Impact behaviour of nylon–rubber blends: 6. Influence of structure on voiding processes; toughening mechanism

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Dilatometry tests were performed on nylon–rubber blends with various rubber concentrations, particle sizes and types of impact modifier. Whereas rubber concentration and particle size do not affect the onset of voiding in the blends during a tensile test, the type of elastomer used has a considerable effect. A correlation exists between the stress at which the rubber particles cavitate (or detach from the matrix) in the tensile test and the impact behaviour of the blend. A toughening mechanism is proposed in which the cavitation stress of the rubber and the interparticle spacing play crucial roles.

(Keywords: nylon–rubber blend; impact toughness; dilatometry; voiding; shear yielding; toughening mechanism)

INTRODUCTION

In a previous paper[1] the influence of rubber concentration and rubber particle size on the impact behaviour of nylon–rubber blends was studied. It turned out that with increasing concentration and decreasing particle size the brittle–tough (BT) transition temperature decreases and hence the impact behaviour improves. A relationship between the BT temperature and the interparticle distance (*ID*) was found. However, the preceding paper[2] showed that *ID* is not the only parameter which determines the impact strength of a nylon–rubber blend. The mechanical properties of the impact modifier were shown to have a decisive influence too. On the other hand, the concentration of the coupling agent, maleic anhydride, does not influence the impact toughness of nylon/EPDM (ethylene propylene diene monomer) rubber blends[3]. The observed stress whitening in deformed rubber-modified nylon was found to be due to a voiding process[1,3]. Crazing was not observed as a result of a deformation mechanism, which is confirmed by studies of Ramsteiner[4] and Sunderland *et al.*[5]

The results presented in the preceding paper suggest that the rubber particles toughen nylon-6 not by acting as stress concentrators to nucleate local plastic deformation but rather by relieving the hydrostatic pressure by delamination or internal cavitation, allowing as such excessive shear yielding.

The purpose of this paper is to investigate a possible relationship between the voiding process when a nylon/rubber blend is loaded and the structural parameters which determine the impact behaviour.

A tensile dilatometry technique is used, modelled after that used by Heikens and Sjoerdsma[6]. Three extensometers were used to measure the thickness, width and longitudinal strains. Then, the volume change ΔV during the tensile test can be determined:

$$\Delta V = [(D/D_0)(B/B_0)(L/L_0) - 1]V_0 \quad (1)$$

where V = volume, D = thickness, B = width and L = length of the specimen and subscript 0 denotes an initial quantity. ΔV has an elastic component ΔV_{el} and a plastic component ΔV_{void}:

$$\Delta V = \Delta V_{el} + \Delta V_{void} \quad (2)$$

Now with ν = Poisson's ratio and ε_{el} = elastic strain and since

$$\Delta V_{el} = V_0(1-2\nu)\varepsilon_{el} \quad (3)$$

the volume change due to void processes can be established:

$$\Delta V_{void} = V_0\{[(D/D_0)(B/B_0)(L/L_0) - 1] - (1-2\nu)\varepsilon_{el}\} \quad (4)$$

If the amount of material subjected to elastic deformation is constant, it is assumed[6] that in the plastic region ε_{el} equals approximately σ/E. Then ε_{el} can be calculated at any stress when the initial modulus of the material is known.

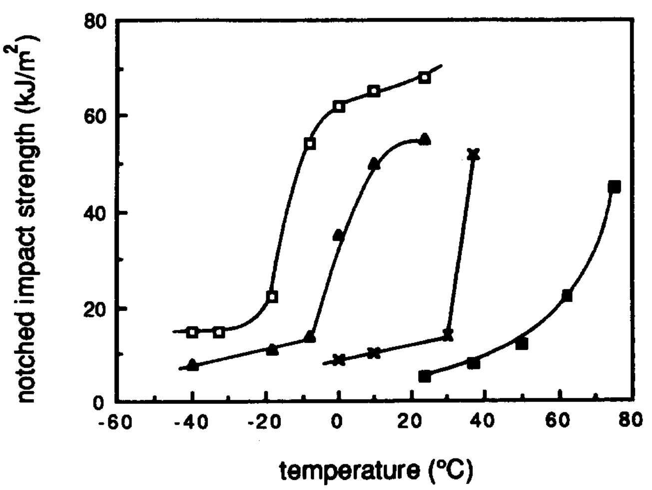

Figure 1 Notched impact strength as a function of temperature for nylon-6/EPDM blends with various rubber concentrations: (■) 0%; (×) 6.4 vol%, weight average particle size d_w = 0.28 μm; (▲) 13.0 vol%, d_w = 0.28; (□) 19.6 vol%, d_w = 0.23 μm

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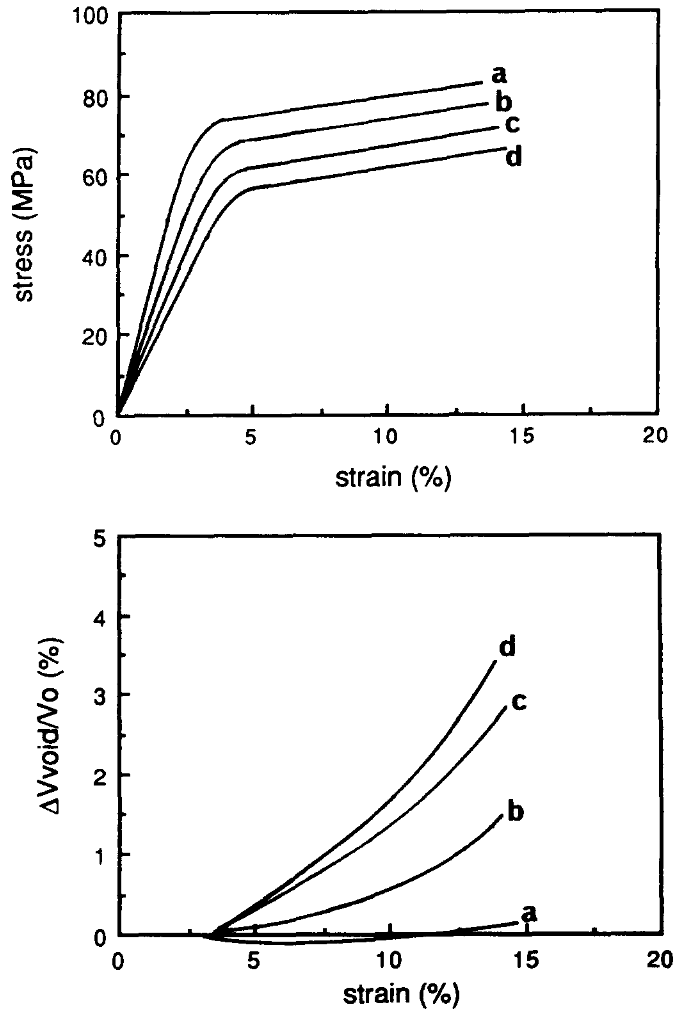

Figure 2 True stress and relative volume change due to voiding in blends with various rubber (EPDM Keltan 740) content, as functions of the applied strain: (a) nylon-6; (b) 6.4 vol%, $d_w = 0.28\,\mu m$; (c) 13.0 vol%, $d_w = 0.28\,\mu m$; (d) 19.6 vol%, $d_w = 0.23\,\mu m$

In this work dilatometry studies were applied to blends with various rubber contents, with a varying average particle size and with different types of impact modifier. The impact behaviour of some of the materials has been tested before[1,2].

EXPERIMENTAL

Materials

The materials used in this study are blends of nylon-6 (Akulon M258) and rubber. More details about the components, the blend preparation and the blend structure are given in the preceding papers[1,2].

The tensile modulus of the elastomers was measured according to DIN 53455-4, with an Instron tensile machine, using a strain rate of 10% min^{-1}. Stress–strain diagrams using a strain rate of 250% min^{-1} and shear modulus–temperature curves of the rubbers were determined as described in the preceding paper[2].

Dilatometry

Dumbbell-shaped samples of blends, obtained with injection moulding, having gauge section dimensions of $40 \times 6 \times 3$ mm and a total length of 80 mm, were dried before testing (vacuum oven, 110°C, overnight). At least three specimens of each material were tested, using an Instron tensile testing machine. Three extensometers with the requisite sensitivity were used to measure the longitudinal, width and thickness strains in the sample. The experiments were performed at a constant extension rate of 12.5% min^{-1}. The load and the three displacements were simultaneously recorded with an Apple IIGS microcomputer. The volume strain due to voiding could be calculated directly via equation (4).

When applying uniaxial tensile dilatometry on rubber-modified epoxies with the aid of extensometers Yee and Pearson[7] were confronted with artefacts. They found a volume maximum and even a decrease in material volume during the tensile test. It was suggested that this was caused by localized shear band formation in the sample induced by the tips of the extensometer pressing on the material. To overcome this problem, in our study thin plates of brass were placed between the sample and the width and thickness extensometers.

Impact testing

The notched Izod impact strength (ISO 180/A) and brittle–tough transition temperature of the blends used in this study are measured as described elsewhere[1–3].

RESULTS

The initial Young's modulus and some mechanical properties of the impact modifiers which were measured before[2] are listed in *Table 1*.

Influence of rubber concentration

Blends were made from nylon-6 and EPDM Keltan 740, modified with maleic anhydride. The rubber concentration was varied from 6.25 to 26.1 vol%. The rubber particle size in the blends was kept constant (about $0.3\,\mu m$) with the procedure described before[1].

In *Figure 1* the notched Izod impact strength of the blends is given as a function of the temperature. With increasing rubber content the BT temperature decreases while the impact energy in both the brittle and the tough regions increases. This is in full agreement with earlier findings[1].

In *Figure 2* the true stress and the relative *plastic* volume change $\Delta V_{void}/V_0$ are plotted *versus* the elongation. As observed before[1], the yield stress of the blends decreases proportionally with the rubber volume fraction. In the neat nylon-6, which has been tested as a reference,

Table 1 Initial Young's modulus (strain rate 10% min^{-1}), maximum stress and elongation at break (strain rate 250% min^{-1}) of impact modifiers used in this study. For polethylene and Arnitel E740 the maximum stress is in the yield stress; the other maximum stresses are stresses at break

Impact modifier	*E* modulus (MPa)	σ_{max} (MPa)	ε_b (%)
EPDM K740	4.8	3.8	700
XX1201 (EPM)	31.9	7.4	550
Keltaflex N35	189.0	4.8	80
Polethylene	265.0	9.7	340
Arnitel EL740	960.0	36.4	360
Arnitel E315	35.6	17.4	850

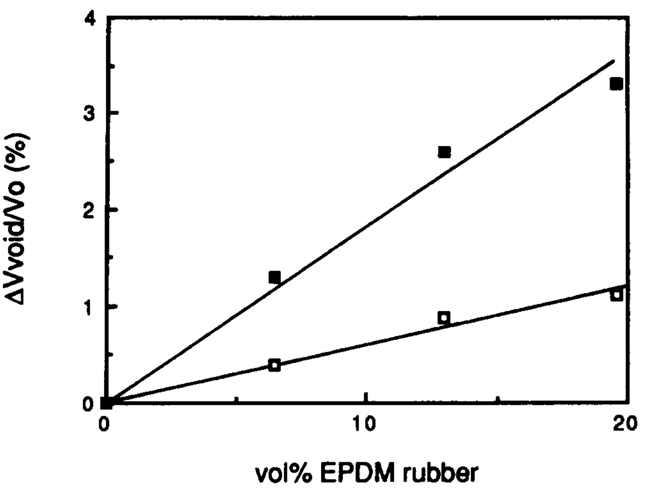

Figure 3 Relative volume change due to voiding as function of the rubber concentration in the blend, at applied strains of 8% (□) and 14% (■)

no voiding can be observed. In each blend, however, plastic dilatation starts at the same strain, independent of the rubber concentration. Apparently, the onset of voiding in or around the rubber particles appears not to be influenced by stress concentration fields induced by neighbouring particles.

In *Figure 3* the volume change in the blend due to voiding at a strain of 8% and 14%, respectively, is plotted *versus* the rubber concentration. In both stages of the tensile test the total void volume increases linearly with rubber concentration. The void volume growth does not seem to be affected by stress concentrations around neighbouring particles.

Influence of rubber particle size

Three blends of nylon-6 and 13 vol% EPDM Keltan 740 (modified with maleic anhydride) with various particle sizes were subjected to the dilatometry test. The production and characterization of these blends was described before[3]. The notched Izod impact strength is given as a function of temperature in *Figure 4*. As was noted before[1,3], a decrease in particle size decreases the BT temperature and increases the impact energy in both the brittle and tough regions.

Figure 5 shows the true stress and the volume change in the blends due to voiding as functions of strain when applied to the uniaxial tensile test. As noticed before[1], the yield stress of the blends is not affected by the rubber particle size (observed slight differences are within experimental error). The voiding starts at the same point of elongation for each blend, notwithstanding the differences in rubber particle size. The stress at which rubber delamination or cavitation begins is not influenced by the particle size, at least for the range of sizes studied. The blends show a slight increase in void volume growth with increasing particle size.

Influence of rubber properties

The production and characterization of blends of nylon-6 and one of the impact modifiers described in *Table 1* was described in the previous paper[2]. It appeared that the type of modifier, as well as rubber concentration and particle size, strongly affects the impact behaviour of nylon–rubber blends. In *Figure 6* the true stress and the plastic dilatation of the blends are plotted *versus* the applied elongation. In the legend of the figure the weight-average particle size of the dispersed phase in the blend is given. The yield stress of the blends is only slightly affected by the type of impact modifier used.

The strain at which voiding in the blend starts, however, is clearly influenced by the type of impact modifier used. The applied strain at which voiding in or around the impact modifier begins decreases in the order: PE–Arnitel–Keltaflex–EPM–EPDM. The void volume growth seems to increase in the same direction.

DISCUSSION

Correlation voiding process and impact properties

In the preceding paper[2] it was found that the impact-modifying effect of the elastomer increases, independent of concentration and particle size, in the order: PE–Arnitel–Keltaflex–EPM–EPDM. Remarkably, this sequence was also found in the previous section of this paper for an increasing ability to generate voids in a nylon matrix during a tensile test.

Figure 7 correlates both observed phenomena by plotting the BT temperature of the blends *versus* the strain at which voiding starts ('cavitation strain'). The BT temperature decreases (and the impact behaviour improves) unequivocally as the strain at which voiding in the blend starts to decrease. Because the average particle size among the blends only varies slightly, *Figure 7* therefore suggests that the effectiveness of an impact modifier depends on its ability to create voids.

It should be noted that the voiding phenomena are measured under low strain-rate conditions whereas the impact test involves a high strain rate. However, although the applied strain rates differ, the stress fields around the rubber particles will be triaxial in both the impact test and the tensile test. It is known that in an impact test ahead of the crack tip a triaxial stress state exists[8]. Owing to the difference in Poisson's ratio the rubber particles will experience a triaxial tension too during the tensile test, provided that the particles adhere to the matrix.

There is thus some evidence now that the function of the rubber particles, in the toughening of polyamides, is

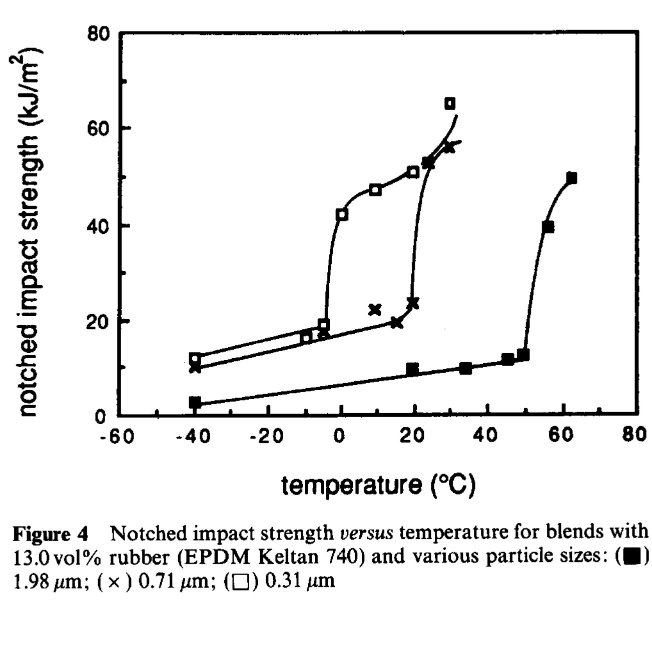

Figure 4 Notched impact strength *versus* temperature for blends with 13.0 vol% rubber (EPDM Keltan 740) and various particle sizes: (■) 1.98 μm; (×) 0.71 μm; (□) 0.31 μm

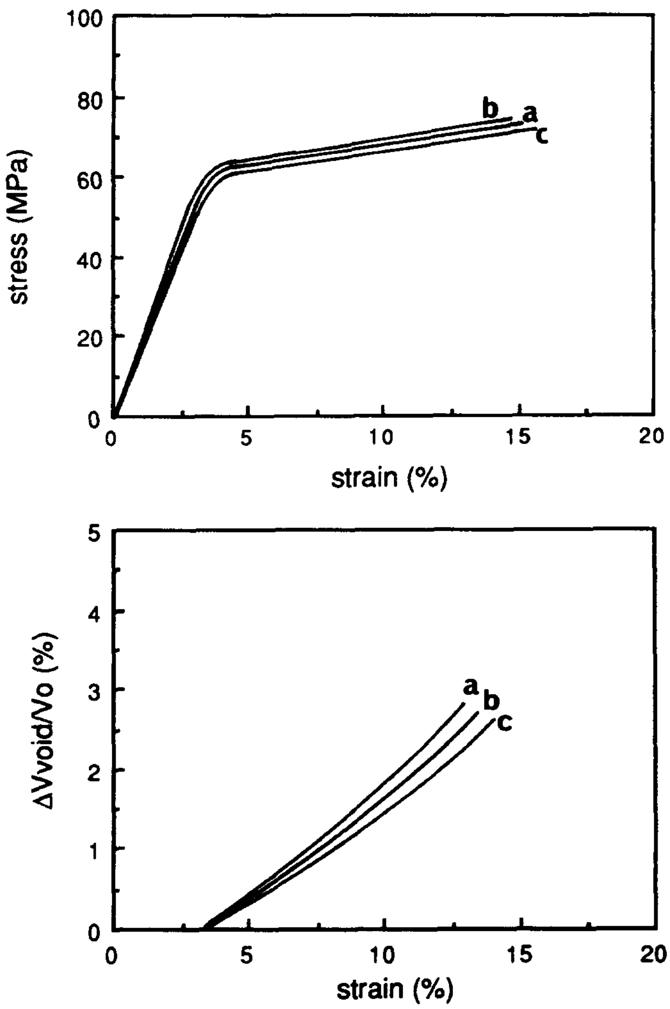

Figure 5 True stress and relative volume change due to voiding, as functions of the applied strain for blends containing 13.0 vol% rubber (EPDM Keltan 740) and various particle sizes: (a) $d_w = 1.98\,\mu m$; (b) $d_w = 0.71\,\mu m$; (c) $d_w = 0.31\,\mu m$

to relieve the hydrostatic tension ahead of the crack tip by creating voids.

Factors affecting the cavitation process in the blends

Because of the relatively high bulk moduli of the rubbers, the particles in the nylon matrix will sustain considerable load under hydrostatic tension. The observed voiding in the blends may be due to either a detachment of the rubber particles from the nylon matrix or to internal rubber cavitation. Ramsteiner[4] demonstrated cavitated rubber particles in a plastically deformed nylon–rubber blend with transmission electron microscopy. Hert[9] showed that the failure in a double-layer structure of nylon-6 and a reactive olefinic copolymer is within the elastomeric phase. However, it should be noted that Hert used a peel test with a uniaxial force whereas during a notched impact test the rubber particles are subjected to triaxial stresses.

In part 4 of this series[3] we found that the degree of interfacial adhesion does not influence the impact toughness of nylon–rubber blends, while in part 5 of this series[2] it has been demonstrated that the type of impact modifier used has a decisive effect. Thus, the results obtained from both literature and our experiments suggest that the voiding in the blends is due to rubber cavitation rather than delamination of the rubber particles.

In order to investigate which mechanical properties of the rubber determine its ability to introduce cavitities in a nylon–rubber blend, in *Figure 8* the strain at which voiding in the blend starts ('cavitation strain') is plotted as a function of respectively the elongation at break, the breaking stress and the initial tensile modulus of the elastomer. It is repeated here that the extension rate for the dilatation test is 12.5% min^{-1}, while the tensile modulus of the rubber is measured at a strain rate of 10% min^{-1} and the stress and elongation at break at 250% min^{-1}.

Although different strain rates were applied, *Figure 8* suggests that there is no relationship between the strain at which cavitation starts in the blend and the elastomer's elongation at break.

Gent[10,11] states that rubber cavitation under triaxial tension is due to the elastic instability of precavities in the rubber and therefore only depends on the elastic modulus of the elastomer. However, the correlation between 'blend cavitation strain' and initial Young's modulus of the impact modifier is just as rough as the correlation between 'blend cavitation strain' and breaking stress of the dispersed phase (*Figure 8*). The deviations in both correlations are caused by PE and the Arnitels.

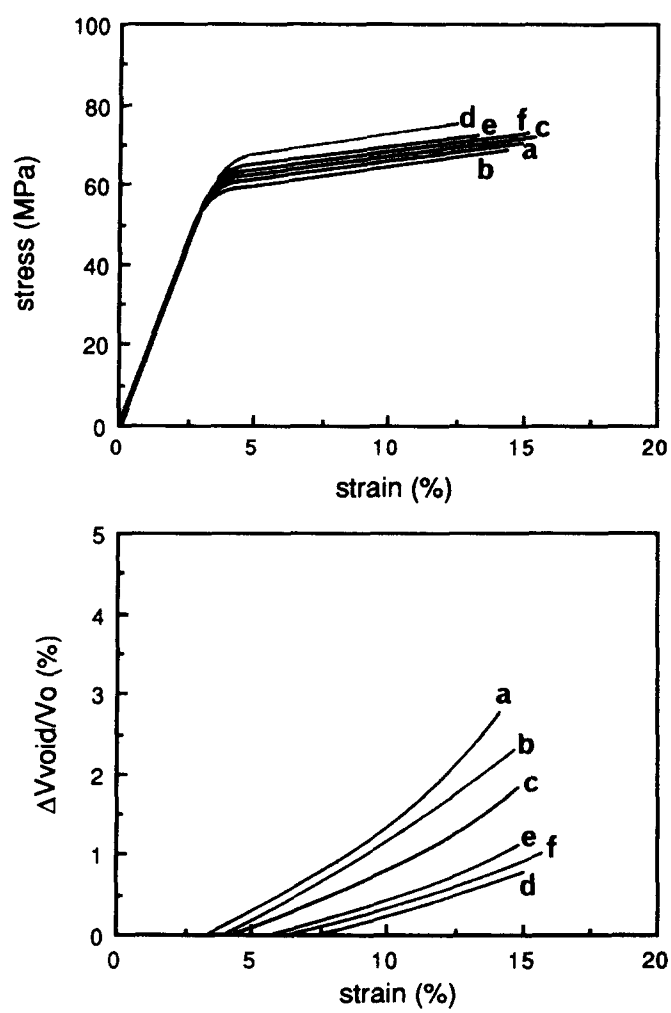

Figure 6 True stress and relative volume change due to voiding, as functions of the applied strain for blends containing 13.0 vol% impact modifier: (a) EPDM Keltan 740, $d_w = 0.31\,\mu m$; (b) XX1201, $d_w = 0.25\,\mu m$; (c) Keltaflex, $d_w = 0.29\,\mu m$; (d) polyethylene, $d_w = 0.49\,\mu m$; (e) Arnite E740, $d_w = 0.25\,\mu m$; (f) Arnite E315, $d_w = 0.28\,\mu m$

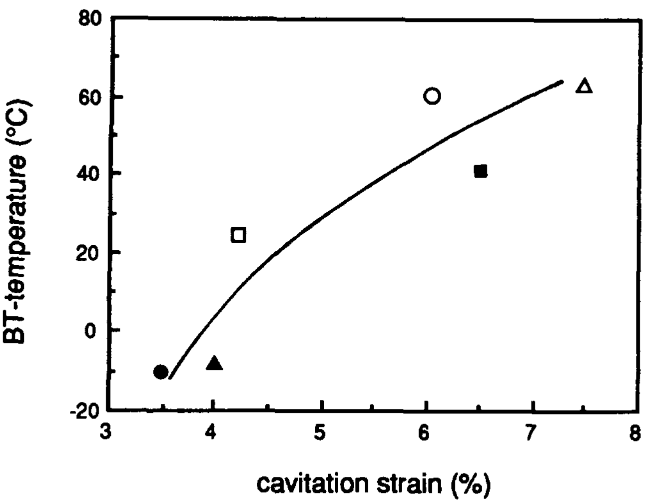

Figure 7 The BT temperature (measured with notched Izod impact tests) *versus* the strain at which voiding starts (data obtained from *Figure 6*): (●) EPDM Keltan 740, d_w=0.31 μm; (▲) XX1201, d_w=0.25 μm; (□) Keltaflex, d_w=0.29 μm; (△) polyethylene, d_w=0.49 μm; (○) Arnitel E740, d_w=0.25 μm; (■) Arnitel E315, d_w=0.28 μm

It should be noted that these impact modifiers are not real elastomers and maybe will not fit Gent's model.

The phenomenon that, for example, the thermoplastic elastomer Arnitel E315 initiates voiding in a blend only at high strain despite its relatively low Young's modulus might be related to its mechanical bulk properties. It can be expected that the Poisson's ratios of the thermoplastic Arnitels are smaller than the Poisson's ratio of a real rubber ($\nu \approx 0.49$–0.50) and consequently the difference with the nylon matrix ($\nu \approx 0.43$) will be smaller. With decreasing difference in Poisson's ratio between matrix and particle, the applied load on the particle decreases and cavitation (or delamination) may be retarded.

Toughening mechanism

Besides the ability of the impact modifier to generate voids in a triaxial stress field, the interparticle spacing *ID* turned out to be a significant factor in determining the impact toughness of a nylon–rubber blend[1]. Since rubber concentration and particle size do not influence the rubber cavitation process, the importance of *ID* must be due to other phenomena.

When in an impact test the elastic constraint is relieved by cavitation, extensive plastic flow in the matrix may occur, provided that the decreased yield stress of the matrix is sufficiently low. For a given applied deformation rate and matrix structure, the yield stress depends on: (a) the temperature, and (b) the applied stress state. It is postulated[12] that after voiding in or around the rubber particles, the yield stress of a matrix ligament between the created voids depends directly on the ligament thickness. Thin ligaments will have a relatively low yield stress since they tend to be in plane stress, whereas thick ligaments have higher yield stresses because of an incompletely relieved plane strain situation. The critical thickness of a ligament is dependent on the matrix structure and might be determined by a typical structural parameter like the lamellar thickness of the crystalline phase.

In a real blend, there is a distribution of thin and thick ligaments. Excessive plastic flow will start in the matrix if a sufficient number of thin ligaments start to yield in order to absorb the elastic energy. In this view, the average interparticle distance indicates whether the criterion for excessive shear yielding is fulfilled.

Remarkably, in 'brittle' matrices like polystyrene, rubber particles under hydrostatic tension usually induce cavitation within the matrix (crazing) by generating stress concentrations. In ductile matrices like polyamides, however, cavitation within the matrix is prevented by a high entanglement density[13]. The elastic constraint in that case is relieved by the internal rubber cavitation (or delamination of the rubber particles). Yielding between

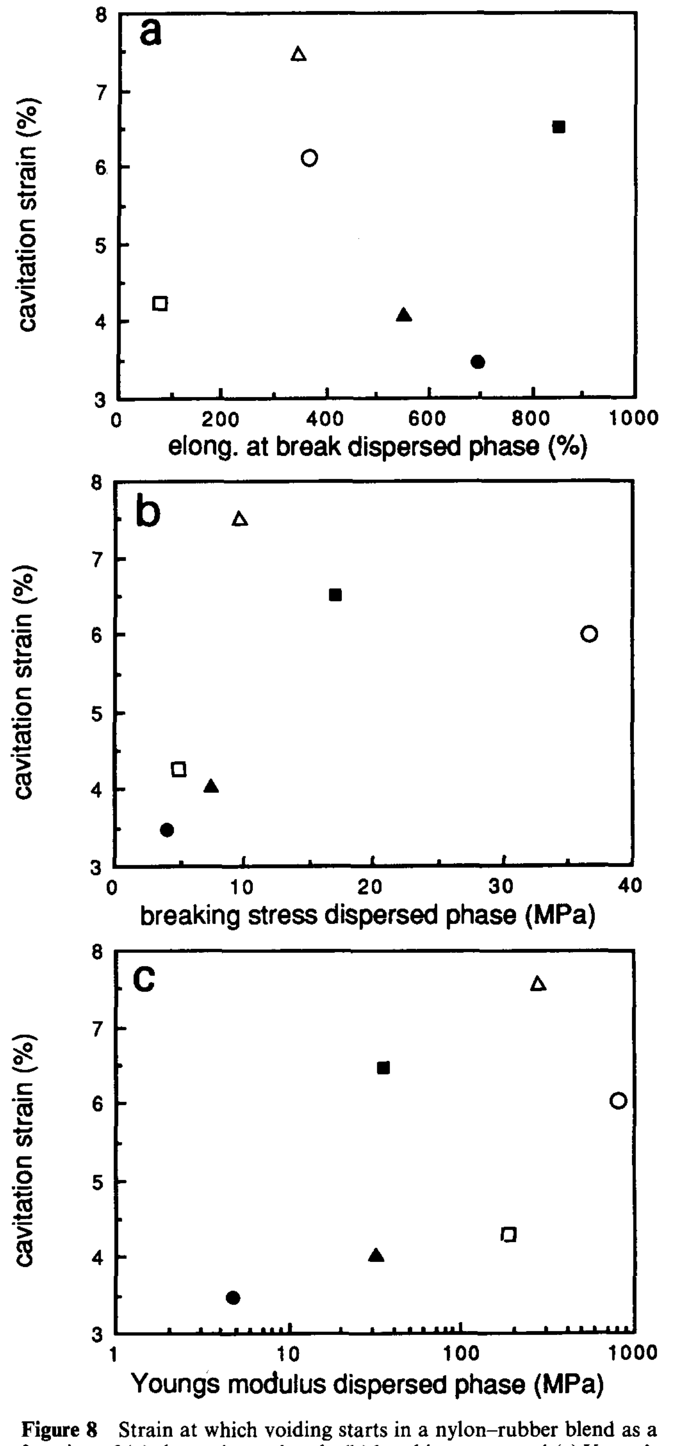

Figure 8 Strain at which voiding starts in a nylon–rubber blend as a function of (a) elongation at break, (b) breaking stress and (c) Young's modulus of the dispersed rubber phase. Dispersed phase: (●) EPDM; (▲) XX1201; (□) Keltaflex; (△) polyethylene; (■) Arnitel E315; (○) Arnitel E740

the cavities may occur in both the ductile matrix and the brittle matrix. However, whereas within a brittle matrix cavities usually coalesce quickly and form a fatal crack ('craze breakdown'), in a ductile matrix shear yielding can take place excessively between the cavitated/delaminated rubber particles without fast crack formation.

CONCLUSIONS

The start of plastic dilatation in nylon–rubber blends is not affected by rubber concentration and particle size. Stress concentrations induced by neighbouring particles obviously do not act upon the rubber cavitation process. However, the onset of voiding has been observed to be strongly influenced by the type of elastomer used.

Although both quantities were measured at different deformation rates, an unambiguous relation was found between the strain at which voiding starts in a nylon–rubber blend during a tensile test and the impact behaviour of that blend. A decrease of stress necessary to cavitate (or detach) the dispersed particles seems to result, at constant interparticle distance, in an increase of the impact toughness.

It is not exactly clear yet which mechanical properties of the impact modifier determine the voiding process in the blend. It is suggested, however, that both a low elastic modulus and a high Poisson's ratio of the elastomer favour voiding within the blend.

Summarizing, the impact toughness of an elastomer-modified polyamide with given matrix structure and specimen geometry depends on: (1) the stress at which rubber particle cavitation or delamination in hydrostatic tension occurs; (2) the average thickness of the ligament between the created cavities, which is equivalent to the average interparticle spacing *ID* in the blend; and (3) temperature.

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