Toughening behaviour of rubber-modified thermoplastic polymers involving very small rubber particles: 1. A criterion for internal rubber cavitation

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The criteria for internal cavitation of rubber particles have been evaluated. It is shown that internal rubber cavitation can be considered as an energy balance between the strain energy relieved by cavitation and the surface energy associated with the generation of a new surface. The model predicts that there exists a critical particle size for cavitation. Very small particles (100–200 nm) are not able to cavitate. This critical-particle-size concept explains the decrease in toughening efficiency in different rubber-modified systems involving very small particles.

(Keywords: rubber toughening; particle size; rubber cavitation)

INTRODUCTION

Many glassy polymers are brittle. For structural applications, this is clearly unwanted and it is well known that the impact properties can be improved by the incorporation of a dispersed elastomeric phase[1,2]. The mechanism by which the toughness is enhanced depends on the intrinsic ductility of the matrix material and on the morphology of the blends[3]. For example, in brittle polymers such as polystyrene (PS) and poly(styrene-*co*-acrylonitrile) (SAN), the rubber particles promote crazing in the matrix, whereas in pseudoductile polymers, such as polycarbonate (PC), poly(vinyl chloride) (PVC) and polyamides, shear yielding is usually the major energy absorbing mechanism.

Under triaxial tensile stress states at low temperatures or high strain rates, the generation of voids within the material is inevitable. Macroscopically, this is manifested by the phenomenon of stress-whitening. In rubber-modified materials under triaxial tensile stresses, voiding can occur in the matrix (multiple crazing in high impact polystyrene (HIPS)) or can initiate inside the rubber particles (rubber cavitation). Once the rubber particles are cavitated, the hydrostatic tension in the material is relieved, with the stress state in the thin ligaments of matrix material between the voids being converted from a triaxial to a more uniaxial tensile stress state. This new stress state is favourable for the initiation of shear bands. In other words, the role of the rubber particles is to cavitate internally, thereby relieving the hydrostatic tension and initiating the ductile shear yielding mechanism.

Many examples are mentioned in the literature to support this concept. The process of rubber cavitation and associated matrix shear yielding is found in rubber-modified PC[4–7], PVC[8–10], poly(butylene terephthalate (PBT)[11], nylon-6[12–15], nylon-6,6[16] and epoxy systems[17–20]. The matrix polymers in these rubber-modified systems are either crosslinked or have a high entanglement density, thus being polymers for which the crazing mechanism is suppressed[21]. This is not to say that rubber cavitation can only appear in high-entanglement-density matrices. A recent paper[7] reveals that rubber cavitation can occur in HIPS to a very large extent, but this does not lead to matrix shear yielding. At first sight, rubber cavitation thus seems only necessary in matrices with a high entanglement density, where it is needed for the promotion of shear yielding.

The ultimate mechanical properties of the material will depend on the blend morphology. Wu established that for blends with pseudoductile matrices the brittle–tough transition occurs at a critical interparticle distance[22]. The average value of the interparticle distance can be calculated for a monomodal particle size distribution by assuming that the particles are arranged as in a cubic lattice. The interparticle distance (*IPD*) is then related to the rubber particle size (d_0) and the rubber volume fraction (Φ_r) by the following:

$$IPD = d_0\left[\left(\frac{\pi}{6\Phi_r}\right)^{1/3} - 1\right] \tag{1}$$

In other words, the critical interparticle distance is the critical morphological parameter controlling the toughness in rubber-modified pseudoductile matrices. The percolation concept is the physical explanation behind this equation[3,23]. If the rubber particles are able to cavitate internally and if the generated voids are close enough, then the thin matrix ligaments between the

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particles will yield locally. When all of the thin matrix ligaments are interconnected, the yielding process propagates over the entire deformation zone and the blend is ductile. This happens when the ligament thickness is smaller than the critical interparticle distance. For a given volume fraction, this is achieved by decreasing the particle size and by improving the dispersion. For most systems, this concept works very well and a decrease in particle size corresponds to a shift in the brittle–tough transition to lower temperatures[15,22]. However, it has been found in a number of systems[8,12,24–28] that there exists a minimum particle size below which the brittle–tough transition no longer shifts to lower temperatures. As a possible explanation for this peculiar behaviour, it has been suggested that particles which are too small are not able to cavitate.

In order to determine whether this could be true, and also because of the importance of rubber cavitation as a precursor for ductile behaviour, the criteria for rubber cavitation are evaluated in this paper. The model explains the increasing resistance against cavitation with decreasing rubber particle size. The consequences for the toughness of blends with pseudoductile matrices with very small particles are discussed. The following paper[28] experimentally verifies the model on a rubber-modified PVC system by determining the strain at which cavitation occurs and by correlating this quantity to the toughening behaviour of the blend.

A MODEL FOR RUBBER PARTICLE CAVITATION

The phenomenon of rubber failure in bulk samples was treated by Gent and coworkers[29,30]. They assumed that failure in bulk rubber samples takes place as the result of elastic expansion of precursor cavities. Under the assumptions of rubber elasticity, a spherical cavity with a size between 0.5 μm and 1 mm expands to an indefinitely large size under an inflating pressure of $5G/2$, with G being the shear modulus. This pressure is higher for smaller precursor void sizes.

In rubber-modified systems with second-phase particle sizes sometimes of the order of 0.1 μm, precursor cavities of the order of 1 μm evidently do not occur. A different approach to the understanding of cavitation in these particles is therefore required. The model outlined below is based on the following assumptions. The rubber particles are spherical in shape with a diameter d_0 and the largest defects in these particles are of the order of a few nanometres. Failure will then initiate from local inhomogeneities on a molecular scale, such as local differences in the crosslinking density. Furthermore, it is assumed that internal rubber cavitation is an instantaneous process, as shown schematically in *Figure 1*, with the hydrostatic tension on the particle as the driving force for cavitation. Consequently, rubber cavitation will occur when the total energy associated with the process (U_{total}) decreases. The criterion for rubber cavitation is then given by the following energy balance equation:

$$U_{\text{total}} = U_{\text{strain}} + U_{\text{surface}} < 0 \qquad (2)$$

where U_{strain} is the elastic strain energy stored in the rubber particle under the applied stress and U_{surface} is the surface energy associated with the cavitation. This equation means that rubber cavitation will only be initiated if the energy gained by relieving the stress (U_{strain}) is greater than the energy needed to create a new surface (U_{surface}).

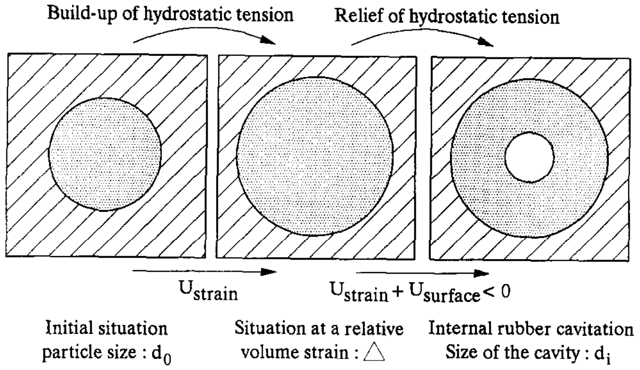

Figure 1 A schematic representation of the different steps in rubber cavitation

The strain energy in one rubber particle is equal to the total work done by the external tension p during the deformation, assuming that no cavity is created:

$$U_{\text{strain}} = \int_{V_0}^{V} -p\,\mathrm{d}V \qquad (3)$$

where p is the hydrostatic pressure in the rubber particle:

$$p = K_{\text{r}}\Delta$$

where K_{r} is the rubber bulk modulus and $\Delta(=\Delta V/V_0)$ is the relative volume strain ($V_0 = \pi d_0^3/6$). Equation (3) can thus be written as:

$$U_{\text{strain}} = \int_{V_0}^{V} -p\,\mathrm{d}V = -K_{\text{r}}V_0\int_0^{\Delta}\Delta\,\mathrm{d}\Delta = -\frac{\pi}{12}K_{\text{r}}\Delta^2 d_0^3 \qquad (4)$$

The strain energy stored in the rubber particle is thus determined by the rubber particle size (d_0), the rubber bulk modulus (K_{r}) and the relative volume strain (Δ). This energy term is negative, indicating that it will be relieved when cavitation occurs.

However, the formation of a void in the rubber particle, as shown in *Figure 1*, requires surface energy, which is given by:

$$U_{\text{surface}} = \Gamma \pi d_{\text{i}}^2 \qquad (5)$$

where d_{i} is the void diameter and Γ is the surface energy per unit area. The internal void diameter (d_{i}) is related to the particle diameter (d_0) and to the relative volume strain (Δ) by:

$$\frac{\left(\frac{\pi}{6}\right)d_{\text{i}}^3}{\left(\frac{\pi}{6}\right)d_0^3} = \Delta V/V_0 = \Delta$$

$$d_{\text{i}} = \Delta^{1/3} d_0 \qquad (6)$$

To a first approximation, the forces of interest on the void surface are the van der Waals intermolecular forces. As a consequence, the corresponding void surface tension is given by $\Gamma = \gamma_{\text{r}}$, where γ_{r} is the van der Waals surface tension of the rubber. However, this approximation is only true when the rubber particle is a liquid. Most rubbers are chemically crosslinked and the generation of a new surface requires the scission of a certain number of skeletal bonds, which is largely determined by the crosslinking density (ν_x) of the rubber. The energy per unit area, associated with chain scission is then[21]:

$$\Gamma_{sc}=\tfrac{1}{4}d\nu_x U \qquad (7)$$

where d is the mesh size of the network between the crosslinks or the root-mean-square end-to-end distance between the crosslinks in the network, ν_x is the crosslinking density, expressed as the number of crosslinks per cubic metre and U is the polymer backbone bond energy. This equation is analogous to the equation for the surface energy term in the crazing of thermoplastics[21]. However, in the latter the physical entanglements play the same role as the crosslinks. In rubbery materials, one can neglect the physical entanglements; the chains will disentangle rather than break and the average force on them will be negligible when compared to the breaking force. This assumption is only valid for 'true' rubbers with a low shear modulus ($G_r \sim 1$ MPa); for polyethylene (PE) for example, with a shear modulus of the order of 100 MPa, the average force on the chains is not negligible, and the total energy required to create the surface energy will be higher. Neglecting this contribution in the present analysis, the surface energy per unit area is then given by the following:

$$\Gamma=\gamma_r+\Gamma_{sc}=\gamma_r+\tfrac{1}{4}d\nu_x U \qquad (8)$$

It should be mentioned here that the crosslinking density in rubbery materials is often of the order of 10^{26} crosslinks per cubic metre[31]. In that case, the contribution from chain scission is of the same order of magnitude as the contribution from the van der Waals surface tension ($\gamma_r \sim 0.035\,\mathrm{J\,m^{-2}}$).

Combining equations (2), (4), (5), (6) and (8), the condition for internal rubber cavitation can be written as follows:

$$\begin{aligned} U_{total} &= U_{strain}+U_{surface} \\ &= -\frac{\pi}{12}K_r\Delta^2 d_0^3+(\gamma_r+\Gamma_{sc})\pi\Delta^{2/3}d_0^2<0 \qquad (9) \end{aligned}$$

This relationship predicts rubber cavitation for a given relative deformation (Δ), and from the elastic properties of the rubber (rubber bulk modulus, K_r), the molecular characteristics of the rubber (γ_r, ν_x, U) and the rubber particle size (d_0).

DISCUSSION

Critical particle size concept

The different energy terms associated with rubber cavitation are depicted in *Figure 2* as a function of the particle diameter for a model system having the following characteristics: $K_r=2$ GPa, $\gamma_r=0.035\,\mathrm{J\,m^{-2}}$ and $\Gamma_{sc}=0.035\,\mathrm{J\,m^{-2}}$, at a relative volume strain of $\Delta=0.0128$. The relative volume strain was taken as the product of $(1-2\nu_m)\varepsilon$ where ν_m is the Poisson ratio of the glassy matrix, which for many polymers is ~ 0.42[32], and where ε is the longitudinal strain, which is typically 0.08 at the yield point. The relative volume strain of $\Delta=0.0128$ can thus be considered as an upper limit if cavitation has to occur prior to matrix yielding.

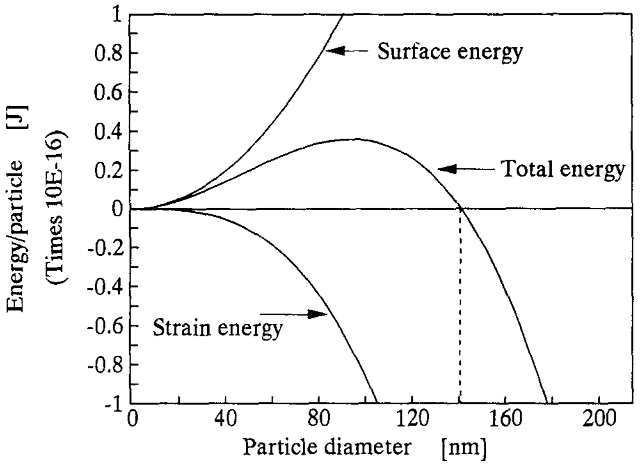

Figure 2 The strain energy, surface energy and total energy associated with internal rubber cavitation as a function of particle diameter (see equation (9)) for a model system with the following parameters: $K_r=2$ GPa, $\gamma_r=0.035\,\mathrm{J\,m^{-2}}$ and $\Gamma_{sc}=0.035\,\mathrm{J\,m^{-2}}$, at a relative volume strain of $\Delta=0.0128$

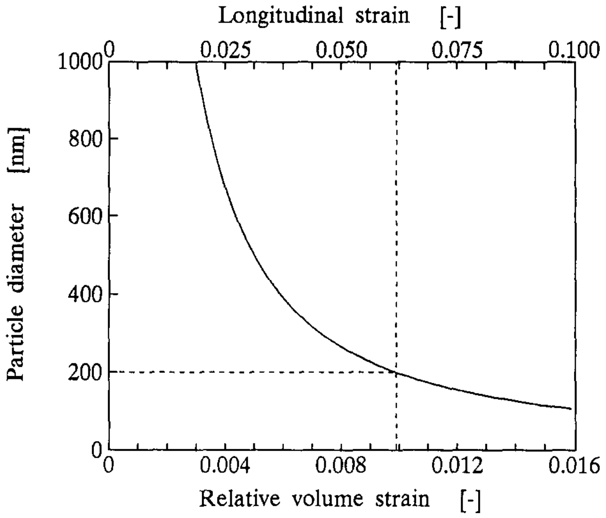

Figure 3 Relationship between the minimum particle diameter required for cavitation and the relative volume strain (Δ) for a model system with the following parameters: $K_r=2$ GPa, $\gamma_r=0.035\,\mathrm{J\,m^{-2}}$ and $\Gamma_{sc}=0.035\,\mathrm{J\,m^{-2}}$. The upper horizontal axis denotes the longitudinal strain in a uniaxial tensile test assuming a Poisson ratio for the material of 0.42, while the dotted lines are the critical conditions corresponding to a particle size of 200 nm and a relative volume strain of 1%

As can be seen from *Figure 2*, our model calculation indicates that the total energy for internal cavitation ($U_{total}<0$) is negative for particles with a diameter larger than 140 nm. The release of the strain energy for particles smaller than 140 nm is lower than the surface energy required to create the void. Therefore, particles smaller than 140 nm are expected not to cavitate at a relative volume strain of 0.0128 or lower.

The condition for particle cavitation is dependent on the relative volume strain. The relation between the particle size required for cavitation and the applied relative volume strain can be found by rearranging equation (9) as follows:

$$d_0=\frac{12(\gamma_r+\Gamma_{sc})}{K_r\Delta^{4/3}} \qquad (10)$$

and is depicted in *Figure 3*, based on the same material parameters as mentioned earlier. Equation (10) predicts that large particles will cavitate in the early stages of the deformation process, while small particles will cavitate at a later stage. In other words, the cavitation resistance of the particle increases with decreasing particle size. The minimum particle size for cavitation (140 nm at $\Delta = 0.0128$) therefore depends on the maximum relative volume strain that can be reached in the material. For example, at a relative volume strain of 1%, the critical particle size for cavitation is 200 nm; this case is shown in *Figure 3* by the dashed lines. In pseudoductile matrices, the maximum relative volume strain equals the relative volume strain where crazing is initiated in the matrix, since this leads to rapid and brittle failure of the sample.

Although the absolute value of the minimum particle diameter required for cavitation might be questioned, it is still expected that the critical particle size is within the same order of magnitude for many different rubber-modified thermoplastic polymers, since the molecular parameter (γ_r, Γ_{sc}), the rubber modulus (K_r) and the glassy matrix Poisson ratio (ν_m) are fairly constant for different systems. The observations reported in the literature on rubber-modified systems dealing with very small rubber particles indicate that this is indeed the case; they will be briefly discussed later. The experimental verification of the criterion for rubber cavitation on a rubber-modified PVC system is given in the following paper[28].

One of the first studies dealing with very small rubber particles was made by Sultan and McGarry[17] on a blend of butadiene-*co*-acrylonitrile (CTBN) elastomer particles suspended in a crosslinked epoxy matrix. At a rubber particle size of ~40 nm, the plastic deformation, the fracture toughness and the mechanical properties in uniaxial and biaxial tests appeared to be very similar to the unmodified matrix material. On the other hand, in the CTBN/epoxy blends with a rubber particle size of ~1200 nm, yielding was reached at a lower stress level, the fracture toughness increased considerably, and the material whitened, while scanning electron microscopy revealed cavity formation at the rubbery particle sites. These data confirm that for particle cavitation with associated yielding and ductile behaviour, the particle size needs to have a minimum value.

The effect of rubber particle size on the cavitation behaviour was also studied on blends of PVC with methyl methacrylate–butadiene–styrene (MBS) graft copolymers by Breuer *et al.*[8], using transmission electron microscopy. The electron micrographs of the stress-whitened zones obtained from a uniaxial tensile test at a strain rate of $1\,\mathrm{m\,s^{-1}}$ revealed that MBS rubber particles with a size of 160 nm or larger showed internal cavitation, while only a few cavities were found in the blend with a particle size of 80 nm. The Izod impact strength of PVC/MBS blends was also investigated[27]. It was found that the impact resistance increases considerably with increasing particle size, up to a particle diameter of 200 nm. Similarly, in a blend of PVC with polybutadiene as the dispersed elastomeric phase (particle sizes in the range from 70 to 450 nm), a maximum in the Izod impact strength was observed in the rubber particle size range from 150 to 200 nm[26].

Borggreve *et al.* showed that the brittle–tough transition temperature in rubber-modified nylon-6 decreased with decreasing particle size, in agreement with the critical interparticle distance concept[15]. This observation was confirmed in a study on nylon-6 which had been blended with maleic anhydride modified ethylene-*co*-propylene rubber (EPR-*g*-MA)[24]. However, in the latter study, the particle size was further decreased down to 100 nm. At very low particle sizes, i.e. below 200 nm, it was observed that the impact strength decreases sharply with decreasing particle size and approaches the value of the unmodified semicrystalline nylon-6 matrix.

The lower limit on particle size for the toughening of nylon-6 was also found in a study on nylon-6 blended with mixtures of styrene–(ethylene-*co*-butylene)–styrene (SEBS) and a maleic anhydride functionalized copolymer (SEBS-*g*-MA)[25]. By varying the ratio of the latter two components, the particle size of the elastomeric phase in the blend could be varied. The critical particle size for toughening was found to be ~250 nm.

Unmodified poly(methyl methacrylate) (PMMA) is a brittle material that deforms by crazing. However, rubber-toughened PMMA deforms by shear yielding. From the relatively low intrinsic brittleness of the matrix (characteristic chain ratio, $C_\infty = 7.9$ for PMMA[3]), it can be understood that the hydrostatic tension required for rubber cavitation can be lower than the hydrostatic tension required for the initiation of crazing in the matrix. Once the rubber particles have been cavitated, the hydrostatic tension in the material is relieved, and shear yielding is induced. Accordingly, a minimum particle size for toughness in this system is expected. The toughening of PMMA with very small particles of a butylacrylate-*co*-styrene crosslinked copolymer (P(BA-*co*-St)) was recently investigated[33]; a lower size limit of 200–250 nm for the toughening of this system was found.

The data presented by Wu[3] on the notched Izod impact toughness of PMMA/rubber blends with 20 wt% rubber might be reconsidered in the light of these ideas. Wu found that the notched Izod impact strength is nearly the same as that of unmodified PMMA (~$16\,\mathrm{J\,m^{-1}}$) when the rubber particle diameter is smaller than 100 nm, or larger than 500 nm. The toughness reaches a maximum at 250 nm. The notched Izod impact strength of rubber-modified PMMA with 20 wt% rubber, as a function of the rubber particle size[3], is shown in *Figure 4*. The critical particle size for cavitation appears to be 200 nm, in accordance with the observation on the PMMA/P(BA-*co*-St) system[33]. Below this limit the toughening efficiency of the rubber is practically zero. Because rubber-modified PMMA deforms by shear yielding, the upper limit should be in accordance with the critical interparticle distance

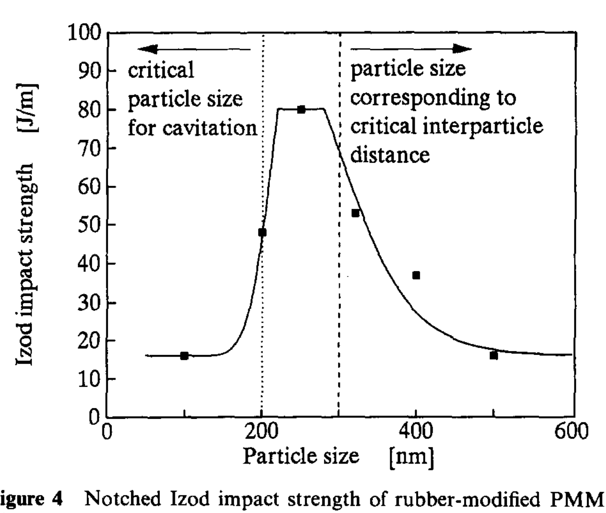

Figure 4 Notched Izod impact strength of rubber-modified PMMA with 20 wt% rubber as a function of the rubber particle size; the critical particle size (200 nm, ...) is shown as the dotted vertical, while the particle size estimated from the critical interparticle distance concept (300 nm, – – –) is shown as the dashed vertical line (data taken from ref. 3)

concept. According to Wu[3], this critical interparticle distance (IPD_c) is related to the characteristic chain ratio of the matrix (C_∞) by the following:

$$\log(IPD_c(\text{in } \mu\text{m})) = 0.74 - 0.22C_\infty \qquad (11)$$

With $C_\infty = 7.9$ for PMMA, one obtains a critical interparticle distance of 100 nm. Together with equation (1) and a volume fraction (Φ_r) of 0.22 (the bulk density of PMMA is $1.17\,\text{g cm}^{-3}$ which is about 20% higher than that of most rubbery materials), the corresponding critical particle size is 300 nm. Both the critical particle size and the critical interparticle distance concepts are indicated by the vertical lines in *Figure 4*. It can be seen that they predict the Izod impact data with great accuracy. Since the dispersed rubber particles toughen the PMMA matrix by changing the deformation mechanism from crazing to shear yielding, we therefore believe that both the critical particle size concept and the critical interparticle distance concept should be used to explain the observed optimum in the curve of *Figure 4*. This is further supported by the observation that even rubber-modified PS tends to deform by shear yielding under the condition where the interparticle (intervoid) distance is below the critical value, as given by equation (11)[34].

The toughness of the different rubber-modified systems (PVC, PMMA, nylon-6) all seem to indicate a universal range of values for the critical particle size for cavitation of 100–200 nm. Although more accurate measurements might show small differences between the different systems, this seemingly universal critical particle size of 200 nm is really not surprising. The value of 200 nm is clearly expected on the basis of equation (9) and by also knowing that the molecular parameters (γ_r, Γ_{sc}), the rubber bulk modulus (K_r) and the glassy matrix Poisson ratio (ν_m) are fairly constant for different systems.

The cavitation resistance of the rubber modifier

The relationship between the resistance against cavitation and the particle size (see *Figure 3*) was used indirectly to explain the effect of very small particles on the toughness in different systems. Direct measurements of the cavitation strain have only been performed in a limited number of systems[4,7,10,12,14].

Borggreve *et al.* measured the cavitation strain in a uniaxial tensile test using tensile dilatometry[14]. It was observed that the brittle–tough transition temperature in a notched Izod impact experiment for the different nylon/rubber blends that were studied showed a correlation with the cavitation strain of the rubber modifier, despite the fact that both quantities are measured at a very different strain rate and stress state. The brittle–tough transition decreases and the impact behaviour improves unequivocally as the strain, at which voiding in the blend starts, decreases. This justifies our earlier comments relating particle size with toughness through the cavitation strain (*Figure 3*). Borggreve *et al.* also investigated the effect of the particle size on the cavitation strain in blends of nylon-6 with EPR[14]. It was found that the strain at which rubber cavitation initiates is not affected by the particle size. This observation was later contradicted by Dijkstra who measured the cavitation strain in a different way[12]. The experimental set-up was based on the principle that cavitation in a blend is accompanied by stress-whitening, so that the intensity of a continuously transmitted (laser) light source will suddenly drop due to the scattering of the cavitated particles. In a study on nylon-6/EPR blends, Dijkstra observed that the cavitation resistance in a blend with a rubber particle size of only 150 nm is substantially higher than that in blends with a particle size of ~300 nm[12]; a critical rubber particle size for cavitation of 200 nm was proposed. This critical particle size was further confirmed by a TEM study on a nylon-6/polybutadiene blend deformed under impact conditions; the resulting micrographs showed that particles with a particle diameter below 200 nm had not cavitated.

In translucent blends, the initiation of rubber cavitation can also be determined by viewing at stress-whitened zones using an optical microscope. This technique was used to determine the criterion for cavitation in blends of PVC with chlorinated polyethylene (CPE)[10]. It was found in this study that the controlling parameter for cavitation is the critical volume strain in the material. In accordance with the criterion for internal rubber cavitation as stated here, stress-whitening occurred when the critical volume strain (Δ) was reached. This quantity was found to be independent of composition and temperature, and had a value of 0.008 in the blend studied. Unfortunately, the CPE particle size was not given.

The technique of optical microscopy to examine the stress-whitened zones was also applied on rubber-modified polycarbonate (PC)[4]. The cavitation resistance of two core–shell modifiers was compared in specimens under a pronounced triaxial stress state. The first modifier (with a particle size of 600 nm) was found to cavitate at a low hydrostatic tension. The second modifier (with a particle size of 200 nm) required a much higher critical hydrostatic stress for cavitation; immediately after cavitation however, the PC matrix started to deform by shear yielding. This indicates again that the critical size for cavitation is ~200 nm in rubber-modified PC. If the particle size had been decreased still further, then voiding in the matrix (crazing), instead of in the rubber particle, might have been the result.

Driving factor for cavitation

So far, it has been shown that the critical particle size for cavitation is around 200 nm and that the driving factor behind cavitation is the volume strain (Δ) applied on the particle. The examples mentioned above deal with 'true' rubbery materials with a Young's modulus (E_r) of ~1 MPa and a Poisson ratio (ν_r) of 0.5. It is tempting to see whether this criterion also holds for polymeric materials with a rubber-like behaviour but with a significantly higher Young's modulus, such as polyethylene (PE) for example. As the Poisson ratio of the second-phase particle decreases towards the Poisson ratio of the matrix, the driving force for cavitation diminishes and Δ should therefore be rewritten as follows:

$$\Delta = (2\nu_r - 2\nu_m)\varepsilon \qquad (12)$$

with

$$\nu_r = 0.5 - \frac{E_r}{6K_r} \qquad (13)$$

where K_r is fairly constant for different polymers. With a decreasing difference in the Poisson ratio between matrix and particle, the hydrostatic stress on the particle decreases and cavitation may be retarded. This was also concluded by Huang and Kinloch using numerical finite element analysis[18]. Moreover, Borggreve *et al.*, in their study on nylon-6/rubber blends with different rubbery material properties, also used the Poisson ratio of the rubbery material to explain the high cavitation strain in nylon-6/PE and in nylon-6/Arnitel blends[14]. However, the variation in the Poisson ratio resulting from a change in the Young's modulus is usually very small. When E_r is varied from 1 to 100 MPa, ν_r changes from 0.4999 to 0.49. This decrease in the Poisson ratio is too small to account for the observed increase in cavitation strain in the nylon-6/PE and nylon-6/Arnitel blends[14]. In addition to the Poisson ratio effect, the elastomeric phase of a high modulus material immediately around an initiating cavity experiences a pronounced biaxial tension for which the energy will be proportional to the rubber shear modulus (G_r) via the equation for rubber elasticity. In 'true' rubbery materials, the chains will disentangle immediately so that this contribution can be neglected. When the shear modulus is high, then the average force on the chains during disentanglement is not negligible and an extra term should be added to the equation for the surface energy (equation (8)). Both the decreasing Poisson ratio, as well as the more notable increase in surface energy, can explain the exceptionally high cavitation strain in nylon-6/PE and in nylon-6/Arnitel blends. The criterion presented in this paper is therefore not able to predict quantitatively the cavitation strain in high modulus second-phase particles.

The effect of the crosslinking density

In the model calculations shown in *Figures 2* and *3*, the contribution from chain scission in the surface energy term was treated as a constant, with a value of $\Gamma_{sc} = 0.035\,\mathrm{J\,m^{-2}}$. This value will depend on the crosslinking density (ν_x) of the rubber. Although little experimental work has been reported on the effect of crosslinking on toughening, it can be expected that crosslinks will hinder easy void formation so that the energy required to create a new surface will increase with an increasing crosslinking density.

If the crosslinking density is not too high, i.e. the chain segments show Gaussian behaviour between the crosslinks, then the network mesh size (d) can be written as follows:

$$d^2 = C_\infty N_x l_b^2 = \frac{C_\infty l_b^2 M_x}{M_0} = \frac{C_\infty l_b^2 \rho N_A}{M_0 \nu_x} \qquad (14)$$

where l_b is the bond length of one freely jointed unit, N_A is the Avogadro constant, ρ is the density of the polymer in $\mathrm{g\,m^{-3}}$, C_∞ is the Flory characteristic ratio or chain stiffness and N_x is the number of monomers between crosslinks, which is equal to M_x/M_0, with M_x being the molecular weight between crosslinks ($M_x = \rho N_A/\nu_x$) and M_0 the molecular weight of the repeat unit. The contribution from chain scission, assuming Gaussian chain segments between the crosslinks (equation (7)), can then be rewritten as follows:

$$\Gamma_{sc} = \frac{1}{4}\left(\frac{C_\infty l_b^2 \rho N_A}{M_0}\right)^{0.5} \nu_x^{0.5} U \qquad (15)$$

so that the chain scission term is found to be proportional to the square root of the crosslinking density.

The contribution from chain scission relative to the contribution from the van der Waals surface tension can be shown in a simple calculation. Let us consider a polybutadiene rubber with divinylbenzene (DVB) as the crosslinking agent. The product, $C_\infty l_b^2$ for polybutadiene can be estimated from group contribution calculations[32,35] and equals $0.204\,\mathrm{nm^2}$. If the weight fraction (x_c) of the DVB that is added is 0.01, then $\nu_x = (N_A \rho x_c)/(M_{DVB}) = 4.3 \times 10^{25}$ crosslinks per cubic metre, while if 4 wt% of DVB is added then $\nu_x = 1.7 \times 10^{26}$ crosslinks per cubic metre.

Using equation (15), the chain scission term for 1 wt% DVB in polybutadiene rubber is equal to $0.035\,\mathrm{J\,m^{-2}}$, and for 4 wt% DVB this becomes $0.071\,\mathrm{J\,m^{-2}}$. Both are to be compared with the van der Waals surface tension for polybutadiene of $0.032\,\mathrm{J\,m^{-2}}$ (ref. 32).

These basic calculations indicate that the contribution from chain scission in crosslinked rubbers cannot usually be neglected. According to equations (9) and (15), a high crosslinking density suppresses the cavitation of the particle, and as a consequence, the impact behaviour is expected to decrease. A recent study on nylon-6/styrene–butadiene–styrene (SBS) blends with different crosslinking degrees of the rubber confirms this statement[31].

CONCLUSIONS

A criterion for the internal cavitation of rubber particles was developed. The condition has been treated as an energy balance between the strain energy relieved by cavitation and the surface energy required to create a new surface. Accordingly, cavitation of the rubber is dependent on the elastic and molecular properties of the rubber, on the rubber particle size and on the applied volume strain. A critical particle size for cavitation in the range 100–200 nm is estimated.

This critical particle size is the minimum size that is required for a rubber particle to be effective in the toughening of pseudoductile matrices that deform by shear yielding. The value of 100 to 200 nm is found in rubber-modified PVC[26,27], nylon-6[24,25], PMMA[3,33] and PC[4]. On the basis of the criterion for rubber cavitation, the decrease in impact behaviour of rubber-modified systems with increasing (rubber) Young's modulus[14] and (rubber) crosslinking density[31] can be qualitatively explained.

In the following paper[28], the strain at which cavitation initiates is determined using real-time stress-whitening measurements during a uniaxial tensile experiment on transparent PVC/MBS blends. The cavitation strain as a function of particle size is then compared with the criterion for internal cavitation developed in this paper and the observation is used to explain the toughening behaviour in these blends.

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