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# Polypropylene–rubber blends: 4. The effect of the rubber particle size on the fracture behaviour at low and high test speed

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**Abstract**

The effect of the rubber particle size and rubber content on the fracture behaviour of polypropylene–EPR blends was studied at low and high test speeds. The particle size was varied by changing the molecular weight of the EPR phase, and ranged from about 0.5 to around 4.0 μm. The fracture behaviour was determined as a function of temperature by the notched Izod impact test (high test speed) and by a tensile test on notched Izod bars at 1 mm/s (low test speed). At high test speed the brittle–ductile transition temperature ($T_{bd}$) increases with increasing particle size. At low test speed the $T_{bd}$ decreases slightly with increasing particle size. The weight average particle size gave a better correlation with the notched Izod results than the number average particle size. This suggests that the larger particles initiate the fracture more easily. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Polypropylene–rubber blends; Fracture; Rubber particle size

## 1. Introduction

Of the structural properties of blends the particle size effects has been studied only in a few instances [1–10]. It was found to be difficult to vary the particle size independent of matrix and dispersed phase properties. In polyamide–EPDM blends where the interface is formed by interfacial grafting the particles are relatively stable [2]. The influence of structural parameters are often studied with the brittle–ductile transition temperature ($T_{bd}$). At the $T_{bd}$ the fracture of a (notched) sample changes form an unstable crack propagation with a very high fracture speed (>200 m/s) to a stable crack propagation with a much lower fracture speed (<50 m/s) and this transition is accompanied by a strong increase in fracture energy. The change in fracture process is also evident from the structure of the fracture plane [11]. In the brittle region hardly any deformation can be observed while ductile fractured samples show massive stress whitening and deformation of material next to the fracture plane. The influence of particle size in polyamide–rubber blends is that with decreasing particle size the $T_{bd}$ as measured by notched Izod shifts to lower temperatures. At very low particle sizes (particles less than 50 μm) however the $T_{bd}$ shift to higher temperatures [3,4]. This has been explained as being due to the more difficult cavitation of small particles. The influence of particle size has also been studied at low test speed [6,7]. At low test speed the bd-transition was found to develop gradually and the $T_{bd}$ to be independent of particle size. The transition from brittle to ductile is now not a process which takes place over a few degrees but over 40–50°C. Thus at low test speed the toughening process proceeds differently than at high test speed.

The effect of particle size and the effect of rubber concentration for the notched Izod data of PA–EPDM blends have been combined to a single parameter, the interparticle distance (ID) [1,2]. At low test speed there is no particle size effect observed [6,7] and thus not a $T_{bd}$–ID relationship. This suggests that although there is, for the notched Izod, a good correlation of $T_{bd}$–ID this relationship probably does not have a physical meaning, unless the ID effect is only effective at higher deformation rates.

The $T_{bd}$ has been correlated with a particle size, but the particles have a size distribution. One might ask whether it is an advantage to have many small particles or does one not want to have a few large particles. This effect can be studied with samples that differ in particle size distribution. As yet this important question has not yet been answered.

In rubber toughened polypropylene, the effect of the particle size on the toughening process has only been studied under impact conditions. According to Jang et al. [8] smaller particles are more effective in this respect than

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Table 1
Starting EPRs (data according to the supplier)

| Rubber code | Ethylene content (mol%) | Intrinsic viscosity[a] (dl/g) |
|---|---|---|
| E40L | 40 | 3.4 |
| E40M | 40 | 6.9 |
| E40H | 40 | 14.9 |
| E60L | 60 | 4.3 |
| E60M | 60 | 8.0 |
| E60H | 60 | 14.1 |

[a] In decaline at 135°C.

larger particles. The authors showed that particles with a size below 0.5 μm initiate yielding, while particles with a size above 0.5 μm initiate crazes. Ramsteiner [9] demonstrated that the impact strength at −40°C increases with increasing particle size, and that crazing is the dominant mechanism at this temperature. Thus, the effect of the particle size of polypropylene seems to depend on the dominant deformation mechanism. If crazing is the mechanism, then the impact strength increases with increasing particle size. If shearbanding is the dominant mechanism, then the impact strength decreases with increasing particle size. The above mentioned studies suggest that crazing occurs in rubber toughened polypropylene. van der Wal et al. [11] studied the deformation mechanism of rubber toughened polypropylene for various test conditions and blend morphologies, using post-mortem SEM fractography. No evidence of crazing was found in their blends, neither for large particle sizes ($\gg$0.5 μm), nor at low temperatures (about −50°C). At ductile fracture, the matrix deforms by yielding. Brittle fracture merely gives rise to voids due to cavitation of the rubber particles. The $T_{bd}$ transition at high test speeds, as measured with notched Izod and with single edged notched (SEN) tensile, is a sharp and discontinuous process. At low test speeds as measured with SEN test the $T_{bd}$ is gradual [12] as was observed with the PA–EPDM system [7]. A complicating factor while explaining the effect of test speed is that the electron micrographs of the deformed material showed that the deformation at high test speeds is accompanied by the formation of a relaxation layer which suggests a thermal blunting process, which is not taking place at low speeds [13].

Wu et al. [10] varied the particle size in PP–EPDM blends by changing the extrusion conditions. They observed with decreasing particle size a decreasing $T_{bd}$, and showed that with these results a good correlation was obtained between the $T_{bd}$ and the ID. However as the particle size was changed by altering the extrusion conditions, serious matrix degradation might have occurred. The molecular weight of the matrix has a considerable effect on the $T_{bd}$ [14].

Another method of altering the particle size is to vary the molecular weight of the rubber. Several studies have demonstrated that the effect of the molecular weight of the rubber phase on the impact strength of polypropylene rubber blends is very small [15–17].

In the present paper, the effect of the particle size on the fracture behaviour of polypropylene–EPR blend is studied at low test speed (SEN tensile test 1 mm/s) and at high test speed (notched Izod impact test).

## 2. Experimental

### 2.1. Materials

The materials used include a commercial polypropylene (GE 7100, Montell; MFI 0.8 (230°C, 21.6 N)) and a series of experimental EPRs supplied by Shell (Shell Research and Technology Centre, Amsterdam, The Netherlands). Respective material properties of the EPR series are listed in Table 1. The EPRs differ in terms of molecular weight, as indicated by the different intrinsic viscosities, and in their ethylene content. The ethylene contents are comparable to that of commercial EPR grades, but the viscosities are much higher than those of commercial grades. The molecular weight of E40H is approximately $3.10^6$ g/mol, based on the relationship between the intrinsic viscosity and the molecular weight found elsewhere [18].

#### 2.1.1. Blending

The EPRs were blended with polypropylene on a Berstorff co-rotating twin screw extruder ($L/D = 33$, $D =$

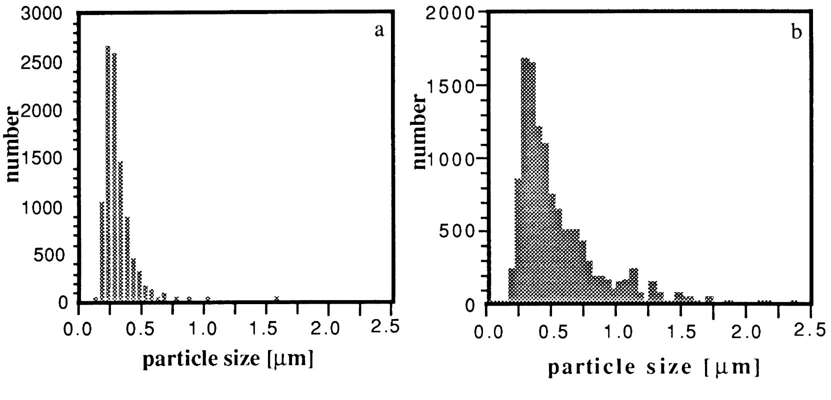

Fig. 1. Particle size distribution for PP–EPR blends: (a) E40H20; and (b) E60H20.

Table 2
Particle sizes for the PP–EPR blends

| Rubber content | Rubber type | $D_n$ (μm) | $D_w$ (μm) | $D_w/D_n$ (–) |
|---|---|---|---|---|
| 5 vol% | E40L | 0.19 | 0.28 | 1.47 |
| | E60L | 0.26 | 0.44 | 1.69 |
| | E40M | 0.59 | 0.80 | 1.36 |
| | E40H | 0.66 | 1.31 | 1.98 |
| | E60M | 0.83 | 1.38 | 1.66 |
| | E60H | 0.63 | 2.35 | 3.73 |
| 10 vol% | E40L | 0.17 | 0.33 | 1.94 |
| | E60L | 0.34 | 0.50 | 1.47 |
| | E40M | 0.74 | 1.20 | 1.62 |
| | E40H | 0.75 | 1.47 | 1.96 |
| | E60M | 0.66 | 1.59 | 2.41 |
| | E60H | 0.93 | 2.40 | 2.58 |
| 20 vol% | E40L | 0.25 | 0.37 | 1.48 |
| | E60L | 0.41 | 0.67 | 1.63 |
| | E40M | 0.65 | 1.34 | 2.06 |
| | E40H | 0.62 | 1.55 | 2.50 |
| | E60M | 0.58 | 2.08 | 3.59 |
| | E60H | 0.52 | 3.83 | 7.37 |

25 mm). A 80/20 vol% PP–EPR master blend was prepared at a barrel temperature of 230°C and a screw speed of 100 rpm. During a second extrusion step, this master blend was diluted to afford blends with EPR contents of 10 respectively 5 vol%. The second extrusion step was carried out over the last quarter of the screws to minimise the change in blend morphology. Conditions during the second extrusion step were identical to those during the first extrusion step.

### 2.1.2. Injection moulding

Rectangular bars and dumb-bell-shaped specimens were injection moulded on a 221-55-250 Arburg Allrounder injection moulding machine. The barrel temperature and the screw speed were 230°C and 300 rpm, and the mould temperature was 40°C. The geometry of the rectangular bars ($74 \times 10 \times 4$ mm$^3$) was according to ISO 180/1A and that of the dumb-bell-shaped specimen (cross-section 10 × 3) according to the ISO R527-1 specifications. The blend code consists of the rubber type listed in Table 1 plus the respective rubber content in vol%. For example E40L20 stands for a blend of polypropylene with 20 vol% E40L EPR.

## 2.2. Analysis

The particle size in the core of the bars were studied. The surface of interest is parallel to the flow direction during injection moulding. The surface was cryotomed with a diamond knife at −110°C, and then etched in *m*-xylene at 80°C for 6 h to dissolve the rubber particles. The surfaces were sputter-coated with a thin gold layer before SEM micrographs were obtained. As a result of the large particle size distribution a number of micrographs were taken at different magnifications. The film negatives from the SEM micrographs were projected onto a graphic tablet. The particle size was determined manually using the graphic tablet. The number ($D_n$) and a weight ($D_w$) average particle size was calculated. These averages were defined as

$$D_n = \frac{\sum n_i d_i}{\sum n_i}, \qquad D_w = \frac{\sum n_i d_i^2}{\sum n_i d_i}. \tag{1}$$

Dynamical mechanical analysis (DMA) was performed on the gauge section of the dumbbell-shaped specimens (50 × 10 × 3 mm) using a Myrenne ATM3 torsion pendulum. Measurements were carried out at 1 Hz at a heating rate of approximately 0.5°C/min for the E40L EPR and at a heating rate of 1.8°C/min for the blends.

## 2.3. Mechanical properties

Tensile measurements were carried out on the dumb-bell-shaped specimens (cross-section 10 × 3) according to ISO R527-1 at 1 mm/s (strain rate $10^{-2}$ s$^{-1}$).

The fracture behaviour was determined by a notched Izod impact test and a tensile test on notched bars. The tensile test on the notched bars is referred to as the single-edge notch (SEN) tensile test. The Izod notched bars ($74 \times 10 \times 4$ mm$^3$) were according to ISO 180/1A and contained a milled 45° V-shaped notch (tip radius 0.25 mm, depth 2 mm). The SEN tests were carried out on the notched Izod bars with a clamping length of 4 cm. Tests were carried out in five-fold.

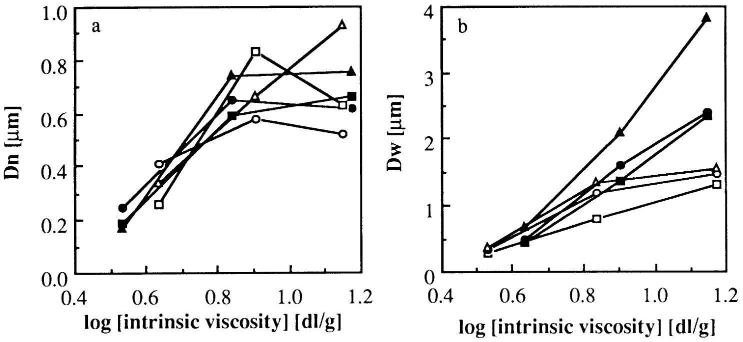

Fig. 2. Number average particles size ($D_n$) (a) and weight average particle size ($D_w$) (b) versus the intrinsic viscosity of the EPR phase for PP–EPR blends. Ethylene content EPR phase: filled symbols: 40 mol%, open symbols: 60 mol%. Rubber content (vol%): ■ and □, 5; ▲ and △, 10; ● and ○, 20.

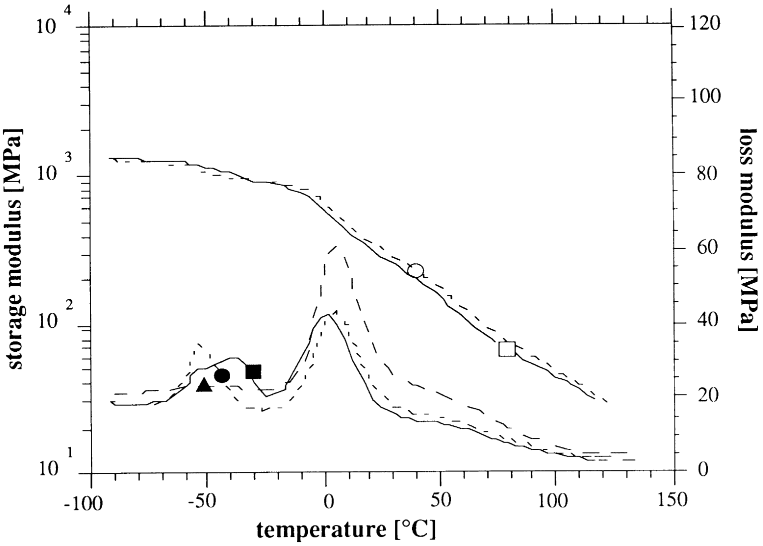

Fig. 3. Storage modulus ($G'$) and loss modulus ($G''$) as a function of the temperature, measured by DMA at 1 Hz: □, $G'$ E40L20; ○, $G'$ E60L20; ■, $G''$ E40L20; ●, $G''$ E60L20; ▲, $G''$ pure polypropylene.

Table 3
$T_g$ values of 20 vol% PP–EPR blends and pure materials

| Material | $T_g$: EPR (°C) | $T_g$: PP (°C) |
|---|---|---|
| Pure polypropylene | – | 5 |
| Pure E40L | −50/−37 | – |
| E40L20 | −50/−37 | −1 |
| 40M20 | −50/−38 | 2 |
| E40H20 | −50/−37 | 2 |
| E60L20 | −54 | 6 |
| E60H20 | −54 | 5 |

## 3. Results and discussion

The particle size distribution of the E40H20 and the E60H20 blend is shown in Fig. 1. Both blends show a unimodal distribution. The other blends also showed a unimodal distribution. The particle size data for the blends are listed in Table 2. The $D_w/D_n$ ratio is a measure of the particle size distribution. The distribution broadens with increasing $D_w$ and is exceptionally broad at a large $D_w$.

The $D_n$ and $D_w$ as a function of the intrinsic viscosity of the EPR phase are shown in Fig. 2. The relationship of $D_n$ with the intrinsic viscosity of the EPR phase is not simple. The $D_w$ increases with the logarithm of the intrinsic viscosity of the EPR phase and with increasing rubber content and increasing ethylene content.

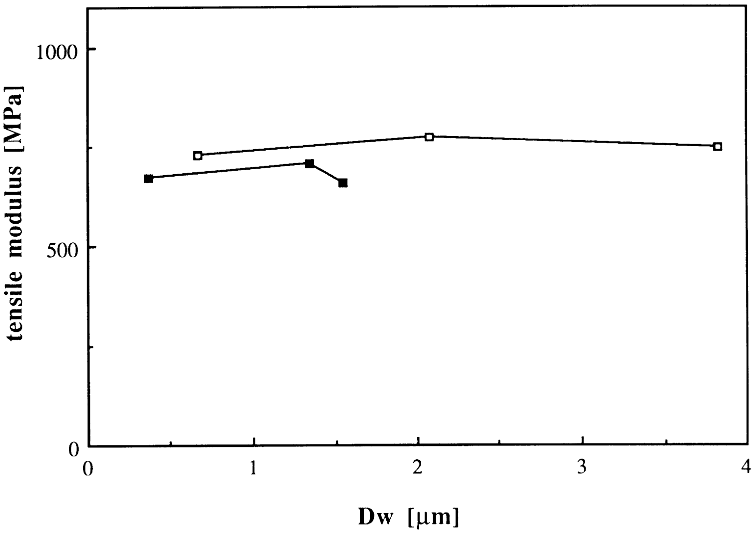

Fig. 4. Tensile modulus versus weighted average particle size for the 20 vol% PP–EPR blends. Ethylene content: ■, 40 mol%; □, 60 mol%.

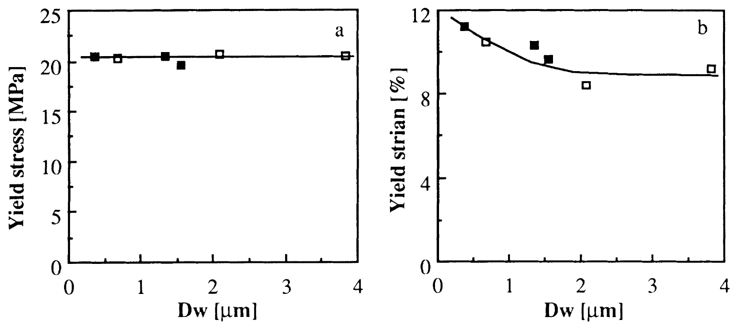

Fig. 5. Yield stress (a) and yield strain (b) versus weighted average particle size for the 20 vol% PP–EPR blends. Ethylene content: ■, 40 mol%; □, 60 mol%.

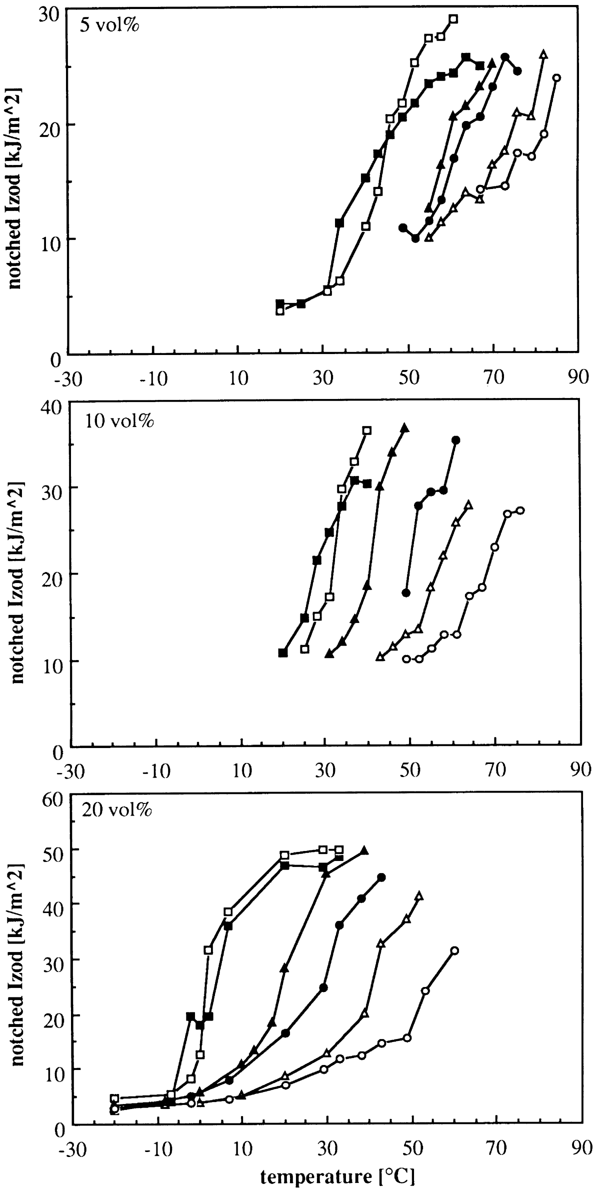

Fig. 6. Notched Izod impact strength versus the temperature for the PP–EPR blends. EPR type: , E40L; □, E60L; ▲, E40M; ●, E40H; △, E60M; ○, E60H. The circle marks the brittle–ductile transition.

### *3.1. Blend properties*

The storage modulus ($G'$) and the loss modulus ($G''$) were measured as a function of the temperature by DMA at 1 Hz. The storage modulus and the loss modulus curves of the E40L20 and the E60L20 blend and the loss modulus curve of polypropylene are plotted in Fig. 3. The $G''$ of dispersed E40 EPR phase shows two peaks, one at about −50°C and one at −37°C. These peaks were also exhibited by pure E40 EPR. The $G'$ curve of E40 EPR (not displayed in Fig. 3) demonstrates that this EPR becomes real rubbery above the second peak at −37°C (Fig. 3). The $G''$ of the dispersed E60 EPR contains just one peak. In this context, the glass transition temperature ($T_g$) is defined as the loss modulus peak temperature. The $T_g$ values of the blends and the pure materials are listed in Table 3.

The double peak seen representing the E40 EPR phase suggests the presence of two phases, one with a high propylene content and one with a high ethylene content. The matrix $T_g$ of E60 blends is not influenced by the dispersed EPR phase. The matrix $T_g$ of the E40 blends shifts towards lower temperatures than the $T_g$ of pure polypropylene. The degree of shifting increases with decreasing molecular weight. Most probably, low molecular weight EPR chains with a low ethylene content dissolve in polypropylene, thus reducing the $T_g$. As a result of a shift of the matrix $T_g$, the storage modulus of the E40L20 blend is slightly lower than that of the E60L20 blend (Fig. 3).

The tensile modulus of the blends is shown in Fig. 4. The modulus is almost entirely independent of the particle size (and rubber molecular weight) and increases slightly with the ethylene content of the EPR phase. A similar effect of ethylene content was observed for the storage modulus (Fig. 3). For this reason, the decreasing modulus with decreasing ethylene content may be attributed to the decreasing $T_g$ of the polypropylene matrix.

The yield stress is independent of the particle size and the ethylene content of the EPR phase (Fig. 5), despite the difference in the matrix $T_g$ between the E40 and E60 blends. Cavitation of the rubber lowers the yield stress of the blend [19]. As the particle size, the molecular weight of the rubber and the ethylene content have no effect on the yield stress, they seem not to have an effect on the cavitational stress.

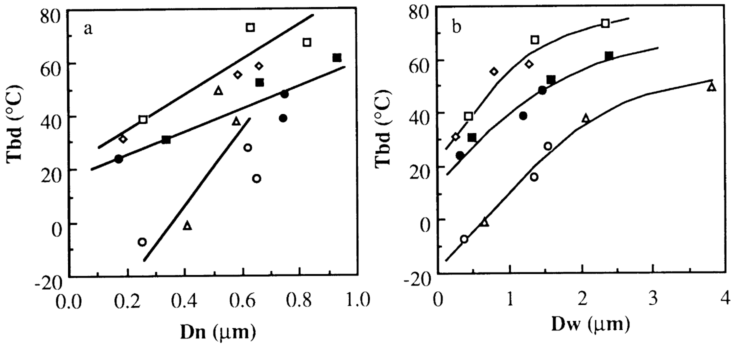

Fig. 7. The brittle–ductile transition temperature ($T_{bd}$) versus number (a) and weighted (b) average particle size for the PP–EPR blends (impact test). Rubber content: ◇ and □, 5%; ● and ■, 10%; ○ and △, 20%.

The ease of cavitation of the rubber particles is a very important step in the toughening process. The yield strain decreases with increasing particle size.

### 3.2. Notched impact

The notched Izod impact strength as a function of the temperature is shown in Fig. 6. The impact strength–temperature curve clearly shows an effect of both the rubber concentration and the particle size. The curves have an S-shape and with increasing rubber concentration and decreasing particle size the curves shift to lower temperatures. The sharp increase in impact strength is typical for the impact behaviour at high speeds of these blends. At the onset of this increase the fracture during crack propagation changes from brittle to ductile [11]. In the brittle region hardly any deformation can be observed while ductile fractured samples show massive stress whitening and deformation of material next to the fracture plane. This onset is for these materials taken as the brittle–ductile transition. The temperature at which this is taking place is the brittle–ductile transition temperature ($T_{bd}$). The $T_{bd}$ as a function of the particle size ($D_n$ and $D_w$) is shown in Fig. 7. The $D_w$ clearly gives a better relationship with the $T_{bd}$ than $D_n$. This may be due to the fact that the larger particles are more influential on the $T_{bd}$ than smaller particles. The $D_w$ is used as a measure of particle size in the sequel. The $T_{bd}$ increases with increasing $D_w$ and decreasing rubber content. The effect of particle size remains largely the same irrespective of the rubber content. Blends containing E40 and E60 rubber gives rise to the same curve, in other words the ethylene content of the EPR phase has little or no effect on the brittle–ductile transition.

As the $T_{bd}$ depends both on the rubber concentration and the particle size we studied whether for this system the $T_{bd}$ has a good correlation with the ID. Assuming regular lattice packing and a mono-dispersed rubber phase affords the following equation:

$$\mathrm{ID} = d\left[k\left(\frac{\pi}{6\phi_r}\right)^{1/3} - 1\right], \qquad (2)$$

where $d$ is the particle size, $\phi_r$ stands for the rubber content and $k$ denotes a geometric constant which depends on the lattice type. In a cubic lattice $k$ equals 1, while in a body centred lattice $k$ equals $(\surd 3)/2$ (and not $2^{1/3}$ as calculated by Wu [1]). The relationship between the brittle–ductile transition and the ID was established with $D_w$ for the ID based on a cubic lattice [1,7].

The ID was calculated assuming the particle size to be mono-disperse with a cubic lattice packing: $\mathrm{ID}_{\mathrm{cubic}}$ and a body centred cubic (BCC) lattice packing: $\mathrm{ID}_{\mathrm{bcc}}$ (Fig. 8). If all data points fall on one line one can say that $T_{bd}$ and the ID correlate. For both the $\mathrm{ID}_{\mathrm{cubic}}$ and the $\mathrm{ID}_{\mathrm{bcc}}$ the 5% and 20% rubber data do not fall on one line and the 10% data are

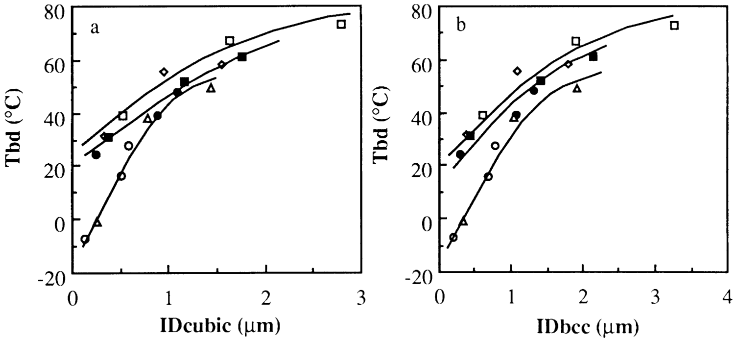

Fig. 8. The brittle–ductile transition temperature ($T_{bd}$) versus the interparticle distance for a cubic lattice (a) and BCC lattice (b) for the PP–EPR blends. Rubber content: ◇ and □, 5%; ● and ■, 10%; ○ and △, 20%.

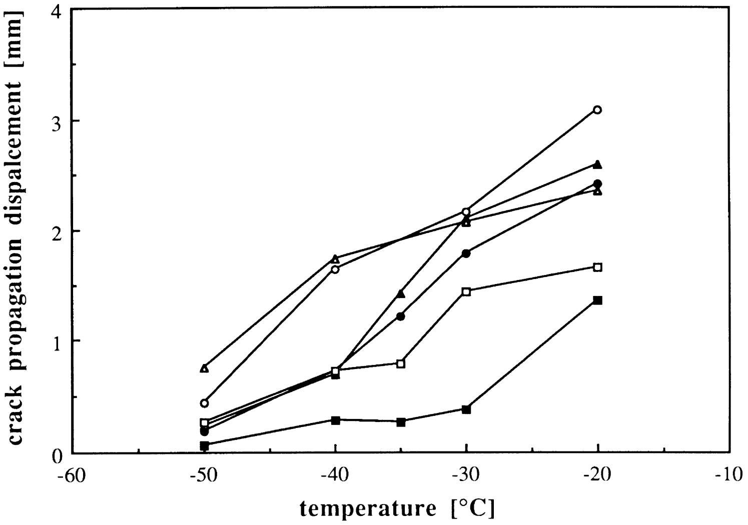

Fig. 9. The crack propagation displacement versus temperature for the 20 vol% PP–EPR blends (SEN tensile test at 1 mm/s). $D_w$ (μm): ■, 0.37; □, 0.67; ▲, 1.34; ●, 1.55; △, 2.08; ○, 3.83. Ethylene content EPR: filled symbols 40 mol%, open symbols 60 mol%. The circle marks the brittle–ductile transition.

in-between. Thus the $T_{bd}$ as measured by the notched Izod for these blends cannot be described with an ID parameter.

### 3.3. Low speed SEN tensile test (1 mm/s)

The fracture behaviour at low test speed was studied by a SEN tensile test at 1 mm/s. The fracture process may be divided into an initiation stage and a crack propagation stage. During the initiation stage the stress builds up at the notch tip, but crack initiation has not yet taken place. In the crack propagation stage the crack runs through the sample. In the case of brittle fracture the crack propagation speed is very high and the displacement (strain) during crack propagation (which is the time needed by the crack to propagate through the specimen, multiplied with the test speed) is very small. In the case of ductile fracture the crack propagation speed is much lower, and displacement during crack propagation considerably exceeds displacement during brittle fracture. The amount of displacement during crack propagation is thus a measure of the ductile crack propagation. Displacement during crack propagation of the 20 vol% blends is studied as a function of temperature (Fig. 9). The crack propagation displacement (CPD) increases gradually with increasing temperature. With increasing particle size the curves are shifted to lower temperatures, this is unexpected. The $T_{bd}$ may pass through a transition with increasing temperature.

As $T_{bd}$ is taken the onset in the rise in the CPD–temperature curve. The blends with the largest particle size were assumed to have a $T_{bd}$ of −50°C. The brittle–ductile transition temperature ($T_{bd}$) versus the $D_w$ is shown in Fig. 10. The $T_{bd}$ decreases with increasing particle size. Considering

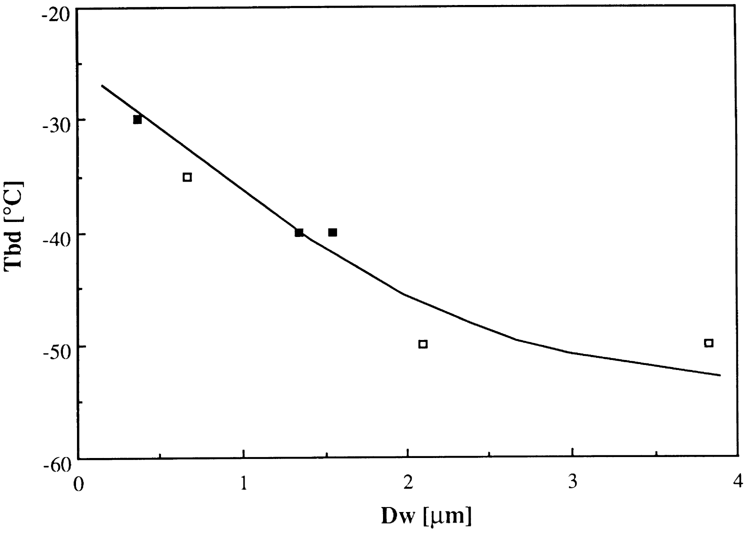

Fig. 10. The brittle–ductile transition temperature ($T_{bd}$) versus the weighted average particle size for the 20 vol% PP–EPR blends (SEN tensile test 1 mm/s). Ethylene content: ■, 40 mol%; □, 60 mol%.

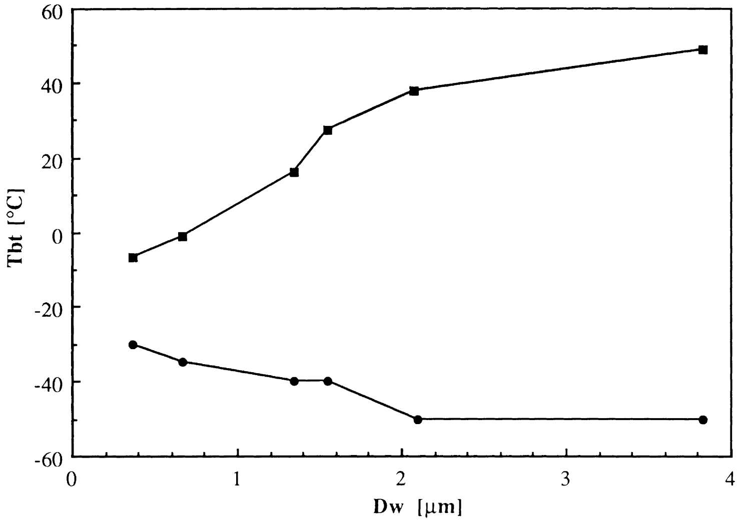

Fig. 11. The brittle–ductile transition temperature ($T_{bd}$) as a function of the weighted average particle size for the 20 vol% PP–EPR blends. ■: high test speed (impact test), ●: low test speed (SEN tensile test 1 mm/s).

the effect of particle size on the CPD-curves (Fig. 9) the relation between $T_{bd}$ and the particle size as shown in Fig. 10 seems reasonable. The $T_{bd}$ values are very low and may be affected by the glass transition temperature of the E40 and E60 EPR of −37 and −54°C, respectively (Table 3). The E40 and E60 blends fall reasonably on one line thus the ethylene content seem to have little effect. The fact that the $T_{bd}$ even decreases with increasing particle size may be due to the ease of cavitation of larger particles [5]. The rubber concentration has both at low and high test speeds a strong effect on the $T_{bd}$ of PP–rubber blends [12]. The decrease in $T_{bd}$ with increasing particle size at low test speed indicates that there cannot be a correlation between the brittle–ductile transition and the ID.

The effect of the test speed and particle size on the $T_{bd}$ of a 20% blend is shown in Fig. 11. At high test speed the $T_{bd}$ increases considerably with increasing particle size, whereas at low test speed in the studied particle size range the $T_{bd}$ decreases slightly. Consequently, the particle size effect depends on the test speed. As both low and high test speed the matrix deforms by a shear yielding, the mechanism of deformation is not changed by the test speed [11]. What might have changed is the onset of fracture. With increasing size of the cavities the possibility of initiating a crack has increased. At high speeds this seems to be the case. At low speeds in the studied particle size range (0.37–3.83 μm) the particles/cavities do not seem to influence the onset of crack initiation. The curious effect of the particle size remains to be further elucidated.

## 4. Conclusions

The ethylene content of the rubber had little effect on the properties of the blends. The molecular weight of the rubber might have an effect on the cavitational behaviour. The yield stress was found to be independent of the type of particles, this suggests that the cavitational stress of the particles as a function of the molecular weight did not change.

In studying the effect of rubber particle size we observed that the $D_w$ had a much better correlation with the brittle–ductile transition in Izod than the $D_n$. This suggests that particularly the larger particles influence the impact behaviour adversely. The function of the rubber particles in a polymer is to relieve the volume strain in a material without introducing inhomogenities from which a fracture can initiate. Large particles form large cavities that are more likely to become unstable. A few large particles might be sufficient to change the fracture behaviour.

At high test speed (impact conditions), the $T_{bd}$ increases considerably with increasing particle size. Surprisingly, at low test speed (SEN tensile test, 1 mm/s) in the studied particle size range (0.37–3.83 μm) the $T_{bd}$ shows even a slight decrease with increasing particle size. It can be expected that with very large particles the $T_{bd}$ increases too at low test speeds. The effect of the particle size on the brittle–ductile transition in the studied region at high test speeds is more critical.

## Acknowledgements

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