

# Effect of multiple morphology on the properties of polypropylene/ethylene-propylene-diene terpolymer blends

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(Received 19 September 1988; revised 19 December 1988; accepted 16 January 1989)

Dynamic mechanical, tensile and impact properties of polypropylene/ethylene-propylene-diene terpolymer (PP/EPDM) blends were investigated in the entire composition range. The composition dependence of the properties reflects the changes of the structure – determined earlier by direct morphological investigations – from a continuous PP phase through a transitional morphology to a continuous elastomer phase at high EPDM content. In the latter composition range, dispersed PP shows greater affinity towards block EPDM than towards statistical copolymer, which results in improved tensile failure properties and better structural stability of the block-copolymer-containing blends.

(Keywords: polypropylene; EPDM rubber; blends; morphology; mechanical properties)

## INTRODUCTION

Because of its poor low temperature impact strength, polypropylene (PP) is often modified by elastomers. Ethylene-propylene-diene (EPDM) terpolymer has proved to be one of the most effective impact modifiers for PP. PP/EPDM blends of low EPDM content, i.e. impact modified PP, have been widely investigated<sup>1-9</sup>. Less, and more contradictory, information is available on the structure and properties of these blends at intermediate composition ranges, where both phase inversion<sup>10-12</sup> and interpenetrating network (IPN) structure<sup>13-15</sup> were reported. Conclusions on the composition dependence of the structure can be deduced directly from morphological investigations or indirectly from changes in the properties of the blends. Both methods have their advantages and disadvantages, and conclusions drawn from them are often contradictory.

In an earlier publication<sup>16</sup> we reported our results on direct morphological investigations of PP/EPDM blends in the entire composition range. We established that blending has only a slight effect on the crystal structure of PP: its melting and crystallization behaviour change only above 80 vol% EPDM. Three types of dispersed morphology were observed at different compositions, involving two structural transitions. Blends of PP prepared with statistical or block copolymers show morphological differences in the case of a continuous EPDM phase, which are the result of the different inherent structure of the copolymers. Block EPDM has a multiphase morphology of its own.

In the present paper the rheological and mechanical properties of the investigated blends are reported. An attempt is made to correlate the results of direct morphological studies with the properties. Special attention is paid to the question of phase inversion *versus* IPN structure and to the observed differences between block and statistical EPDM copolymers.

## EXPERIMENTAL

Materials and blend preparation were described in detail in a previous publication<sup>16</sup>. Rheological behaviour of the blends was evaluated on the basis of recorded torque *versus* time and melt temperature *versus* time curves. Torque, proportional to melt viscosity<sup>17,18</sup>, was determined at 190°C. The method of Goodrich and Porter<sup>17</sup> was used to determine flow activation energy of the blends.

Tensile tests were carried out on an FPZ 10 universal testing machine at 5 mm min<sup>-1</sup> cross-head speed. The specimens for the tests were cut from the 1 mm thick compression moulded plates also used for the morphological studies<sup>16</sup>. Young's modulus, tensile yield stress, tensile strength and elongation at break were determined from the recorded force *versus* elongation curves. Impact strength was measured on notched Charpy specimens of 4 × 6 × 50 mm. Dynamic mechanical spectroscopy was carried out on a DuPont 980 dynamic mechanical analyser (DMA). Measurements were made at 5°C min<sup>-1</sup> heating rate between -150 and +150°C. Oscillation amplitude was 0.2 mm.

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## RESULTS

It is widely accepted that mechanical properties reflect the morphology of polymer blends. Their composition dependence usually gives additional information on the morphology: it helps to determine the composition range of phase inversion or to decide on the possible existence of an IPN structure. If in PP/EPDM blends phase inversion takes place, properties must show one abrupt change at a well defined narrow composition range<sup>10,11</sup>. For IPN two transitions can be expected, one from continuous PP/dispersed EPDM to IPN and the other from IPN to continuous EPDM/dispersed PP structure.

The torque, proportional to the viscosity of the blends, does not show any transition as a function of the composition, but increases continuously with increasing EPDM content (Figure 1). Blend viscosity seems to be governed by the viscosity and volume fraction of the elastomer. Statistical and block copolymers have a similar effect on the viscosity of the blend.

Contrary to melt viscosity, flow activation energy shows two transitions, indicating IPN structure (Figure 2). These results, however, must be treated very carefully. Determination of the flow activation energy is difficult and it can be measured only with considerable experimental error. Although for thermoplastics the method gives the same values as determined in a capillary viscometer<sup>17</sup>, in blends the results might be biased by the homogenization process during which the size of the dispersed morphological units changes. The observed tendency, however, is clear and the composition range of the transitions can be easily defined. Because of the considerable experimental error, possible differences between the effect of the statistical and block copolymers cannot be distinguished.

Young's modulus, as expected, decreases with increasing elastomer content (Figure 3). It is difficult to detect any particular changes or regions on the curve. There is no noticeable difference between the effect of block and statistical copolymers either. To facilitate the evaluation of the results and the determination of a possible phase

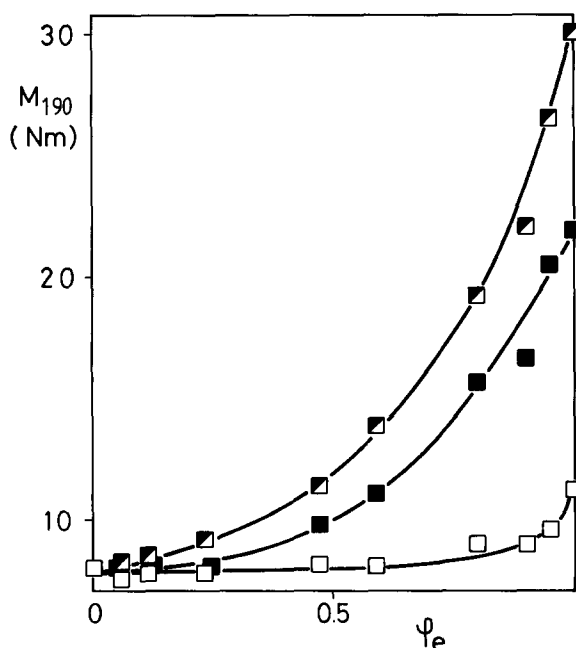


Figure 1 Composition dependence of the torque (proportional to melt viscosity) measured at 190°C: □, AP 251; ■, AP 341; ■, AP 541

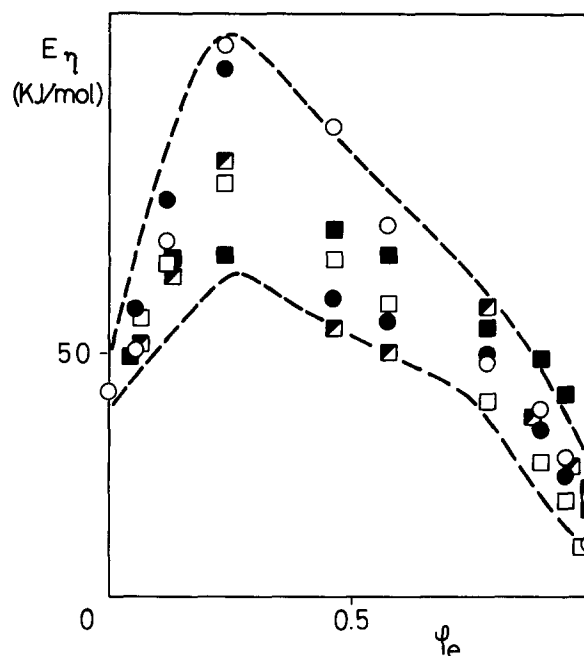


Figure 2 Flow activation energy of PP/EPDM blends as a function of EPDM volume fraction: ○, AP 147; ●, AP 447; □, AP 251; ■, AP 341; ■, 541

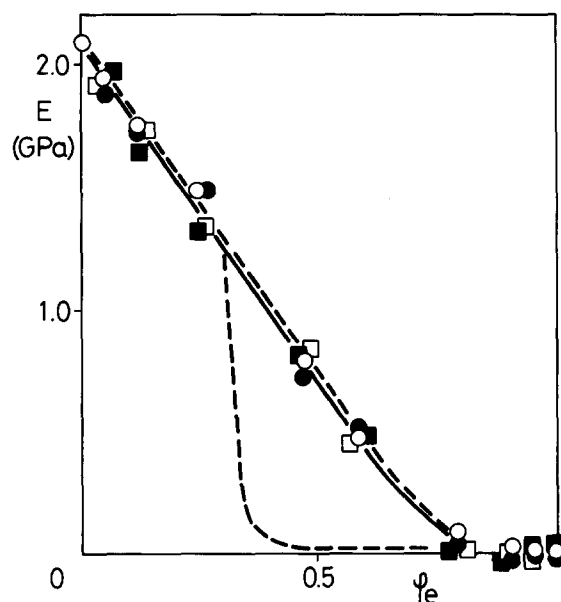


Figure 3 Young's modulus of PP/EPDM blends plotted against composition. ○, AP 147; ●, AP 447; □, AP 251; ■, AP 541; -----, Lewis-Nielsen equation

inversion, moduli were also calculated by the Lewis-Nielsen equation<sup>19</sup>, which has the form:

$$G = G_p(1 - B\psi\phi_e)/(1 + AB\phi_e) \quad (1)$$

for a continuous PP phase. Here  $A = (8 - 10\nu_p)/(7 - 5\nu_p)$ ,  $G$  and  $G_p$  are the shear moduli of the blend and the continuous PP phase, respectively,  $\nu_p$  is the Poisson ratio of PP and  $\phi_e$  is the volume fraction of the dispersed elastomer in the blend. For a continuous elastomer phase the equation takes the form:

$$G = G_e(1 + AB\phi_p)/(1 - B\psi\phi_p) \quad (2)$$

Here  $A = (7 - 5\nu_e)/(8 - 10\nu_e)$ ,  $G_e$  is the shear modulus of the elastomer,  $\nu_e$  its Poisson ratio and  $\phi_p$  is the volume

fraction of the dispersed PP.  $B$  takes the same form in both cases:

$$B = (G_p/G_e - 1)/(G_p/G_e + A)$$

$\psi$  is a correction function which reflects the influence of the maximum packing fraction of the dispersed phase,  $\phi_d^{\max}$ , and is written as

$$\psi = 1 + [(1 - \phi_d^{\max})/\phi_d^{\max}]^2 \phi_d$$

where  $\phi_d$  is the volume fraction of the dispersed component in the blend. The relation of the Young's and shear moduli can be expressed by the well known equation

$$E = 2G(1 + \nu) \quad (3)$$

In the calculations the following values were used for the parameters:  $E_p = 2.09$  GPa,  $E_e = 3.6$  MPa,  $\nu_p = 0.27$ ,  $\nu_e = 0.49$ ,  $\phi_d^{\max} = 0.79$  for continuous PP phase and 0.7 for continuous elastomer phase. The calculated values are plotted as broken lines in Figure 3.

A comparison of the measured and calculated values indicates phase inversion. According to these results, up to 0.8 volume fraction EPDM, polypropylene is the continuous phase, while at higher EPDM content it is the elastomer phase.

Tensile yield stress of the blends decreases monotonously with increasing elastomer content (Figure 4). Above a certain EPDM content, distinct yield stress cannot be defined, since the elastomer does not show the characteristic yielding phenomena of the thermoplastics. Thus, the disappearance of the maximum in the load versus deformation curve can be regarded as an indication of phase inversion.

The two types of copolymer show slight, but characteristic differences. The yield stress of the two block-copolymer-containing blends is always larger than that of the blends with statistical copolymers. In Figure 4 the yield stresses calculated by the Nicolais-Narkis equation<sup>20</sup> are also plotted. This equation

$$\sigma_y = \sigma_{y0}(1 - 1.21 \phi_d^{2/3}) \quad (4)$$

where  $\sigma_y$  and  $\sigma_{y0}$  are the yield stresses of the blend and

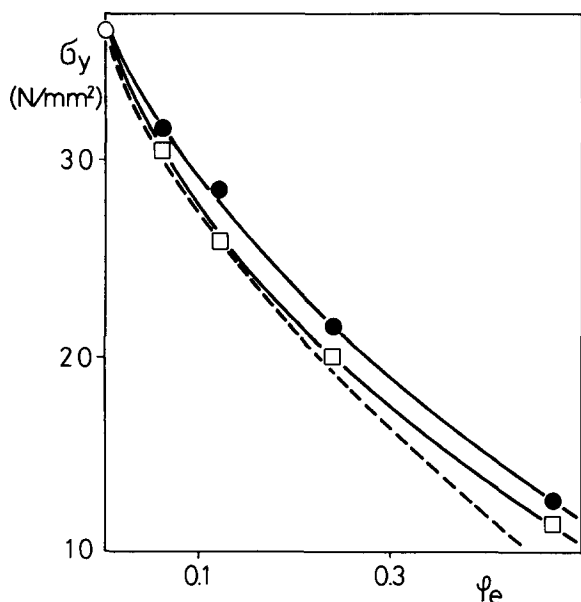


Figure 4 Composition dependence of the tensile yield stress of PP/EPDM blends: ●, AP 447 (block); □, AP 541 (statistical); ----, Nicolais-Narkis equation

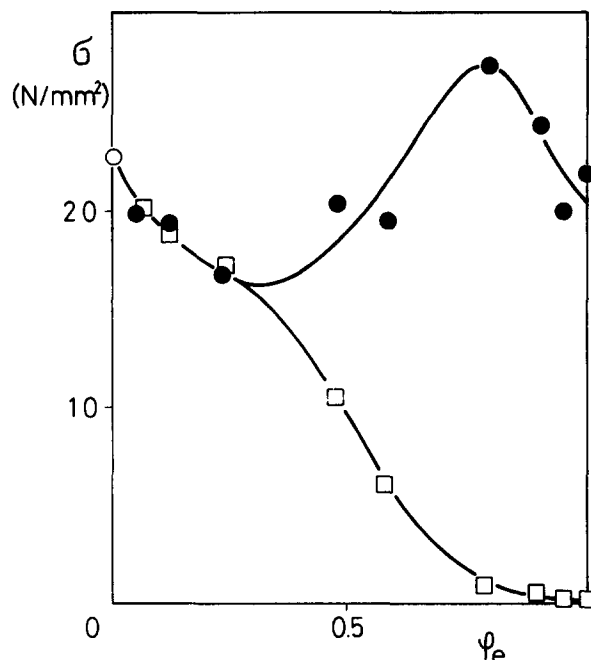


Figure 5 Tensile strength of PP/EPDM blends plotted against composition. Symbols as in Figure 4

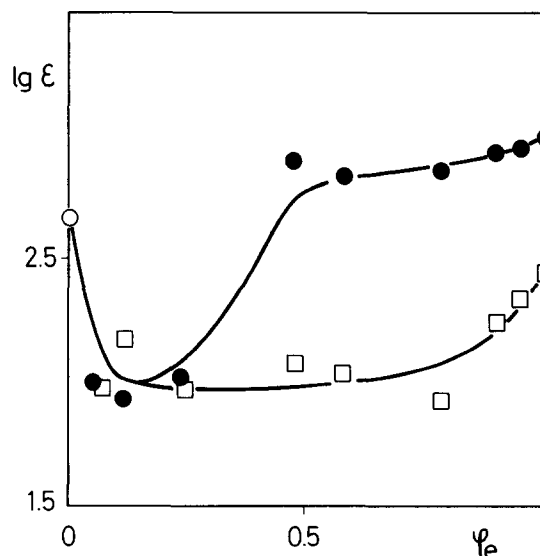


Figure 6 Elongation at break of PP/EPDM blends as a function of EPDM content. Symbols as in Figure 4

the dispersed phase, respectively, and  $\phi_d$  is the volume fraction of the dispersed component, was originally derived for filled composites. Nevertheless, it was also successfully applied to polymer blends of a dispersed morphology<sup>21,22</sup>. The equation assumes zero adhesion between the components. An analysis of the yield stresses in thermoplastic composites has shown that deviation from the zero adhesion curve can occur as an effect of increased contact surfaces and increased adhesion between the components<sup>23</sup>. In our case, the viscosity of the two elastomers is nearly the same, and therefore similar sizes of the dispersed elastomer phases can be expected. Thus the differences in the yield stresses indicate stronger adhesion between PP and block EPDM than between PP and the statistical copolymer.

Tensile strength and elongation at break show particular behaviour as a function of composition (Figures 5 and 6). In the composition dependence of these

properties two transitions can be observed indicating IPN structure. There are also significant differences between the blends prepared with block and statistical copolymers.

In Figure 7 the notched Charpy impact strength of the blends is plotted as a function of elastomer content. The impact strength increases and at about 0.25–0.3 volume fraction elastomer content the specimens stop breaking, i.e. one transition can be observed in this property. There are some differences in the effect of the elastomers, but these are much smaller than the effect of the composition. Copolymers of lower viscosity are more effective impact modifiers than those with high viscosity. This result is in accordance with data in the literature which indicate that a lower melt viscosity of the elastomer will result in smaller dispersed particle size and higher impact strength<sup>4,9</sup>. Also, statistical copolymers seem to increase the impact strength more effectively than block copolymers. This observation is also in agreement with published data<sup>24</sup>. The more rigid, phase separated

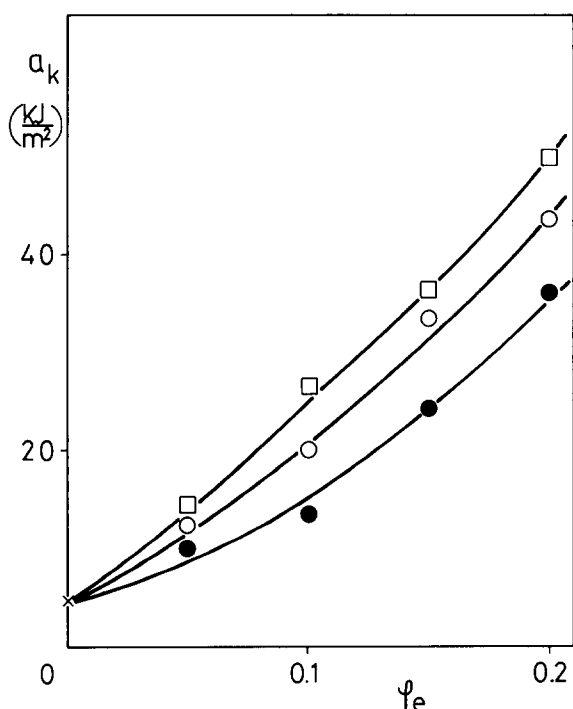


Figure 7 Notched Charpy impact strength of PP/EPDM blends as a function of blend composition: ○, AP 147; ●, AP 447 (block copolymers); □, AP 251 (statistical copolymer)

structure as well as better adhesion of block copolymers to the matrix<sup>25</sup> might be the main reason for the lower impact strength.

The above results are obviously contradictory concerning both the structure of the blends and the possible differences between copolymer types. Some properties indicate phase inversion, while others suggest IPN structure. Also, the compositions at which a property change can be observed differ from the property to property. Block and statistical copolymers influence some mechanical characteristics similarly, while their effect on other properties is different.

## DISCUSSION

### Composition dependence of the structure

The properties listed in Table 1 show significant differences from the point of view of their change as a function of composition. Some show one change and several exhibit two or more less abrupt changes in their composition dependence. It is remarkable, however, that irrespective of the number of transitions their composition range is the same, i.e. 0.25–0.3 volume fraction EPDM for the lower and  $\approx 0.8$  for the upper one. For a phase inversion, a single, rather narrow transition range could be expected. Thus the wide,  $\approx 0.5$  volume fraction, gap between the two transitions hints at the existence of two continuous phases. The question still remains why in some cases only one transition is observed or none at all.

The composition dependence of the torque, proportional to viscosity, does not show any characteristic change, but it can still give information on the possible melt morphology of the blends. Even if the components were miscible in the melt, addition of an elastomer of higher viscosity would increase blend viscosity. Flow activation energy and deviation from log additivity<sup>13</sup> indicate, however, that there is also dispersed morphology in the melt. The correlation of Van Oene<sup>26</sup>, which describes the dependence of blend viscosity for a dispersed morphology, expresses the importance of the viscosity of the dispersed phase. If the Mooney equation<sup>27</sup>

$$\ln(\eta/\eta_0) = \frac{A\phi_d}{1 - B\phi_d} \quad (5)$$

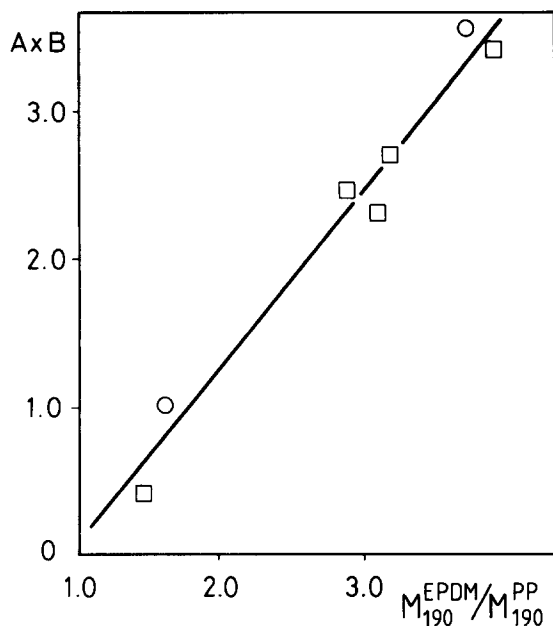
where  $\eta$  and  $\eta_0$  are the viscosities of the blend and the matrix, respectively,  $\phi_d$  is the volume fraction of the

Table 1 Phase structure indicated by blend properties, composition range(s) of property change and differences between statistical and block copolymers

Property	Indicated structure	First transition	Second transition	Differences between copolymer types
		EPDM vol. fraction		
Viscosity	?	—	—	No <sup>a</sup>
Flow activation energy	IPN	0.2	0.8	No <sup>b</sup>
Young's modulus	Phase inversion	—	0.8	No
Yield stress	Phase inversion	—	0.6–0.8	Yes
Tensile strength	IPN	0.25	0.75	Yes
Elongation at break	IPN	0.2	0.8	Yes
Notched Charpy impact strength	Phase inversion	0.30	—	Yes

<sup>a</sup> Viscosity of EPDM determines blend viscosity

<sup>b</sup> Standard deviation of determination is large, differences cannot be shown



**Figure 8** Dependence of the parameters of the Mooney equation on the relative blending torque of the elastomer:  $\circ$ , block copolymers;  $\square$ , statistical copolymers

dispersed component and  $A$  and  $B$  are constants, is fitted to the experimental data, it also reflects the same tendency. In *Figure 8*, the product of the parameters of the equation is plotted against relative melt viscosity. (We plotted the product of the parameters because in exponential correlations they are not independent of each other.) The figure demonstrates the determining role of elastomer viscosity in the melt flow of PP/EPDM blends. Thus an increase of melt viscosity of the blends can be expected with increasing elastomer content, especially since there is a continuous or semi-continuous PP phase up to high EPDM content.

Young's modulus of the blends shows only an upper transition at about 0.8 volume fraction of EPDM. Young's modulus of PP is at least two orders of magnitude larger than that of EPDM, and thus it dominates the modulus of the blend as long as there is a continuous or semi-continuous PP phase. Similarly, PP having higher strength and a definite yield stress is the load-bearing component in the deformation process: as long as it is continuous a yield stress will be detected. Note, however, that because of the larger deformation involved in the yielding process, the transition moved to a lower composition range (0.6–0.7 volume fraction EPDM). Semi-continuity of PP at higher EPDM content obviously does not suffice to resist higher loads and deformation. This further corroborates our assumption that no regular IPN, but a transitional structure, exists in these blends, i.e. areas with continuous PP phase containing dispersed EPDM and vice versa.

Contrary to modulus and yield stress, impact strength of the blends is not determined by the component of high strength, but by the one with better energy absorption capability. Therefore, as soon as EPDM is continuous or even partially continuous, cracks are arrested and the specimens do not break. The composition range where this occurs is at 0.25–0.3 volume fraction EPDM, i.e. the transition is observed at low EPDM content.

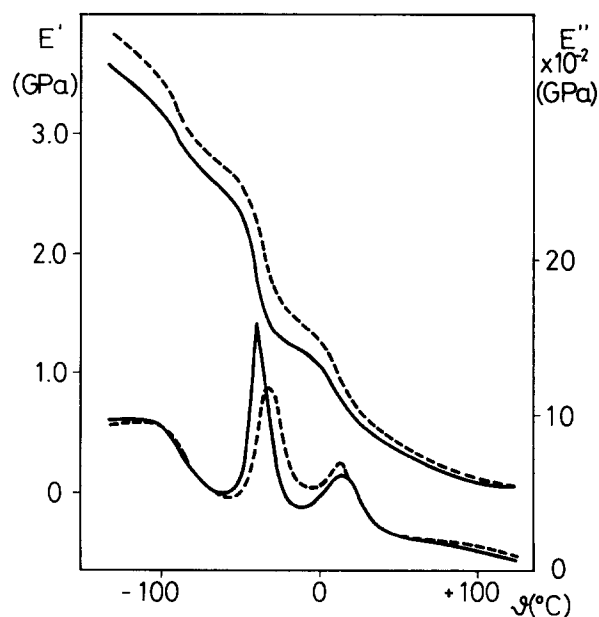
The results presented and the above considerations thus prove that there is close correlation between the

structure and properties of PP/EPDM blends. The properties of the blend reflect the dispersed morphology described in our earlier paper<sup>16</sup> on the grounds of direct morphological investigations. Since under different deformation and loading conditions, the role and significance of the two components is different, great care must be taken, when we want to draw conclusions about the structure on the grounds of the composition dependence of a single property.

#### Comparison of statistical and block copolymers

Similarly to the composition dependence of the properties, in *Table 1*, contradictions can be found concerning the effect of block and statistical copolymers. Young's moduli of blends prepared with the different kinds of elastomer do not show any differences; yield stress and impact strength show slight differences, while failure properties differ widely. In spite of the fact that the two types of EPDM copolymer have a similar effect on the melting and crystallization characteristics of PP, significant differences were observed in the morphology of their blends above 80 vol% EPDM content. From direct morphological studies we concluded that these differences are caused by an increased interaction of the amorphous phases of block EPDM and PP.

This assumption, however, is corroborated by the results of the dynamic mechanical analysis (DMA). According to the DMA spectra of the blends containing different copolymers, especially significant differences can be observed in the EP glass transition peak of the elastomers (*Figure 9*). For the block copolymers this peak is much broader and is situated at a higher temperature than that of the statistical copolymers. In blends prepared with block copolymers, the PP relaxation peak also shifts slightly to lower temperatures. These differences are the consequences of the phase separated internal structure of block EPDM, resulting in hindered EP segment movement on the one hand and better interaction with PP on the other. The effect of this better interaction, i.e. adhesion of the components, was observed in the



**Figure 9** DMA relaxation spectra of PP/EPDM blends containing 47 vol% elastomer: —, AP 251 (statistical copolymer); ---, AP 147 (block copolymer)

**Table 2** EP glass transition peak temperatures and copolymer composition of different EPDM copolymers; and failure properties of 80 vol% elastomer-containing PP/EPDM blends

Trade name of copolymer	Type	EP glass transition peak temperature (°C)	Ethylene content (mol%)	$\sigma_{0.8}$ (N mm <sup>-2</sup> )	$\epsilon_{0.8}$ (%)
Buna AP 251	Statistical	-36.5	55	0.6	90
Buna AP 541	Statistical	-37.5	60	0.6	85
Buna AP 147	Block	-27.0	75	3.8	1012
Buna AP 447	Block	-23.0	72	27.5	739



**Figure 10** Photographs showing the phase structure of PP/EPDM blends after 6 months storage: (a) statistical copolymer, coalescence of EPDM droplets; (b) block copolymer, stable structure

increased tensile yield stress and decreased impact strength values as well.

The differences in the interaction of the amorphous phases of PP and statistical or block copolymers result in the difference in the structure of their blends, characterized by finely dispersed PP droplets in the case of statistical copolymers and large islands in block copolymers. These relationships are surprisingly well represented by the EP glass transition peak temperatures. These are listed in *Table 2* together with the failure characteristics of the 80 vol% EPDM-containing blends, where the largest differences were observed. Molecular structure of EPDM copolymers seems to determine blend structure and properties. EP glass transition peak temperatures and mechanical properties are in close

correlation and the size of the dispersed PP droplets also changes accordingly. It is large in the block copolymers (8–10  $\mu\text{m}$ ) and small in the statistical copolymers (0.5–1  $\mu\text{m}$ ).

According to the scanning electron micrographs and the mechanical properties, the large PP islands form physical crosslinks in block copolymers, significantly improving their strength and extensibility. The existence of the physical crosslinks is also proved by the structural stability of these blends. After several months of storage, statistical-copolymer-containing blends show advanced coalescence of EPDM droplets, while those prepared with block copolymers do not show any change in their structure. These differences in the structural stability of the blends are well demonstrated even by the visual observation of the compression moulded plates (*Figure 10*).

## CONCLUSIONS

Our investigations have proved that close correlation exists between the structure and properties of PP/EPDM blends. Direct morphological studies indicated and the composition dependence of various mechanical properties confirmed that there is not just a single phase inversion with increasing EPDM content. Instead, three structures can be observed in PP/EPDM blends: continuous PP phase at low (<25–30 vol%) and continuous elastomer phase at high (>80 vol%) EPDM content, and a transitional structure in between. In the latter, regions of a continuous PP phase containing dispersed EPDM particles intermix with regions of a continuous EPDM phase in which PP droplets are dispersed. In this range, composition of the blends does not alone determine the structure and properties of the blends. The molecular structure of the components and blending, as well as processing conditions, also play an important role.

Changes in the melting and crystallization characteristics of PP are brought about by the transitions in the dispersed morphology which take place with increasing EPDM content<sup>16</sup>. These changes, however, hardly influence the properties of the blends, which are determined by the prevailing dispersed structure.

Block copolymers exhibit greater affinity towards PP, resulting in the formation of a special morphology. At high EPDM content, dispersed PP forms physical crosslinks, resulting in superior failure properties in a tensile test and better structural stability.

Although close correlation has been found between structure and properties of PP/EPDM blends, evaluation of a single blend property may lead to erroneous conclusions concerning the structure.

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