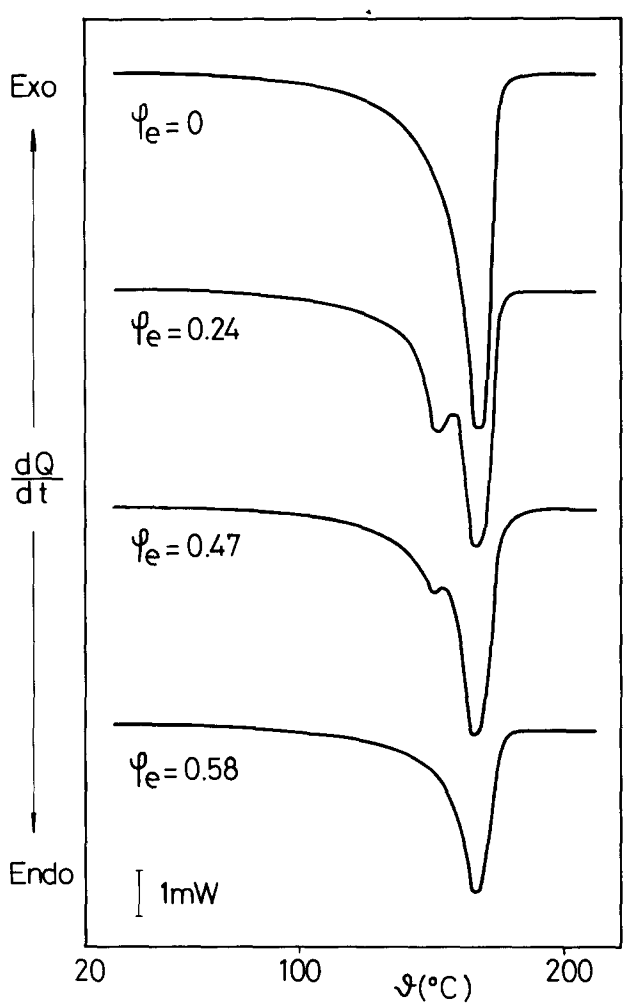

Figure 3 Melting endotherms of PP/EPDM (Buna AP 541) blends of different composition crystallized at 10°C min^{-1} cooling rate

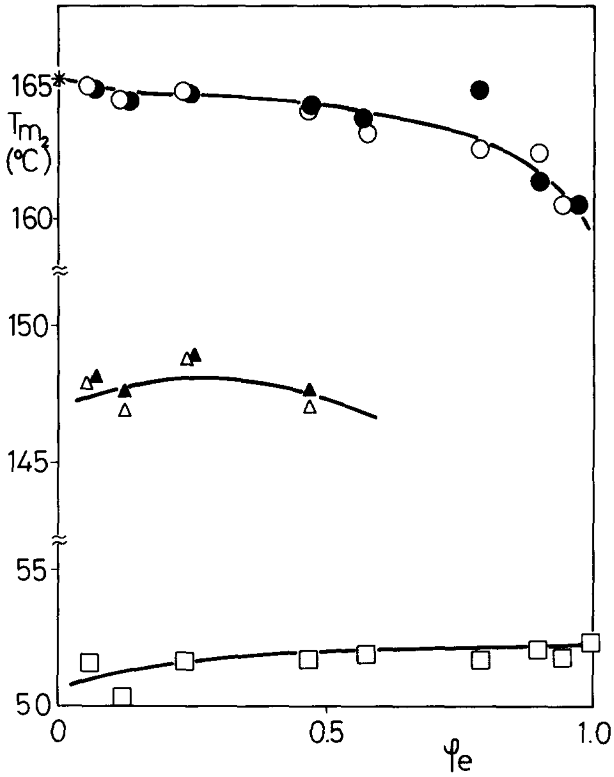

Figure 4 Melting peak temperatures of PP/EPDM blends crystallized at 10°C min^{-1} cooling rate as a function of EPDM content: ○, ●, α PP; △, ▲, β PP; □, EPDM; ○, △, □, block copolymer (AP 447); ●, ▲, statistical copolymer (AP 541)

decreases only slightly up to 80 vol% elastomer content. This indicates a small decrease in the lamellar thickness. SAXS measurements show a similarly slight increase of the long period. From these results one can conclude that the blending results in a decrease of the size and perfection of the PP crystals and in an increase of the amorphous regions between the lamellae. The results agree with data in the literature, which show that the further the conditions are from equilibrium, the less perfect are the crystals[27], i.e. the presence of elastomer somewhat hinders PP crystallization. The observed small nucleation effect of EPDM will influence similarly the size and perfection of the PP crystals. A similar tendency can be observed in the crystallization peak temperature of the block copolymer (≈52°C), although the changes are even smaller than for α PP.

The melting peak temperatures of the components show only slight changes as an effect of blending. Their crystallinities do not change significantly either (*Figure 5*). For the calculation of EPDM crystallinity we assumed PE crystalline phase and used 293 J g^{-1} (ref. 28) as the heat of fusion. The crystallinity of EPDM does not change at all, while that of PP shows significant changes only above 80 vol% elastomer content.

A similar effect of the blending was observed in the crystallization experiments. *Figure 6* shows that only above 80 vol% elastomer content can any changes be detected in the crystallization behaviour of the blends and, more specifically, in that of the PP. Above this EPDM content, the crystallization of PP slows down and a new peak appears at about 50°C on the d.s.c. thermograms. The appearance of this peak and the significantly increased supercooling indicate that the crystallization process changes at around this concentration. This change can be followed well in *Figure 7*, where the different peak temperatures are plotted as a function of composition. A similar observation was made by Ghijsels *et al.*[3] in PP/styrene–butadiene thermoplastic elastomer blends. From their results they concluded that, with increasing elastomer content, the morphology changes and this results in a change of the crystallization process. At a certain elastomer content the elastomer becomes the continuous phase and in the dispersed PP droplets only homogeneous nucleation takes place instead of the earlier heterogeneous nucleation. A similar decrease of the heterogeneous nucleation was observed by Galeski *et al.*[29] in PP/PE blends.

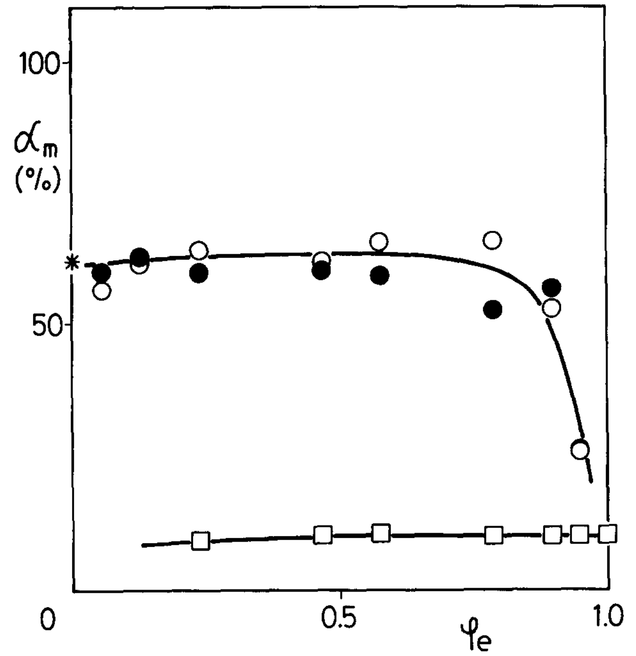

Figure 5 Crystallinity of PP/EPDM blends as a function of composition: ○, ●, PP; □, EPDM; ○, □, block copolymer (AP 447); ●, statistical copolymer (AP 541)

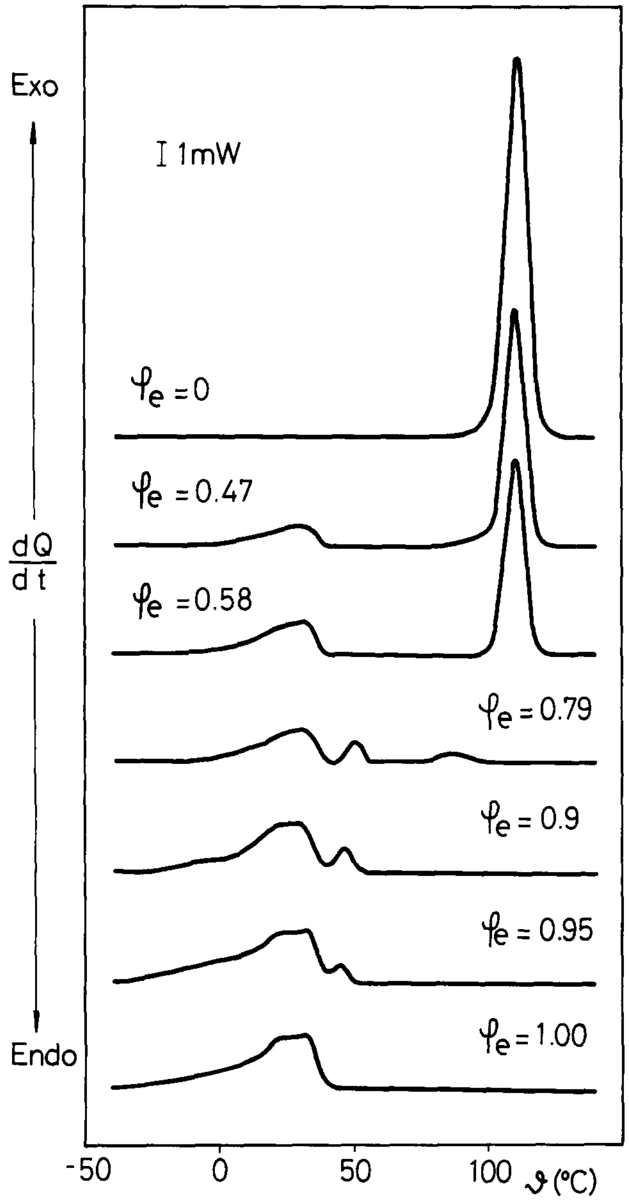

Figure 6 Crystallization exotherms of PP/EPDM (AP 447) blends of different compositions

There is practically no change in the crystallization behaviour of the EPDM block copolymer. The change in the PP crystallization peak temperature, i.e. the change of the nucleation mechanism, is independent of EPDM type. At lower EPDM content, PP crystallization peak temperature increases slightly, showing a small nucleation effect of the elastomer. Increased nucleation usually results in decreased spherulite sizes[4].

The results presented above show only small changes in the crystalline structure, melting and crystallization behaviour of the components in PP/EPDM blends. More

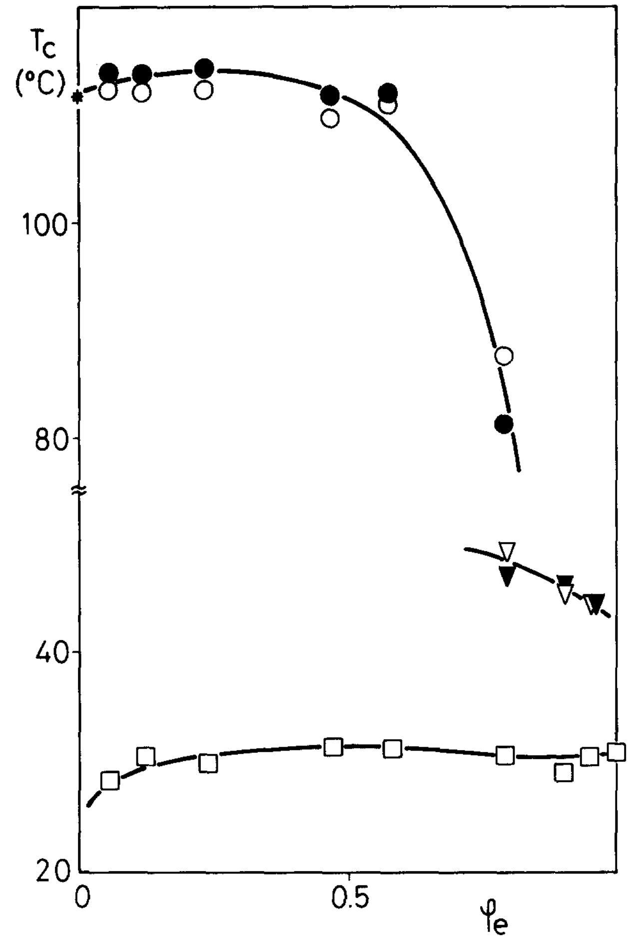

Figure 7 Crystallization peak temperatures of PP/EPDM blends as a function of composition: ○, ●, PP first peak; ▽, ▼, PP second peak; □, EPDM; ○, ▽, □, block copolymer (AP 447); ●, ▼, statistical copolymer (AP 541)

significant changes can be observed only above 80 vol% elastomer content. Although EPDM block copolymers show some internal structural organization, which is absent from the statistical copolymers, the two EPDM types have a similar effect on the crystalline properties of PP. According to these results, some changes in blend properties can be expected above 0.8 volume fraction of EPDM and no differences can be expected between the effect of the statistical and the block copolymers.

Disperse morphology

At room temperature PP and EPDM are immiscible, so mixing of the two polymers will result in a dispersed two-phase structure. At low EPDM content, which is generally used to improve the low temperature impact strength of PP, EPDM is dispersed in PP. The size of the dispersed particles depends on the relative PP/elastomer viscosity and on the conditions of the mixing[18,21,22]. Such dispersed structure was also observed by us, as shown in *Figure 8*. (On the TEM microphotographs dark areas represent OsO_4 stained EPDM and lighter areas the PP phase.) The structures of the blends prepared with statistical or block copolymers do not show any significant differences.

At large EPDM content (>80 vol%), as can be expected, EPDM elastomer is the matrix and PP droplets are dispersed in it (*Figure 9*). From the TEM micrographs, differences could not be found between the structures of the statistical- and block-copolymer-containing blends in this composition range either.

The structure of the PP/EPDM blends in the extreme composition ranges is not surprising and corresponds to that already described in the literature[17,19,21]. More contradictory statements can be found, however, concerning the intermediate composition range: both phase inversion[18,19] and interpenetrating networks[17,21,22] were observed. If we study *Figure 10* we understand the difficulty of phase structure determination on the evidence of such electron micrographs. On the micrograph, both PP and EPDM seem to form continuous phases, i.e. it is easy to assume a regular IPN structure. A closer scrutiny, however, reveals that the structure of this blend is not perfectly regular, but contains regions with different composition and different continuous phase. In some areas EPDM is the continuous phase in which PP droplets are embedded,

Figure 8 Dispersed two-phase morphology of a 10 vol% Buna AP447 EPDM-containing PP blend (TEM)

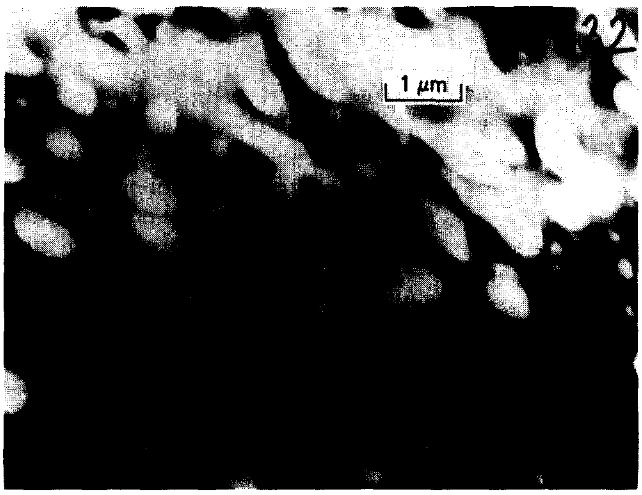

Figure 9 20 vol% PP dispersed in an EPDM (AP 447) matrix (TEM)

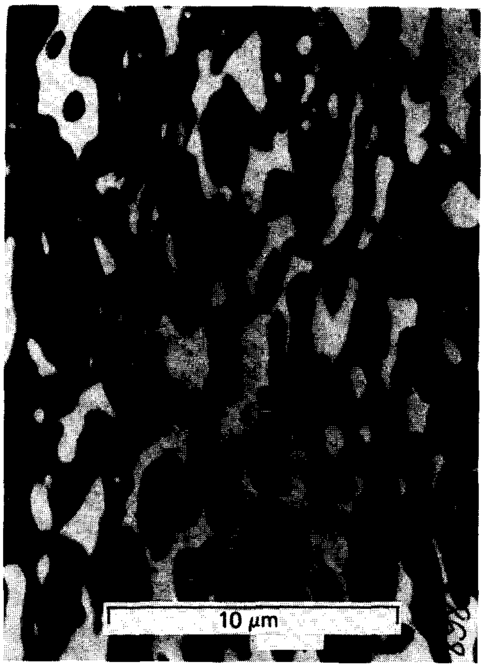

Figure 10 Transitional morphology of a 60 vol% EPDM (AP 447) containing PP blend (TEM)

while there are regions where PP is the continuous matrix containing EPDM islands. In this range, composition alone does not define the structure and the size, shape and distribution of these regions depend both on the relative viscosity of the components and on the blending conditions. A regular IPN structure is a rarely attainable, special form of this morphology.

The composition limits of this transitional morphology are hard to define. Completely dispersed structures were detected below 0.24 and above 0.79 volume fraction EPDM content. In the former case continuous PP phase was observed, while in the latter continuous EPDM phase was observed. Although definite limits of transitions from one structure to the other cannot be determined, we must note the fact that special melting and crystallization behaviour of PP was also observed in these composition ranges. A maximum in the amount and melting peak temperature of β PP was observed at 24 vol% EPDM content. Above 80 vol% elastomer a new crystallization peak of PP appears, which was related to a completely dispersed PP phase[3]. Further evidence of the coexistence of continuous and dispersed PP phases is provided by the appearance of two PP crysallization peaks in *Figure 6*. From these observations the conclusion can be drawn that the compositions where the transitions take place are really at about 0.25 and 0.8 volume fraction EPDM content and that dispersed morphology results in special crystallization and melting phenomena. The exact nature of these phenomena and their relation to dispersed two-phase morphology must be further investigated. Melt viscosity of the elastomer influences somewhat the size of the different morphological units, but otherwise no differences could be detected between the effect of the elastomers, i.e. between statistical and block copolymers. The inherent inhomogeneous structure of the block copolymers does not seem to influence the overall dispersed morphology of the blends.

Scanning electron micrographs of fracture surfaces show the general characteristics of a dispersed blend morphology. In the composition range 0–0.8 volume fraction EPDM, additional information could not be obtained on the structure of the blends by this method and no difference could be observed between statistical and block copolymers. At and above 80% EPDM content, however, distinct differences were detected between the two kinds of elastomer. In a statistical copolymer matrix, PP can be found as finely dispersed droplets (*Figure 11*). In the block copolymer, however, PP forms large islands (*Figure 12*). These contain some smaller elastomer particles, shown by the small craters of dissolved EPDM on the surface of the islands (*Figure 13*). The size of the islands does not depend on the type of the elastomer; only their size distribution seems to differ somewhat in the blends prepared with the two different block copolymers (*Figure 14*).

On the basis of the available information it is difficult to explain unambiguously the formation of this

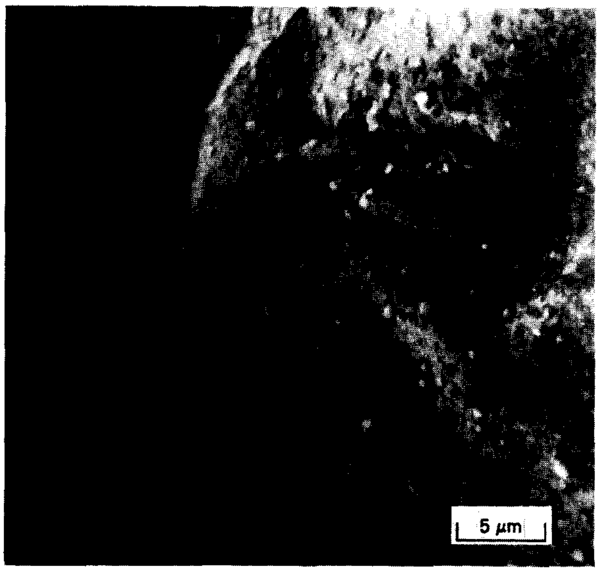

Figure 11 Finely dispersed PP droplets in a statistical copolymer (AP 541) matrix. Composition: 20/80 vol% PP/EPDM (SEM)

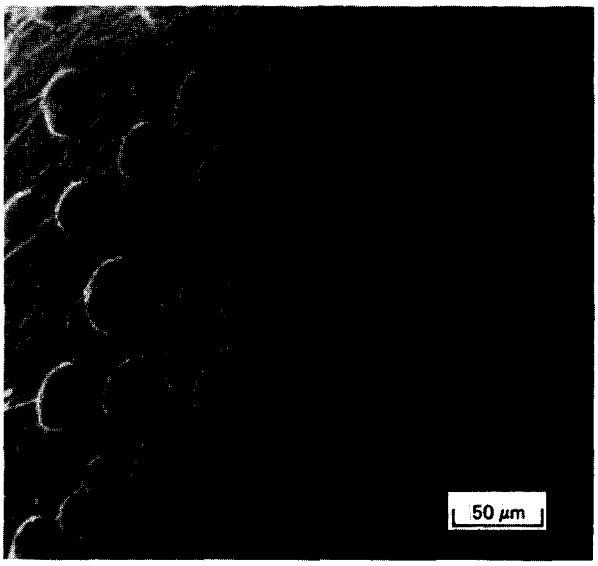

Figure 12 PP islands in a block EPDM (AP 147) copolymer matrix. Composition: 20/80 vol% PP/EPDM (SEM)

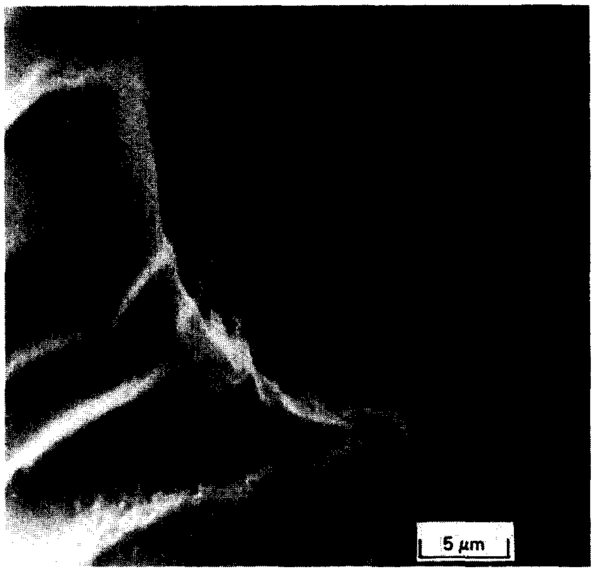

Figure 13 Small EPDM inclusions of the PP islands in a PP/EPDM block copolymer (AP 147) blend. Composition: 20/80 vol% PP/EPDM (SEM)

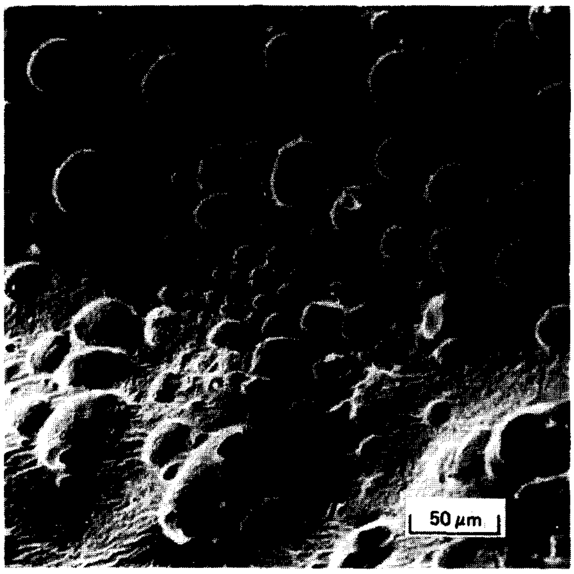

Figure 14 Dispersed PP islands in a block EPDM copolymer (AP 447) matrix of 20/80 vol% PP/EPDM composition (SEM)

morphology and the differences between statistical and block copolymers. The explanation obviously lies in the inherent heterogeneous structure of the block copolymer. This heterogeneity results in the melting peak of about 52°C. However, strong interactions between crystalline phases can hardly be expected since crystallization and melting behaviour of the two components and especially that of the elastomer were only slightly affected by the blending. Also, the two elastomers had the same effect on these properties of PP. According to *Table 1*, only the Mooney viscosities of the two block copolymers differ significantly. But AP 447 has higher viscosity, resulting in increased shear stress, which consequently should result in a finer dispersion of PP.

The only explanation found is that the small-scale crystallinity of block EPDM together with a strong interaction of its amorphous phase with that of PP gives rise to the different behaviour of the blends prepared with the statistical and block copolymers. It was shown earlier that both in EPR and EPDM block copolymers and in PP/EPDM/PE blends a special phase structure can develop. In these multiphase systems, EP elastomer phase[30] (truly random copolymer fraction in the block EPDM) or EPDM[10,31–33] surrounds the minor component and these morphological units are dispersed in the major component forming the continuous matrix. Thus, in our block copolymers, these morphological units can exist in two forms: in the EPDM matrix, the phases are organized as small PP aggregates surrounded by an EP layer and dispersed in a matrix of PE blocks, i.e. PE(EP(PP)), while in PP islands PP(EP(PE)) structure can be found. In the latter structure EPDM, similarly to a detergent or a compatibilizer, can stabilize the dispersed PP islands. The differences between the effects of the two block copolymers might originate from their different molecular structures, which result in different extents of phase separation and thus interaction between the components.

CONCLUSIONS

Investigation of PP/EPDM blends in the entire composition range revealed that as an effect of blending there are only slight changes in the crystalline structure of PP in blends quickly cooled from the melt. Under crystallization conditions which are closer to equilibrium, EPDM seems to promote the formation of hexagonal β modification of PP in the composition range 5–50 vol% EPDM. About 80 vol%, the crystallization process of PP changes, crystallization rate decreases and supercooling increases. Block and statistical EPDM copolymers have similar effects on the crystalline structure, melting and crysallization properties of PP. EPDM block copolymers have some structural organization of their own, which appears as a melting endotherm at about 52°C.

In the two-phase dispersed morphology of the blends, three main structures can be distinguished as a function of composition: (1) continuous PP phase with dispersed EPDM; (2) an intermediate, transitional structure of which IPN is a particular and rarely attainable case; (3) continuous EPDM phase containing dispersed PP. Block and statistical copolymers show differences only above 80 vol% EPDM content, where PP is finely dispersed in statistical copolymers and forms large islands in block copolymers. In such blends, the appearance of these islands shows increased interaction between the amorphous phases of the components, i.e. between PP and EPDM.

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