

Polypropylene–rubber blends: 1. The effect of the matrix properties on the impact behaviour

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The effect of matrix properties, i.e. crystallinity and molecular weight, on the impact behaviour of polypropylene–EPDM blends was studied. The blends were made on a twin-screw extruder. The impact strength was determined as a function of temperature, using a notched Izod impact test. The matrix crystallinity was varied by varying the matrix isotacticity, and ranged from 33 to 50 wt%.

With increasing temperature the polymers show a sharp brittle–ductile transition. This brittle–ductile transition temperature (T_{bd}) shifts to higher temperatures with increasing crystallinity of the polypropylene. However, the balance of properties and the modulus– T_{bd} relationship were better with blends made with higher crystalline PP.

The matrix molecular weight was decreased by treating a high molecular weight PP–EPDM (85/15 vol%) master blend with peroxide. In this way blends were obtained with a high MFI and a small rubber particle size. The matrix MFI of the blends thus obtained ranged from 2 to 30 dg min⁻¹. With decreasing matrix molecular weight the T_{bd} increased. The peroxide treated blends exhibited a considerably lower T_{bd} than comparable blends made in the standard way with a similarly small particle size. Peroxide treatment of a master blend is an effective method of preparing blends with a high MFI, small particle size and good ductility. © 1998 Elsevier Science Ltd. All rights reserved

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INTRODUCTION

Polypropylene (PP) is a semi-crystalline polymer with very interesting mechanical and thermal properties, but its toughness, and in particular its notched toughness, is not sufficient for application as an engineering plastic. Polypropylene shows a clear brittle–ductile transition with increasing temperature under notched impact conditions¹. This transition is seen as a sharp increase in the impact strength/temperature curve, and may be described as a competition between the yield and the fracture stress². With increasing temperature the yield stress drops below the fracture stress and the fracture type changes from brittle to ductile. The brittle–ductile transition of polypropylene is affected by its material properties such as molecular weight and crystallinity^{1,3}. With increasing molecular weight and decreasing crystallinity the temperature at which the brittle–ductile transition occurs (T_{bd}) decreases^{1,3}. Increasing the crystallinity increases the yield stress and decreases the fracture strain^{1,3}. Decreasing the molecular weight does not affect the yield stress but decreases the fracture stress and the fracture strain¹.

By adding a rubber phase the ductility of PP can be enhanced and the T_{bd} can be shifted towards lower temperatures⁴. The rubber phase has two functions: it relieves the volume strain by cavitation and, after cavitation, it acts as a stress concentrator. Cavitation of the rubber particles decreases the von Mises yield stress^{5,6}. This decrease seems to be the dominating mechanism in the blends.

PP with higher crystallinity has poorer ductility. To

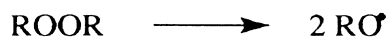
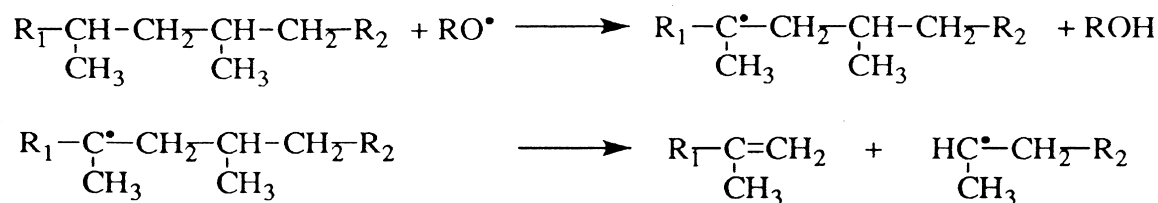
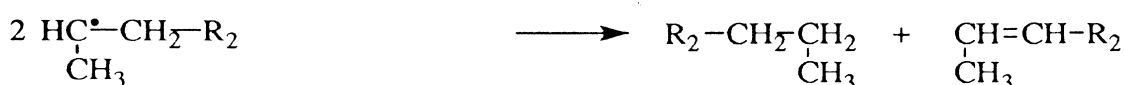
improve the ductility by adding a rubber seems to be a logical step. However, by adding rubber the tensile properties such as modulus and yield stress decrease and, as more rubber is needed for the higher crystalline material, it is a question whether in the end a better balance of properties is obtained.

In the blends, attempts to establish the effect of the matrix molecular weight are hampered by the problem of maintaining a constant particle size at varying molecular weight. The rubber particle size has an effect on the ductility⁷. A constant particle size with decreasing matrix molecular weight can be achieved by changing the molecular weight of the rubber phase⁸. An alternative method may be to treat a master blend with peroxide during extrusion, so that the peroxide degrades the polypropylene matrix. Peroxide treatment is often used for controlled degradation of polypropylene^{9–12}. The peroxide radicals preferentially abstract the tertiary hydrogen atoms of the main chain and cause chain scission. A simplified reaction scheme is given in *Figure 1*. As a result of peroxide degradation, the average molecular weight decreases and the molecular weight distribution narrows⁹. The melt flow index (MFI) of degraded polypropylene increases linearly with the peroxide concentration^{9–11}. Tzoganakis *et al.*¹² showed that peroxide degradation of polypropylene had little effect on the modulus, i.e. little effect on the crystallinity.

We studied the effect of the matrix crystallinity and the matrix molecular weight on the brittle–ductile transition of polypropylene–EPDM blends. The matrix crystallinity was studied with polypropylenes having differing isotacticity. The matrix molecular weight was lowered by treating a master blend with peroxide.

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Initiation*Hydrogen Abstraction and Chain Scission**Termination***Figure 1** Simplified reaction scheme for peroxide degradation of polypropylene (according to Xanthos¹¹)**Table 1** Starting materials

Polypropylene						
	MFI ^a (dg min ⁻¹)	Density (kg m ⁻³)	Modulus (MPa)	Yield stress (MPa)	M_w^b (kg mol ⁻¹)	M_w/M_n^b
Novolen 1300L	5	898	650	21		
Eltex P HCS 580	5	915	2075	40		
Vestolen P2000	37.5				164	4.7
Vestolen P6000	5.5				316	6.0
Vestolen P7000	2.4				362	5.7
Vestolen P8000	1.1				427	5.2
Vestolen P9000	0.3	901	1400	34	657	8.4
EPDM						
	Mooney ^c	Density (kg m ⁻³)	Ethylene content (wt%)	Termonomer (wt%)		
Keltan 320	33	860	55	DCPD (4.5)		
Keltan 820	74	860	55	DCPD (4.5)		
Peroxide						
	Molecular weight (g mol ⁻¹)	Density (kg m ⁻³)	Active O ₂ content (%)	Viscosity (MPa s)		
Trigonox 101	290.4	870	11.02	6.4		

All data taken from data sheets¹⁴⁻¹⁸, except where mentioned otherwise

^a230°C, 21.6 N

^bPersonal communication, Vestolen GmbH

^cML (1 + 4), 125°C

MATRIX CRYSTALLINITY*Experimental*

The materials used included a low isotactic (Novolen 1300 L, BASF) and a high isotactic polypropylene (Eltex PHCS 580, Solvay) with a similar MFI, and an EPDM elastomer (Keltan 820, DSM). The materials were kindly supplied by the suppliers and used as delivered. *Table 1* lists the pertinent material specifications.

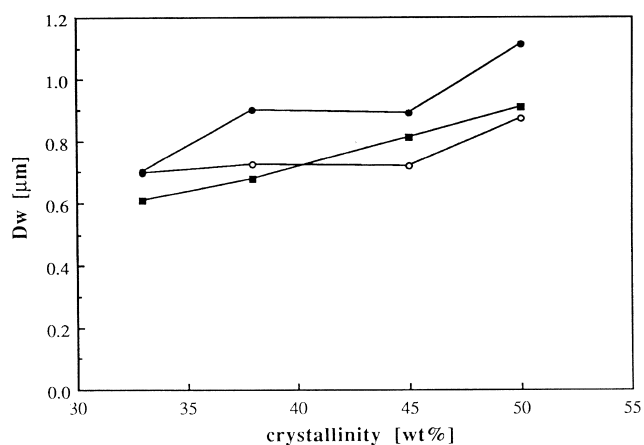
Polypropylene-EPDM blends with PP of differing isotacticity were prepared in a three-step extrusion process. First the low and high isotactic polypropylene were mixed, followed by a step in which 30 vol% EPDM was added to

the mixture. In the final step the 30 vol% blends were diluted to blends containing 30, 20 and 10 vol% EPDM. The mixing was carried out on a co-rotating Berstorff twin-screw extruder. The code for the blends is XXEYY; XX stands for the rubber content and YY represents the Eltex content. From the blends, rectangular bars and dumbbell-shaped specimens were injection moulded on a 221-55-250 Arburg Allrounder injection moulding machine.

Samples for particle size analysis were cut from the core of the bars. The surfaces were cryotomed, etched and sputter-coated with a thin gold layer before SEM micrographs were taken. The particle size was determined manually, using a graphic tablet. The weighted average

Table 2 Crystallinity of the pure matrices (data after Van der Wal *et al.*³)

Matrices	X_c (wt%)
E0	31
E33	38
E67	43
E100	53

**Figure 2** Weighted average particle size *versus* matrix crystallinity for the blends. Rubber content (vol%): ● 10, ■ 20, ○ 30

particle size (D_w) was determined. These averages were defined as

$$D_w = \frac{\sum n_i d_i^2}{\sum n_i d_i} \quad (1)$$

Tensile tests were carried out on the dumbbell-shaped specimens (ISO R527-1, $10 \times 3 \times 115$ mm) with an Instron tensile machine at 0.5 min^{-1} . This tensile test was performed six times. Notched Izod impact tests were carried out on rectangular bars (ISO 180/1A, $74 \times 10 \times 4$ mm) with a milled single-edge 45° V-shaped notch (tip radius 0.25 mm, depth 2 mm), using a Zwick pendulum equipped with a 4 J hammer. To vary the test temperature, the specimens were placed in a thermostatic bath. All measurements were performed five times.

Results and discussion

The matrix crystallinity was varied by taking a low and high isotactic polypropylene and mixtures thereof. The

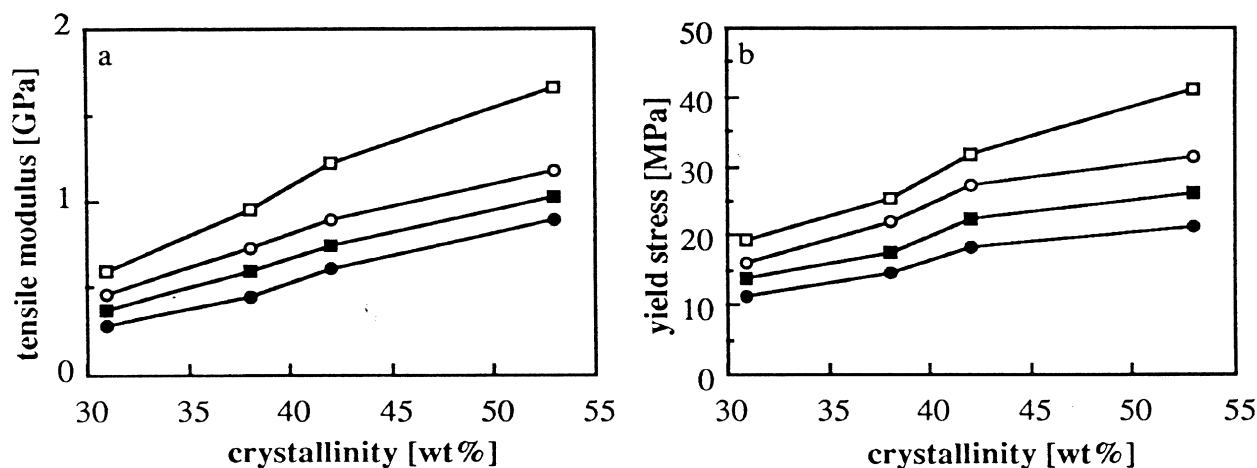
crystallinity of the matrices is listed in *Table 2*. The rubber content has little or no effect on the matrix crystallinity⁴; therefore, the matrix crystallinity was assumed to be equal to the crystallinity of the pure matrix.

The particle size of the blends as a function of the matrix crystallinity is shown in *Figure 2*. The weighted average particle size (D_w) increases with matrix crystallinity and rubber content. The increase in particle size with increasing matrix crystallinity suggests that under the blending and injection moulding conditions the melt viscosity of the matrix decreases with increasing Eltex content, despite the fact that the starting polypropylenes have the same MFI.

The modulus and the yield stress *versus* matrix crystallinity are shown in *Figure 3*. The modulus and the yield stress increase with increasing matrix crystallinity and decrease with rubber content. The effect of crystallinity is somewhat stronger for the PP than for the blends.

The notched Izod impact strength *versus* temperature curve for the blends is shown in *Figure 4*. The impact strength at low temperatures is relatively low ($5\text{--}10 \text{ kJ m}^{-2}$) and the fracture is brittle. At high temperatures the impact strength is very high ($20\text{--}40 \text{ kJ m}^{-2}$) and the fracture is ductile. The transition from brittle to ductile is sharp (stepwise)⁴.

The brittle–ductile transition temperature (T_{bd}) was taken as the intersection of the tangent line of the sharp increase with the tangent line of the linear part in the impact strength curve prior to the sharp increase. It should be noted that this T_{bd} is not a material property but depends on the sample geometry, test set-up etc. The T_{bd} of the blends as a function of the matrix crystallinity is shown in *Figure 5a*. As the blends studied were not of constant particle size (*Figure 2*), and as the particle size has an effect on the Izod impact strength¹³, a correction is made for the variation in particle size (*Figure 5b*). The particle sizes (D_w) were normalized to $0.60 \text{ }\mu\text{m}$. As a result of the normalization the T_{bd} of the larger particle sizes shifts to lower temperatures. The shift due to the larger particles is only 5°C . The effect of increasing crystallinity on the PP and the blends is an appreciable increase in T_{bd} . The increase in crystallinity ($31 \rightarrow 53\%$) gives, for PP, an upward shift of T_{bd} of 70°C and, for the blends, $40\text{--}60^\circ\text{C}$. The 30 vol% blends show a lower limit for T_{bd} at -40°C . This lower limit may be imposed by the glass transition temperature of the EPDM phase ($T_g = -54^\circ\text{C}$, 1 Hz)⁴. The effect of crystallinity is thought to be an effect of the change of yield stress

**Figure 3** Tensile modulus (a) and yield stress (b) at 50 mm min^{-1} *versus* matrix crystallinity for the blends. Rubber content (vol%): □ 0, ○ 10, ■ 20, ● 30

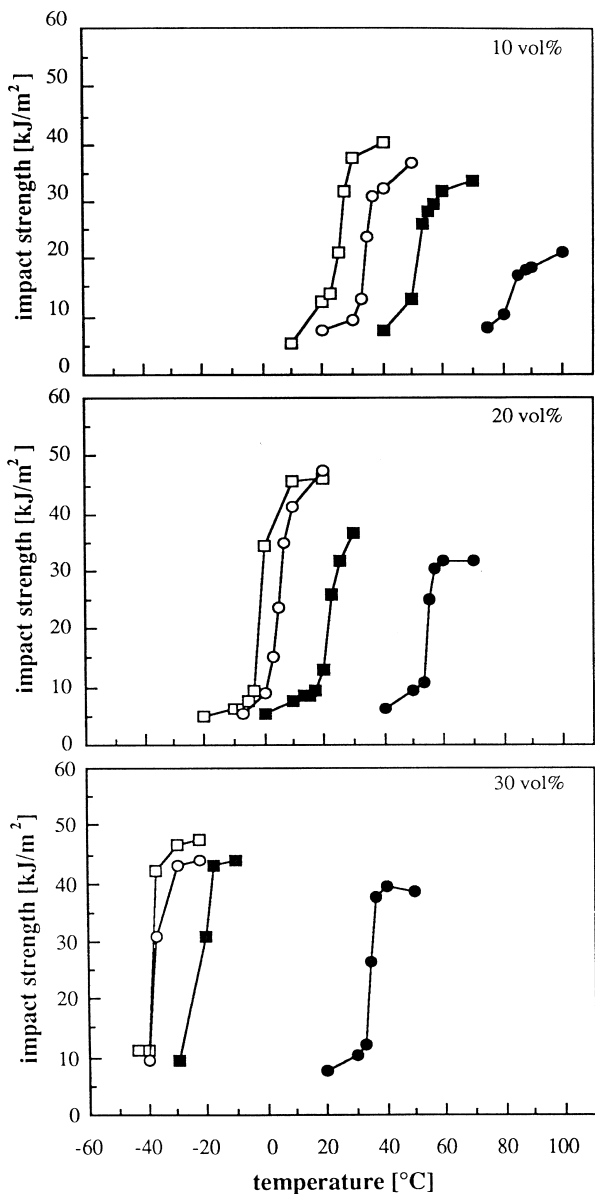


Figure 4 Notched Izod impact strength versus temperature for the blends. Matrix crystallinity (wt%): □ 31, ○ 38, ■ 43, ● 53

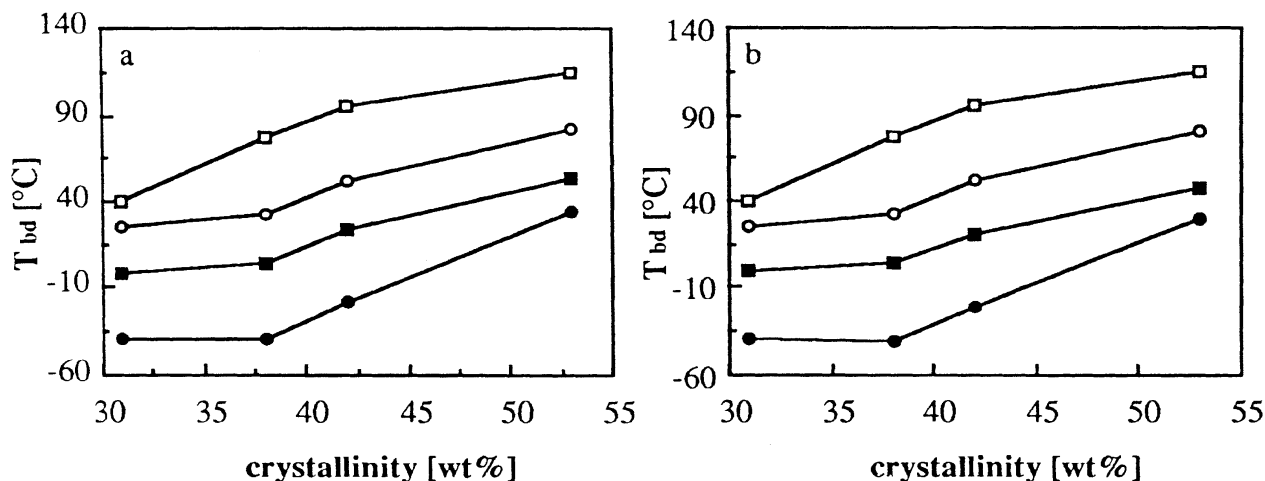


Figure 5 Brittle/ductile transition temperature (T_{bd}) versus matrix crystallinity for the blends at (a) varying particle size, (b) constant particle size ($D_w = 0.4 \mu\text{m}$). Rubber content (vol%): ■ 0, ○ 10, ■ 20, ● 30

(Figure 3)³. What is noteworthy is that at low temperatures, below the T_g of the PP, the crystallinity still has an effect, although at these temperatures the modulus and yield stress have little dependence on crystallinity. Possibly this is due to adiabatic heating of the deformation layer during fracture¹³.

Of practical interest is the balance of properties. It is important to have a high toughness combined with a high modulus and a high yield strength. As the more crystalline materials are less ductile, more rubber has to be added for low temperature ductility (Figure 5b). With increasing rubber content both the modulus and the yield strength decrease (Figure 3). From the above data the T_{bd} as a function of the modulus can be derived (Figure 6). The high crystalline PP has a high modulus and a high T_{bd} . With increasing rubber content the modulus and the T_{bd} are lowered. The modulus for a particular T_{bd} has a higher value for high crystalline PP. The same holds for the yield strength- T_{bd} relationship. The effect of rubber is more than a lowering of the yield stress. Blending with a high crystalline PP has a clear advantage in the balance of properties.

MATRIX MOLECULAR WEIGHT

Experimental

PP-MFI variation. EPDM (10 vol%) was blended with a range of polypropylenes (Vestolen P series), which differ in their MFI, on the Berstorff co-rotating twin-screw extruder. The materials used were an EPDM (Keltan 820) and a series of polypropylenes with varying molecular weight (Vestolen P8000, P7000, P6000 and P5000) (Table 1). The properties of these polypropylenes are described in detail elsewhere¹. The MFI of these polypropylenes ranges from 1.1 to 10.5 dg min⁻¹ (230°C, 21.6 N).

Peroxide treated blends. In a first extrusion step, an 85/15 vol% PP-EPDM (P9000/Keltan 320) master blend was prepared. In a second extrusion step, this master blend was treated with peroxide. Both extrusion steps were performed on a Berstorff co-rotating twin-screw extruder (diameter = 25 mm, length/diameter = 33). The extrusion temperature during the peroxide treatment (220°C) was selected such that complete decomposition (>99%) of the peroxide was obtained in the shortest residence time (~30 s), based on the

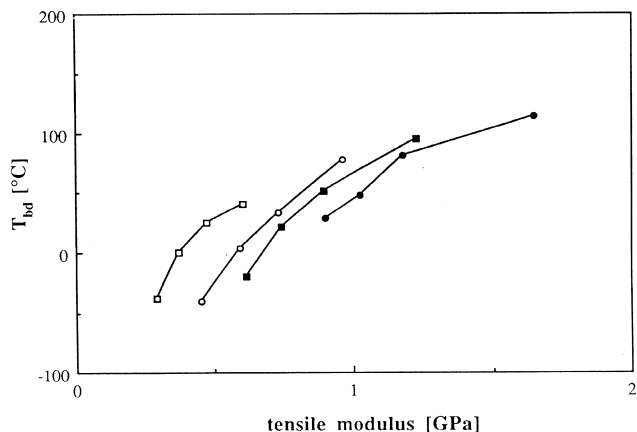


Figure 6 Relationship of tensile modulus and brittle ductile transition temperature of 15 vol% blends with varying percent crystallinity: □ 32, ○ 38, ■ 45, ● 54

decomposition kinetics of peroxide in LDPE¹³. The starting polypropylene (P9000) was subjected to the same peroxide treatment as the master blend. The materials used for the peroxide treated blends encompass a polypropylene (Vestolen P9000, Vestolen GmbH), an EPDM (Keltan 320, DSM) and a peroxide (Trigonox 101-7.5PP-cd, AKZO NOBEL). The peroxide consists of 2,5-bis(*ter*-butylperoxy)-2,5-dimethylhexane on a polypropylene carrier, with a peroxide content of 7.5 wt%. This product is used normally for the production of polypropylene of controlled rheology.

All materials were commercially available and used as delivered, and were kindly supplied by the suppliers. Table 1 lists the pertinent material specifications.

Material characterization, tensile test and notched Izod impact test are described in the previous experimental section.

Results and discussion

A series of blends with varying matrix molecular weight was prepared in two ways: by varying the starting molecular weight of the PP, and by treating a master blend with peroxide. The particle size cannot be kept constant by changing the MFI of the matrix material during blending. The objective of the blends prepared by the peroxide route is that weight-average particle size should remain constant while the MFI of the blend increases.

The effects of peroxide concentration on the MFI of PP and a PP blend are shown in Figure 7. For this method a PP was used with an MFI of 0.3 dg min⁻¹; with such low MFI PP very fine dispersions can be obtained. Blends usually have a lower MFI than the matrix polymer. The MFI of the PP and the blend increases with peroxide concentration, being stronger at higher concentrations. A linear MFI increase with peroxide concentration was reported previously⁹⁻¹¹. The slightly lower increase at low peroxide concentrations is possibly due to the presence of stabilizers. The MFI of the blend is lower over the whole concentration range. This is due to the lower MFI of the starting blend and possibly also due to the fact that a part of the peroxide is absorbed by the EPDM.

The effect of MFI on particle size is shown in Figure 8. The particle size of 'PP-MFI variation' blends increases linearly with the logarithm of the matrix MFI. Surprisingly, the particle size of 'peroxide treated' blends first increases with MFI, as with the PP-MFI blends, but at higher MFI a decrease in particle size is observed. The first increase in

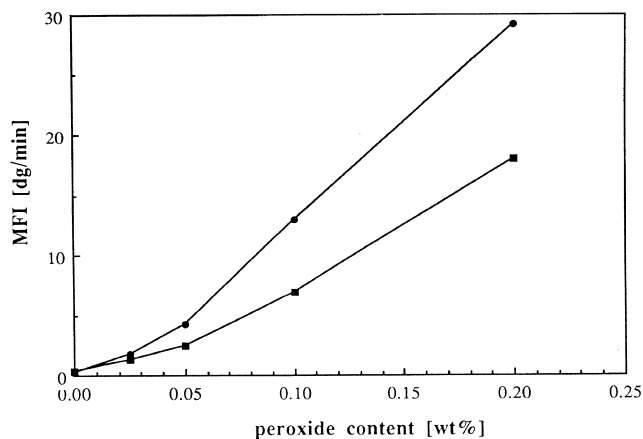


Figure 7 Effect of peroxide on MFI: ●, PP; ■, blend

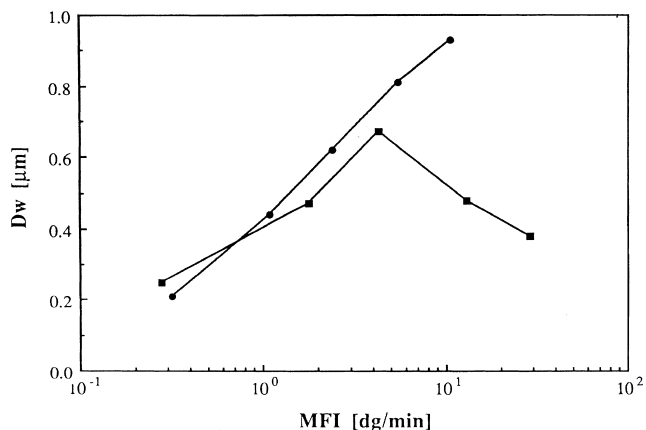


Figure 8 Weighted average particle size (D_w) as a function of MFI: ●, MFI varied; ■, peroxide treated

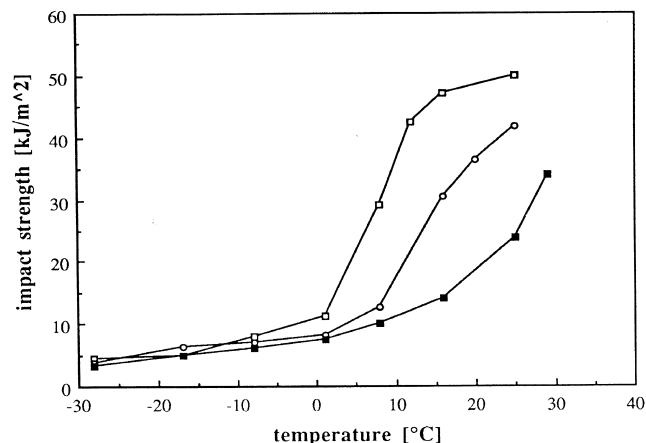


Figure 9 Notched Izod impact strength versus temperature for peroxide treated blends (15 vol%) with a D_w of approximately 0.4 μm . Matrix MFI (dg min⁻¹): □ 1.8, ○ 12.9, ■ 29.2

particle size shows that coalescence takes place and that the particle size is dependent only on the end viscosity of the matrix. The decrease in particle size with the strong peroxide treated blends indicates that here the rubber is modified. Thus, in the peroxide treated blends, the peroxide has reacted not only with the matrix. One possible side-effect is the formation of a compatibilizer by a graft reaction between a polypropylene radical and EPDM, and another

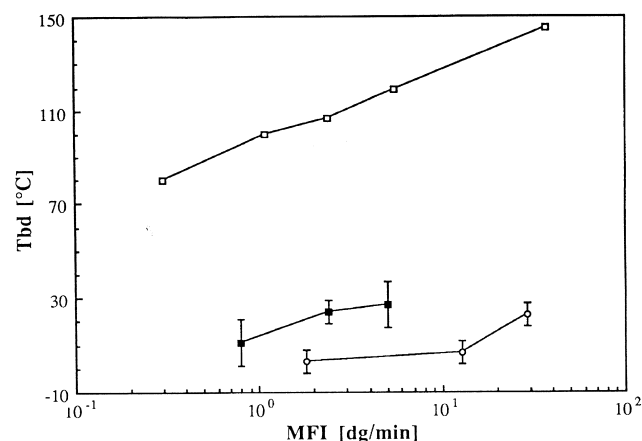


Figure 10 Influence of matrix MFI on the brittle–ductile transition temperature (T_{bd} of 15 vol% blends: \square , PP; \blacksquare , MFI varied; \circ peroxide treated)

Table 3 Control blends II (rubber content 15 vol%, $D_w = 0.4 \mu\text{m}$)

Matrix MFI ^a	Rubber type	T_{bd} (°C)
0.8	EPR	11 ± 10
2.4	EPDM	24 ± 5
5.0	EPDM	27 ± 10

^adg min⁻¹, 230°C and 21.6 N

effect is the crosslinking of the EPDM. In both cases, the blend morphology is stabilized by a reduced coalescence rate.

The impact strength was studied on samples with 15 vol% EPDM. For the peroxide treated blends three samples were taken which had a particle size (D_w) of $0.4 \mu\text{m}$. The notched Izod impact strength curves of these samples shifts to higher temperatures as the MFI is increased (Figure 9). As a measure of the impact improvement, the brittle–ductile transition temperature was taken as obtained from notched Izod measurements.

The T_{bd} for PP and the peroxide treated 15% blends decreases with MFI ($D_w \sim 0.4 \mu\text{m}$) (Figure 10). The T_{bd} of ‘PP–MFI variation’ blends ($D_w 0.40 \mu\text{m}$) increases too with MFI. This effect of MFI is probably due to a decrease in fracture strength with decreasing molecular weight.

The T_{bd} of the PP–MFI variation blends with a rubber content of 15 vol% and a D_w of $0.4 \mu\text{m}$ was derived by interpolation of previously published data^{4,7}. Data for the blends are listed in Table 3. The T_{bd} values were derived as follows.

- (1) *MFI 0.8*: by interpolation of the T_{bd} – D_w curves at 10 and 20 vol%¹³, at a D_w of $0.4 \mu\text{m}$.
- (2) *MFI 2.4*: the T_{bd} for a blend with a rubber content of 15 vol% and a D_w of approximately $0.7 \mu\text{m}$ ⁴ was converted to a D_w of $0.4 \mu\text{m}$, using the known correlation between T_{bd} and particle size¹³. This correlation was derived from an extensive study on the relation between particle size and T_{bd} for PP–EPR blends containing 5, 10 and 20 vol% and covering a particle size range from 0.5 to $4 \mu\text{m}$.
- (3) *MFI 5.0*: by interpolation of the curves shown in Figure 4 at a matrix crystallinity of 45 wt%, which is the crystallinity of a regular polypropylene³.

The T_{bd} s of these unmodified blends are slightly higher than those of the peroxide treated blends (Figure 10). Thus

the peroxide treatment not only influences the particle size but also seems to improve the impact behaviour. The T_{bd} values for PP are at a much higher level but the trend is the same. The effect of MFI on the T_{bd} is strong. The effects of peroxide treatment on the EPDM may be to stabilize the particle size by crosslinking and/or by improving the interface.

CONCLUSIONS

Increasing the matrix crystallinity increases the modulus and yield strength but decreases the impact behaviour. The effect of matrix crystallinity on the brittle–ductile transition is strong. The increase in T_{bd} in the polypropylene–EPDM blends is nearly as strong as for polypropylene. By increasing the crystallinity from 31 to 53% the T_{bd} is shifted 40–70° higher. For a particular T_{bd} , more rubber has to be added to the highly crystalline material. Of practical interest is the balance of properties, and the modulus– T_{bd} relationship is important. The higher crystalline material needs a higher rubber content for a particular T_{bd} , but it still has a higher modulus. A similar behaviour is observed for the yield strength– T_{bd} relationship. For a balance of properties there is thus a clear advantage in having a matrix material with a high crystallinity.

With decreasing matrix molecular weight the T_{bd} of the blends increases. This is probably due to a decrease in the fracture stress. In practice this effect is amplified by the fact that the particle size increases with decreasing molecular weight. At the same time, with decreasing molecular weight of the PP the rubber particle size increases and this is not wanted either. Peroxide treatment of a master blend is an effective method of preparing blends with a high MFI and a small particle size. Compared to reference blends with the same MFI and particle size, it is even the case that peroxide treated blends exhibit a significantly lower T_{bd} . With this method, blends can be made with a high MFI and a low T_{bd} . The effect of the peroxide on the rubber structure and rubber cavitation properties remains to be elucidated.

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