

# Nylon-6–rubber blends

## Part IV Cavitation and yield in nylon–rubber blends

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The macroscopic cavitation and yield behaviour of nylon-6/rubber blends was studied. The type of rubber (poly(butadiene), ethylene propylene copolymer (EPDM) or polyethylene (LDPE), the rubber concentration and the rubber particle size was varied. The onset of cavitation was determined by measuring the intensity of the transmitted light from an incident laser beam. Both the yield stress and the cavitation stress appeared to increase with increasing strain rate and rubber modulus. No linear relation between the shear modulus and the cavitation stress was found. The data indicate that blends with a very small particle size have a relatively high cavitation stress. In all cases, a high cavitation stress of the elastomer resulted in a high yield stress of the blend.

### 1. Introduction

In the deformation mechanism of nylon/rubber blends, cavitation of the rubber phase plays an important role. It is believed that cavitation leads to the relief of the triaxial stress ahead of a notch or a running crack. In this way the size of the plastic zone can be increased drastically, and tough behaviour can also be observed under impact conditions.

The importance of cavitation was demonstrated by the work of Borggreve *et al.* [1] who found a strong dependence of the brittle-to-tough transition temperature (as measured with a notched Izod impact test) on the type of impact modifier used. Since the stress field around a rubber particle in a nylon matrix is hardly affected by the mechanical properties of the elastomer [2], this can only be explained by differences in the cavitation stress of the different types of rubber.

From a theoretical viewpoint, the phenomenon of the cavitation of elastomers was first treated by Gent and Tompkins [3]. They assumed that cavitation started from microvoids and calculated that for a neo-Hookean material, with microvoids large enough for the surface energy terms to be neglected, the critical stress for cavitation is a linear function of the shear modulus (Equation 1). For very small microvoids the surface energy also has to be overcome; this will result in a higher cavitation stress, which is dependent on the size of the microvoid.

$$\sigma_{\text{cav}} = \frac{5}{2}G \quad (1)$$

More recently, this result was confirmed for a homogeneous material by Ball [4] who used a non-linear elastic analysis and described cavitation as a bifurcation problem. The problem of cavitation in two-phase systems was treated by Horgan and co-workers [5–7].

This paper deals with cavitation in nylon-6/rubber blends. A new test method was developed to determine the cavitation stress of an elastomer dispersed in a nylon matrix. Using this test method, cavitation stresses can be measured over a broad range of strain rates. Specific attention was paid to the relationship between cavitation and yield in rubber-modified nylons.

### 2. Determination of the cavitation stress

There are few studies reported in the literature concerning the determination of the cavitation stress of elastomers. A direct approach is to subject a rubber sample to a hydrostatic stress and to detect the point where cavities are formed in the sample. The main problem with this kind of test is the generation of hydrostatic tension in the sample. Examples of solutions to this problem are: tensile tests on cylindrical rubber samples with a high diameter/height ratio which are bonded to metal end-pieces [8], the dissolving of a gas under pressure in a rubber sample after which the pressure is suddenly released [9]; and the use of the stress concentration around a hard, well-bonded spherical inclusion in an elastomeric matrix which is perfectly hydrostatic just above the pole of the inclusion [10].

Despite the fact that the data obtained with the test methods mentioned above generally give a good agreement with the predicted relation (Equation 1) between the modulus and cavitation stress [11, 12], there are still some phenomena which remain unexplained. Gent and Lindley [8] found that the cavitation stress of short cylindrical rubber samples, bonded to metal end-pieces, increased with increasing diameter/height ratios. This is opposite to what was

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expected, since a high diameter/height ratio is more effective in generating a triaxial stress. The authors can explain this fact by supposing that small specimens can only contain small initial voids as precursors to cavitation. This, however, seems unlikely since these microscopic voids have never been demonstrated, which indicates that their size is orders of magnitude smaller than the specimen size. Also the presence and size of initial voids is expected to be more dependent on the fabrication process than on the final size of the specimen.

For a better understanding of the role that cavitation plays in the rubber toughening of plastics it seems more appropriate to study the cavitation of rubber particles blended in a plastic matrix rather than to study the cavitation of macroscopic rubber samples. The cavitation behaviour of the latter can be different for two reasons. First, the size of the particles is more than three orders of magnitude smaller than that of the specimen which are normally used in mechanical tests. The work of Gent suggests that this size can play a crucial role in the onset of cavitation. Secondly, the relation between the applied stress and the real cavitation stress of a rubber particle can be complicated due to stress-field overlap and thermal stresses caused by a mismatch in the thermal expansion coefficients of the matrix and dispersed phase.

The method used most often for studying the cavitation behaviour of rubber particles in a thermoplastic matrix is *tensile dilatometry*, since cavitation goes together with an increase in volume. This method was applied by Borggreve *et al.* [13]. They found that the strain where a sudden increase in volume was observed was independent of the rubber-volume fraction and the rubber particle size. There appeared to be a correlation between the cavitation strain and the brittle-to-tough transition temperatures as measured with a notched Izod impact test. It has to be noted, however, that not all the materials in the work of Borggreve can be regarded as real rubbers (some thermoplastics elastomers (TPEs) and a low density polyethylene (LDPE) were also used as impact modifiers).

More recently, similar studies on nylon-6/EPR (ethylene propylene rubber) and nylon-66/EPR blends with varying particle sizes and rubber contents were performed by Lazzeri [14]. In this study, the temperature and strain rate were also varied. It was concluded that the cavitation stress was practically independent of the strain rate but it seemed to decrease with increasing temperature. Lazzeri also concluded that the rubber particle size had no influence on the onset of cavitation.

In principle, tensile dilatometry has two drawbacks. Firstly, it will not be possible to use the normal technique with strain gauges over a broad range of deformation rates. Particularly in the impact regime, it will be impossible to conduct tensile dilatometry. Secondly, it is difficult to measure changes in volume accurately. Therefore, it will be hard to determine precisely the onset of cavitation in the blend.

To overcome these problems, we have developed a new technique to determine the onset of cavitation in a nylon/rubber blend over a broad range of deforma-

tion rates. The underlying principle of the method is that cavitation in a blend is accompanied by a change in transparency (stress whitening). This stress whitening is caused by the scattering of the incident light by cavitated particles. This scattering will mean that only part of the incident light will pass through.

When a strong light source (for example, a laser) is positioned on one side of a specimen, it is expected that at the onset of cavitation the intensity of the transmitted light will drop suddenly due to the extra scattering of the cavitated particles. This drop can be detected using a photodiode. The basic method described here is relatively simple to carry out. Determining cavitation by this method also has the advantage that the cavitation can be studied at high strain rates.

Fig. 1 demonstrates that cavitation is indeed accompanied by a clear drop in the intensity of the transmitted light, as measured with a photodiode. In this test, the transmittance was measured for dumbbell-shaped specimens with different degrees of pre-deformation over the entire gauge. It is clear that the transmittance decreased with increasing strain and that for the higher strains this was not constant over the parallel section of the gauge. The minimum in the curves coincided with the point where the neck was formed.

The cavitation measurements were performed on a Schenck hydropuls 25 VHS high-speed hydraulic tensile tester with a maximum piston velocity of  $12.5 \text{ ms}^{-1}$ . The laser used was a helium-neon laser with an output power of 30 mW and a wavelength of 633 nm. The data were sampled using a transient recorder after which they were dumped to a computer. Data processing was done using the software delivered by Schenck. The test set-up is given schematically in Fig. 2.

A typical example of the test results from the cavitation measurements is given in Fig. 3. It is clear that at a certain point a sudden drop in the output voltage of the photodiode can be observed. The point where cavitation starts is defined as the point where a change in the output voltage is caused by the cavitation process with more than 95% reliability. Cavitation tests have been performed in fivefold. The standard deviation was usually less than 5% of the average value.

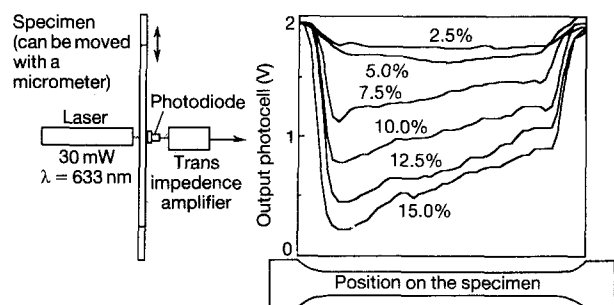


Figure 1 The intensity of the transmitted light versus the position on the gauge for predeformed dumbbell-shaped specimens (nylon-6/EPR, 20 wt %;  $d_w = 0.35 \mu\text{m}$ ) with different applied strains (the strain is given by the numbers in the graph).

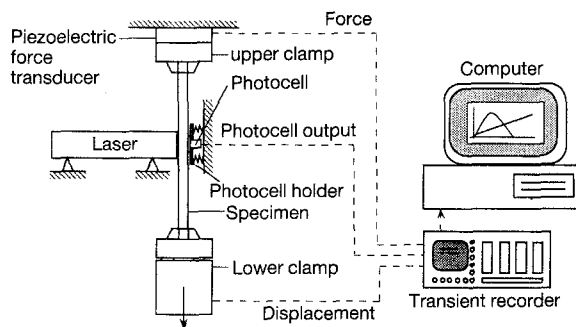


Figure 2 The test set-up for measuring the onset of cavitation.

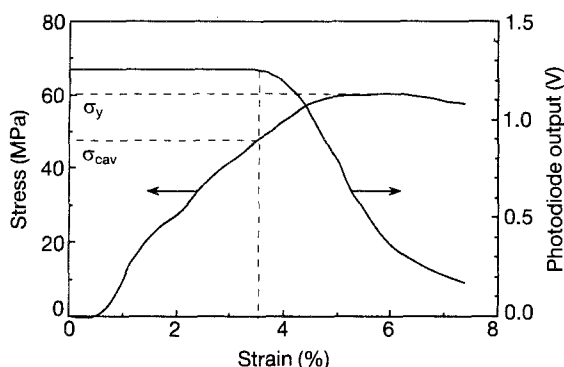


Figure 3 An example of the stress/output voltage-strain curve (piston speed =  $1 \text{ m s}^{-1}$ ,  $\dot{\epsilon} = 9.32 \text{ s}^{-1}$ , where  $\epsilon$  is the strain rate). The material is the nylon-6/BR blend given in Table I.

It will be clear that the cavitation stress as measured in this test is the stress acting on the blend when the rubber starts to cavitate. This stress will not be the same as the stress in the rubber particles at the point of cavitation. Therefore, a distinction must be made between the cavitation stress as measured with the test set-up given in Fig. 3, which will be called the macroscopic cavitation stress, and the real cavitation stress of the rubber.

### 3. Effect of the type of rubber

#### 3.1. Experimental procedure

The nylon-6/LDPE and the nylon-6/ethylene propylenediene rubber (EPDM) blends were prepared by blending nylon-6 (Akulon M258,  $\eta_{rel} = 5.8$  in 96%  $\text{H}_2\text{SO}_4$ ,  $\rho = 1.14 \text{ g/ml}$ , obtained from AKZO) with 20 and 19.5 wt % rubber respectively on a Berstorff ZE25 corotating twin-screw extruder, screw diameter 25 mm and a length/diameter ( $L/D$ ) of 33. The poly(ethylene) used was a maleic-anhydride (MA) modified LDPE, Stamydan LD 1808AN00, supplied by DSM. The EPDM, Royaltuf 465A, 2.0 wt % MA, was supplied by UniRoyal.

The extrusion conditions were set to result in blends with a weight-average particle size of about  $0.4 \mu\text{m}$ . It appeared that the nylon-6/PE blend still had a poorly distributed morphology after extrusion. Therefore, this blend was extruded another time under the same conditions. After the second extrusion step, no particle clusters could be seen on the micrographs.

The nylon-6/polybutadiene (BR) blend was prepared by diluting a 30 vol % nylon-6/BR master blend, Durethan BC303, obtained from Bayer, with

Akulon M258 to the desired rubber content. Also, in this case, blending was done on a Berstorff twin-screw extruder.

Dumbbell-shaped specimens according to the ISO R527-1 standard were injection moulded on an Arburg Allrounder 221-55-250. Before testing, the specimens were dried overnight at  $110^\circ\text{C}$  under a vacuum.

The dynamical-mechanical properties of the rubbers were determined as a function of temperature using a Myrenne torsion pendulum. Specimens (length  $\times$  breadth  $\times$  depth =  $60 \times 9 \times 2 \text{ mm}^3$ ) were prepared from the rubber granules by compression moulding. The mechanical spectrum was measured at 1 Hz with a heating rate of  $1^\circ\text{C min}^{-1}$ . The  $\alpha$ -transition temperature is defined as the temperature where the loss modulus reaches a maximum. The dynamical-mechanical properties of poly(butadiene) given in Table I are not the properties of the BR in the Durethan master blend but those of another type of BR (Cariflex BR1202 D, supplied by Shell).

In order to determine the particle size, the particle-size distribution and the particle distribution, a sample was taken out of an injection-moulded specimen. On this sample a smooth surface was prepared with a diamond knife on a CryoNova LKB 2285-050 microtome. The sample temperature during microtoming was  $-110^\circ\text{C}$ .

The rubber was extracted from these samples from the surface by etching in boiling *m*-xylene for about 12 h. After drying the samples at  $110^\circ\text{C}$  under a vacuum, for one night, they were covered with a layer of gold and examined with a Jeol-JSM-35CF scanning electron microscope. The particle size was determined from the micrographs.

#### 3.2. Rubber properties and blend morphology

#### 3.3. Results and discussion

In Fig. 4 it can be seen that the macroscopic cavitation stress as well as the yield-stress increased with increasing strain rate. For the nylon-6/PE blend, the macroscopic cavitation stress was very close to the yield stress over the entire range of strain rates tested. The nylon-6/BR blend and the nylon-6/EPDM showed similar behaviours. For low strain rates, the macroscopic cavitation stress was only slightly lower than the yield stress. When the strain rate was high, however, the macroscopic cavitation stress was considerably lower than the yield stress.

When the different rubbers were compared, it appears that the rubber with the lowest stiffness had the lowest macroscopic cavitation stress and that with increasing rubber modulus there was an increase in the macroscopic cavitation stress. Also, the macroscopic cavitation stress appeared to be less rate dependent when the modulus of the disperse phase was low. When the specimens were observed, it was obvious that the stress whitening in the BR blends was much more intense than that in the EPDM blend. The PE blend hardly showed any stress whitening. This indicates that a low rubber modulus cavitates to a higher degree.

TABLE I The rubber properties (as measured with a torsion pendulum) and the blend morphology of the prepared nylon-6/rubber blends

Impact modifier	$G'_{\text{rubber}}$ (MPa) at 1 Hz, 20°C	$T_g$ (°C) at 1 Hz	Rubber content (vol %)	$d_n$ (μm)	$d_w$ (μm)	$d_w/d_n$
BR	0.7	-102	23.5	0.28	0.35	1.25
EPDM	5.6	-45	23.5	0.26	0.40	1.53
PE	131	-23	23.5	0.30	0.46	1.53

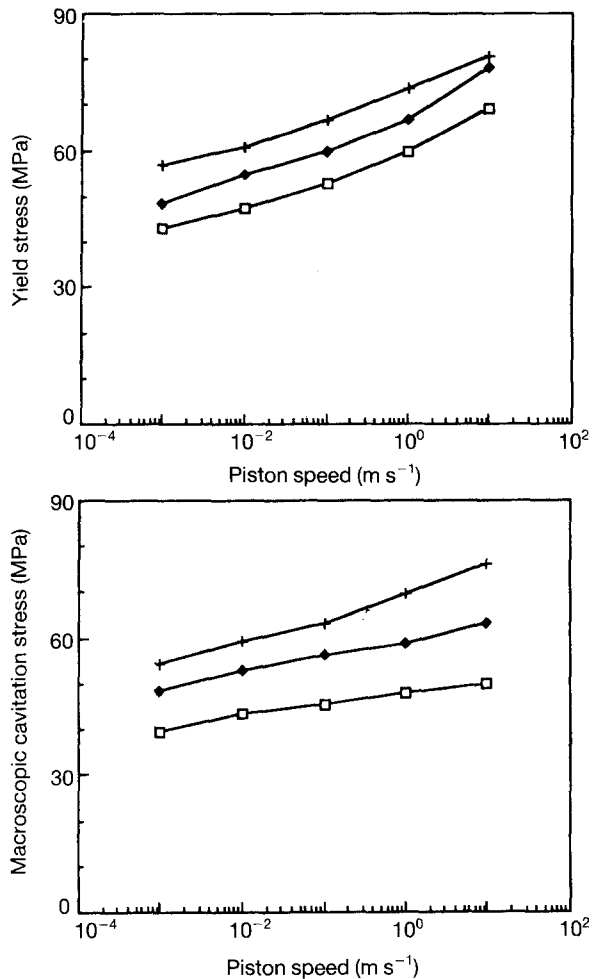


Figure 4 The yield and macroscopic cavitation stress versus the piston speed for the blends given in Table I for the following impact modifiers: (+) PE, (◆) EPDM, and (□) BR.

It is notable that the yield stress is also dependent on the type of impact modifier used. This effect has already been mentioned by Borggreve and co-workers [13] but no special attention was paid to this remarkable point. Until now, it has commonly been believed that when the ratio of the moduli of the dispersed phase and the matrix are below 0.1, there will not be a significant difference between a rubber-modified and a completely voided system [15]. When the rubber volume fraction and the rubber particle size are constant, this would mean that the yield stress should be independent of the mechanical properties of the elastomer. Dijkstra and ten Bolscher [2], however, demonstrated that this only holds when the rubber is under a plane stress. From finite-element calculations it was concluded that with additional uniaxial loading and a plane-strain condition cavitation increased the von

Mises stress around a particle significantly. This indicates that, at least for the nylon-6/PE and nylon-6/EPDM blends, a plane-stress assumption does not hold, even when the loading is uniaxial.

For two of the three blends tested, the macroscopic cavitation strain was also determined, the results are given in Fig. 5. It can be seen that this macroscopic cavitation strain decreased for both blends with increasing draw speed. The reason for this behaviour is not yet clear.

When the yield stress and the macroscopic cavitation stress are plotted as a function of the storage

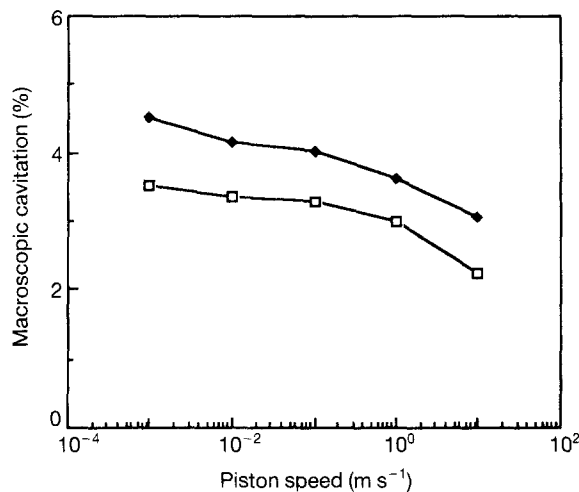


Figure 5 The macroscopic cavitation strain versus the piston speed for the blends given in Table I for the following impact modifiers: (◆) EPDM, and (□) BR.

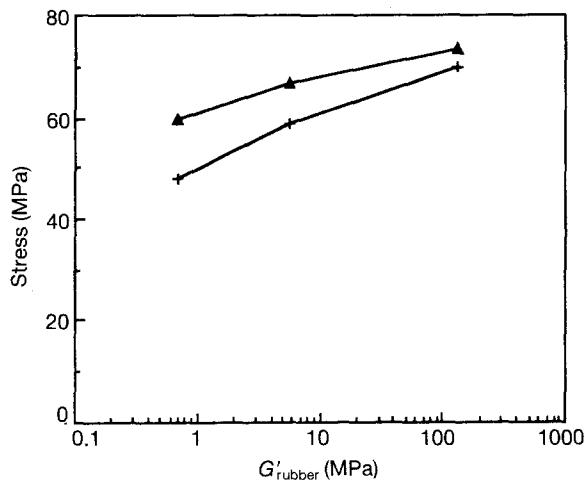


Figure 6 The macroscopic cavitation stress and yield stress versus the storage modulus (measured at 1 Hz and 20°C) of the dispersed phase,  $G'_{\text{rubber}}$  for the blends given in Table I (▲) yield stress, and (+) macroscopic cavitation stress. (The piston speed was 1 m s<sup>-1</sup>.)

TABLE II An approximation of the thermal stresses in nylon-6/rubber blends (for the details, see the text)

Rubber	$K_2$ (MPa)	$\alpha_2$ ( $\times 10^{-6} \text{ K}^{-1}$ )	$\alpha_1$ ( $\times 10^{-6} \text{ K}^{-1}$ )	$\Delta T$ (K)	$\sigma_{\text{thermal}}$ (MPa)	$\sigma_{\text{cav}}$ (MPa)	$\frac{5G_2}{2\sigma_{\text{cav}}}$	$\frac{K_2}{\sigma_{\text{cav}}}$
BR	2500	150	83	40	20.1	40.22	0.04	65.1
LDPE	3500	120	83	40	15.5	47.65	6.88	73.4

modulus of the rubber, it can be seen that both increase approximately linearly with the logarithm of the modulus. Of course, the macroscopic cavitation stress given in Fig. 6 is not the real cavitation stress of the elastomer – it is the uniaxial stress the complete system is subjected to at the point of cavitation. The connection between the real cavitation stress and the macroscopic cavitation stress is dependent on two parameters.

To start with, it has been demonstrated [2] that the relationship between the stress in the rubber and the applied stress far away from the particle is determined by the bulk modulus of the elastomer. At this moment we do not have actual knowledge of the bulk moduli of the impact modifiers used. However, the bulk moduli for all polymers are of the same order of magnitude, and estimated values can be found in the literature [16]. From this, it can be concluded that the ratio of the hydrostatic stress in the particle to the remote applied stress varies from 0.42 to 0.46 when the bulk modulus is raised from 2.5 GPa (for BR) to 3.5 GPa (for LDPE) [2]. This implies that the relationship between the applied stress and the internal stress in the rubber is approximately the same for all the rubbers tested.

A second effect is that the thermal-expansion coefficient of elastomers is usually higher than that of thermoplastics. This will mean that at room temperature the rubber particles will already be subjected to a hydrostatic tension before loading. When cooling is done infinitely fast and the matrix is regarded to be infinitely stiff, the thermal stress can be calculated using

$$\sigma_{\text{thermal}} = 3K_2\Delta T(\alpha_2 - \alpha_1) \quad (2)$$

where  $K_2$  is the bulk modulus of the rubber,  $\Delta T$  is the temperature difference and  $\alpha$  is the linear thermal-expansion coefficient. The subscript 2 denotes the dispersed phase and the subscript 1 denotes the matrix. The actual values of the expansion coefficients of the rubbers used are unknown. When the values found in the literature [17] for nylon-6, LDPE and BR are used, the order of magnitude of the thermal stresses can be estimated. The results are given in Table II.

In the results given in Table II it is assumed that stress relaxation above the glass transition temperature ( $T_g$ ) of the matrix will be fast enough to prevent significant thermal stresses building up. Therefore,  $\Delta T$  is taken to be the difference between the glass-transition temperature of nylon-6 and room temperature. Also, with this relatively small drop in temperature, considerable thermal stresses are generated in the rubber. The stresses given in Table II are overestimated since stress relaxation will continue below  $T_g$  and

the matrix is not infinitely stiff compared to the rubber. Nevertheless, thermal stresses can play an important role in the cavitation behaviour of nylon-6/rubber blends, although it appears that the stress level is similar for the blends tested.

With these estimated values for the relationship between the applied stress and the hydrostatic stress in the rubber particles, together with the thermal stresses in the material, it is possible to calculate the real cavitation stress as a function of the applied cavitation stress using the following simple addition of stresses

$$\sigma_{\text{cav}} = \phi \sigma_{\text{cav, b}} + \sigma_{\text{thermal}} \quad (3)$$

where  $\sigma_{\text{cav}}$  is the real cavitation stress of the rubber,  $\sigma_{\text{cav, b}}$  is the macroscopic cavitation stress of the blend and  $\phi$  is the ratio between the hydrostatic stress in the rubber and the remote applied stress [2]. The results are also given in Table II, together with the value of  $5G/2$ , predicted by Gent. It is obvious that there is a large mismatch between the values predicted by Gent and the experimental data presented here. The correlation with the bulk modulus is much better; this is demonstrated in the last column of Table II, where the ratio between the bulk modulus of the rubber and  $\sigma_{\text{cav}}$  is given. This is also what might be expected since it was already demonstrated that the bulk modulus determines the magnitude of the stresses in the rubber.

## 4. Effect of the rubber volume fraction

### 4.1. Experimental procedure

The nylon-6/BR blend was prepared by diluting a 30 vol % nylon-6/BR master blend, Durethan BC303, obtained from Bayer, with Akulon M258, obtained from AKZO, to the desired rubber content. This blending was done on a Berstorff corotating twin-screw extruder with a screw diameter of 25 mm and an  $L/D$  of 33. The extrusion conditions were barrel temperature 260 °C; screw speed, 100 rev min<sup>-1</sup>, feeding rate, 2 kg h<sup>-1</sup>.

Dumbbell-shaped specimens according to the ISO R527-1 standard were injection moulded on an Arburg Allrounder 221-55-250. Before testing, the specimens were dried overnight at 110 °C under a vacuum.

### 4.2. Blend morphology

The blends appeared to have a very stable morphology. The particle size for all the blends was approximately the same, with a number-average particle size,  $d_n$ , of  $0.31 \pm 0.06 \mu\text{m}$  and a weight-average particle size,  $d_w$ , of  $0.36 \pm 0.06 \mu\text{m}$ ;  $d_w/d_n = 1.16$ . Since the morphology of the master blend appeared to be very inhomogeneous, the pure BC303 was also extruded using the same extrusion conditions as the diluted

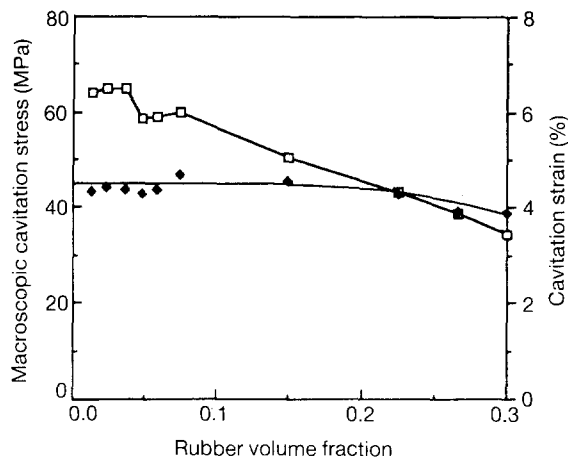


Figure 7 (□) The macroscopic cavitation stress and (◆) the cavitation strain versus the rubber volume fraction of nylon-6/BR blends. The draw speed was  $1 \text{ mm s}^{-1}$ .

blends. After this, the morphology of all the blends was comparable, and particle clustering was no longer observed.

### 4.3. Results and discussion

It can be seen in Fig. 7 that the macroscopic cavitation stress decreased with increasing rubber content. This might be expected, since the total stress level in the material decreased with rubber modification. More important is the fact that the cavitation strain stays approximately constant and it only seems to decrease a little at high rubber contents. This is in agreement with the conclusions of Borggreve *et al.* [13] who also found that the cavitation strain was independent of the rubber content. A constant cavitation strain implies a constant real cavitation stress; apparently the stress in the rubber phase only gets a little higher with high volume fractions of rubber. It seems that only at the high rubber concentration the cavitation of a particle is influenced by a (cavitated) neighbouring particle and this then due to stress-field overlap.

## 5. Cavitation and yield in nylon-6/EPR blends with an extremely small particle size

### 5.1. Introduction

The rubber particle size is an important parameter in the impact behaviour of rubber-toughened nylon. Borggreve *et al.* [18] showed that the brittle-to-tough transition temperature,  $T_{BT}$ , decreased linearly with the particle size while the impact level in the tough and brittle region was unaffected by the particle size. In the work of Borggreve an under limit for the particle size was not reached. It was also shown by Borggreve that the yield stress and the cavitation strain were independent of the particle size for low deformation rates [13].

More recently however, Oostenbrink *et al.* [19] prepared blends of nylon-6 with an EPR which could be very easily dispersed in nylon-6. They prepared blends with extremely small rubber particle sizes and found that below a certain critical particle size  $T_{BT}$  increased again and that the impact strength

in the tough region decreased again. The weight-average critical particle diameter was found to be  $0.2 \mu\text{m}$ . This was confirmed in a more recent article by Oshinski *et al.* [20].

As a possible explanation for this behaviour, it was postulated that very small particles cavitate at higher stresses than larger particles. Gent and Tompkins [3] indeed predicted that for small inclusions the surface energy effects will become important. When some of the particles do not take part in the impact mechanism, the effective rubber content will decrease, with a consequent rise in  $T_{BT}$ . The data of Gent and Lindley [8], however, suggests that surface-energy effects are already important in rubber specimens with dimensions three orders of magnitude above the critical particle size.

In order to check the hypothesis that the cavitation stress of blends with very small particles is higher than the cavitation stress of blends with a particle size above the critical size, blends of nylon-6/EPR were prepared with various particle sizes by varying the extrusion conditions. The results of the cavitation measurements are presented here.

### 5.2. Experimental procedure

The nylon-6 used was an injection-moulding grade, type Akulon K124, obtained from AKZO. The relative viscosity in 96%  $\text{H}_2\text{SO}_4$  was 2.4, the density  $\rho = 1.14 \text{ g ml}^{-1}$ . The impact modifier was an ethylene-propylene (75/25 wt %) copolymer, type VA1801, supplied by Exxon. The rubber was modified with 0.7 wt % maleic anhydride; the density of the rubber was  $0.89 \text{ g ml}^{-1}$ .

The blends were prepared on a Berstorff corotating twin-screw extruder with a screw diameter of 25 mm and an  $L/D$  of 33. The extruder consisted of seven zones and feeding of the rubber and nylon granules was possible at the first and the fifth zone. The extrusion conditions were varied to change the rubber particle size. The feeding rate was  $2 \text{ kg h}^{-1}$  for all blends.

Dumbbell-shaped specimens (according to R527-1) were injection moulded on an Arburg Allrounder 221-55-250. Before testing, the specimens were dried at  $110^\circ\text{C}$  under a vacuum overnight.

### 5.3. Blend morphology

It can be seen in Table III that the EPR, despite the relative low melt viscosity of the nylon-6 used, dispersed very easily. Also, under very mild extrusion conditions the particle size was still submicrometre. With the extreme extrusion conditions, a weight-average particle size of  $0.15 \mu\text{m}$  was obtained. This value may, however, have been overestimated, since it is possible that the extremely small particles ( $< 10 \text{ nm}$ ) could not be seen on the micrographs.

### 5.4. Results and discussion

From Fig. 8 it follows that the two blends with the larger particles both had the same macroscopic

TABLE III The extrusion conditions and the blend morphology of the nylon-6/EPR blends

Blend code	Rubber content (vol %)	Extrusion conditions			Blend morphology		
		$T$ (°C)	Screw speed (rev min <sup>-1</sup> )	Feeding zone	$d_n$ (μm)	$d_w$ (μm)	$d_w/d_n$
A1	24.3	240	400	1	0.13	0.15	1.12
A2	24.3	290	400	5	0.21	0.26	1.22
A3	24.3	290	100	5	0.25	0.32	1.26

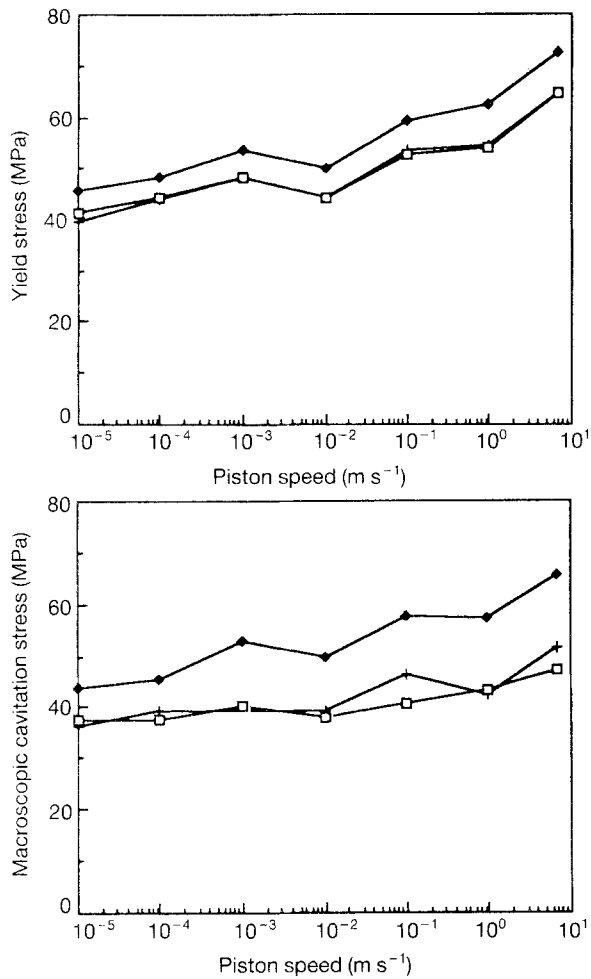


Figure 8 The yield and cavitation stress for 20 wt % nylon-6/EPR blends with different particle sizes: (◆)  $d_w = 0.14 \mu\text{m}$ , (+)  $d_w = 0.25 \mu\text{m}$ , and (□)  $d_w = 0.32 \mu\text{m}$ .

cavitation and yield stress. The blend with  $d_w < d_{w, \text{crit.}}$ , however, had a higher macroscopic cavitation stress and a higher yield stress than the two blends with  $d_w > d_{w, \text{crit.}}$ . These results are in agreement with the results given earlier in this paper that a higher cavitation stress of the dispersed phase leads to a higher yield stress of the blend.

The range of particle sizes studied was too small to be able to draw strong conclusions. The results, however, indicate that the poor impact behaviour of nylon-6/rubber blends is indeed caused by the fact that very small particles cavitate at higher stresses than larger particles.

### 5.5. TEM studies on nylon-6/BR blends

Using scanning electron microscopy (SEM), it was not

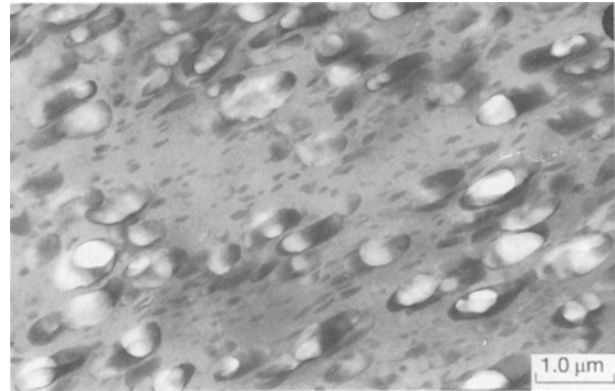


Figure 9 A TEM micrograph of a deformed nylon-6/BR blend (15 vol %). The poly(butadiene) was stained with  $\text{OsO}_4$  (micrograph by H. Janik).

possible to estimate the size below which the particles did not cavitate. Therefore, transmission electron microscopy (TEM) studies were performed on deformed nylon-6/BR blends. Poly(butadiene) was chosen as the impact modifier for these studies instead of the EPR which was used in Section 5.4. This was done because it is much easier to stain poly(butadiene), due to its higher unsaturation (compared to EPR).

For the TEM studies, samples were taken from nylon-6/BR (15 vol %) specimens which were deformed under impact conditions (with a draw speed of  $1 \text{ m s}^{-1}$ ) in a notched tensile-impact test [21]. The sample preparation is described elsewhere [22]. From these samples, slices were cut using a CryoNova LKB 2288-050 cryotome. The specimen temperature during microtoming was  $-120^\circ\text{C}$  and the knife temperature was  $-100^\circ\text{C}$ . The poly(butadiene) was stained with  $\text{OsO}_4$ ; the staining procedure is described elsewhere [23].

A micrograph of the deformation zone is shown in Fig. 9. There is a clear distinction between the matrix, the rubber particles and the voids. It is clear that voids are only present in the larger particles. The very small particles appear to be elongated, but no cavities can be seen in these particles. From Fig. 8 it can be estimated that particles with a particle size below  $0.2 \mu\text{m}$  have not cavitated.

## 6. Conclusions

A new method for determining the cavitation stress of nylon/rubber blends has been described. It has been possible to use the test set-up to measure macroscopic

cavitation stresses over a broad range of strain rates. The cavitation stresses measured were reproducible within 5% of the mean value.

It has been demonstrated that, under uniaxial loading, cavitation of the dispersed phase is able to reduce the yield stress significantly. A consequence of this is that blends with an impact modifier with a high cavitation stress show a higher yield stress than blends with rubbers which easily cavitate. The measured cavitation stresses did not track with the shear modulus but seemed to correlate with the bulk modulus. The number of rubbers tested, and the absence of exact data for bulk moduli and thermal-expansion coefficients make it impossible to draw strong conclusions at this point.

The results of the cavitation tests on blends with different particle sizes indicate that the poor impact behaviour of blends with very fine dispersions is caused by the higher cavitation stress of extremely small particles. TEM studies on deformed nylon-6/BR blends supported the hypothesis that very small particles do not cavitate.

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