

A model for particle cavitation in rubber-toughened plastics

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An energy-balance criterion for cavitation of rubber particles, which was proposed in an earlier paper [A. Lazzeri and C. B. Bucknall, *J. Mater. Sci.* **28** (1993) 6799], is developed by including a term for the energy stored in the matrix and released during expansion of the voids. The model relates the critical volume strain at cavitation to the radius of the rubber particle, and to the shear modulus, surface energy and failure strain of the rubber. The effects of temperature, strain rate and type of stress field upon cavitation behaviour and the resulting toughness of the two-phase polymer are discussed in terms of the model.

1. Introduction

Cavitation of the rubber particles has been observed in toughened polymers over many years. Electron microscope evidence of cavitation has been found in both thermoplastics and thermosets, including toughened grades of nylon [1–7], polystyrene [8,9], polycarbonate [10,11], PVC [12,13], epoxy [14–18] and urethane–methacrylate resin [19]. Both SEM and TEM have proved useful in studying the phenomenon. However, some commentators continue to question whether particle cavitation makes a significant contribution to the toughening mechanism and there is considerable debate about the conditions under which void formation occurs.

Several authors [8, 20, 21] have concluded that rubber particle size is one of the main factors controlling cavitation: tests on blends containing rubber particles with a range of sizes have shown that voids form preferentially in the larger particles. Recent work by Sue and Garcia-Meitin [22] on rubber toughened epoxies suggests that voids are more likely to form within rubber particles when the stress conditions are highly triaxial, as they are near crack tips, and that cavitation will not take place before a certain volume strain is reached. Similar results have been reported for other matrix–rubber systems, including PC/MBS [10], PC/PE [11], nylon-6,6/olefin rubber [3] and PVC/CPE [13]. From the mean stress and bulk modulus, Tse *et al.* [13] also calculated a critical volume strain for stress whitening, which was independent of composition and temperature; however, they gave no information about rubber particle size.

Lazzeri and Bucknall [20] have recently developed a new treatment of rubber particle cavitation based on an energy-balance approach. An outline of their model is given below. The underlying principle is that the particle will cavitate when the energy released during cavitation is greater than the energy needed to form the void. In the original analysis, only energy stored within the particle itself was taken into account

and no allowance was made for work done by the matrix as the void expanded. This paper considers the effect of introducing additional terms for the energy input from the matrix and surroundings and examines the relationship between cavitation resistance and the properties of the rubber, as predicted by the model.

2. Theory

The two basic assumptions of the model are that the largest defects within a typical rubber particle are microvoids with dimensions in the order of a nanometre, and that these microvoids will expand only if the resulting release of stored strain energy is sufficient both to increase the surface area of the void and to stretch the surrounding layers of rubber biaxially. For convenience of calculation, the rubber-toughened polymer is treated as an assembly of composite spherical elements, consisting of a rubber particle of radius R surrounded by a concentric shell of the matrix polymer, with an external radius Q , as illustrated in Fig. 1. The volume fraction of rubber, ϕ , is therefore R^3/Q^3 . The two phases are assumed to be homogeneous, isotropic and well bonded to each other. Their elastic properties are defined by shear moduli G_m and G_r and bulk moduli K_m and K_r , where subscripts m and r refer to matrix and rubber, respectively.

Rubbers have very low shear moduli but high bulk moduli: typical values are $G_r = 0.4$ and $K_r = 2000$ MPa. Therefore, under uniaxial or biaxial tension, they can reach extension ratios in excess of 5 at relatively low stresses, which are capable of producing only small volume strains, ca. 0.5%. By contrast, the rubber particles in a toughened plastic are constrained by the surrounding rigid matrix, so they can easily be subjected to substantial triaxial tensile stresses. If the rubber is well bonded to the matrix, volume strains of 1% can be generated within the rubber particles at low overall strains (ca. 5%) in the toughened polymer.

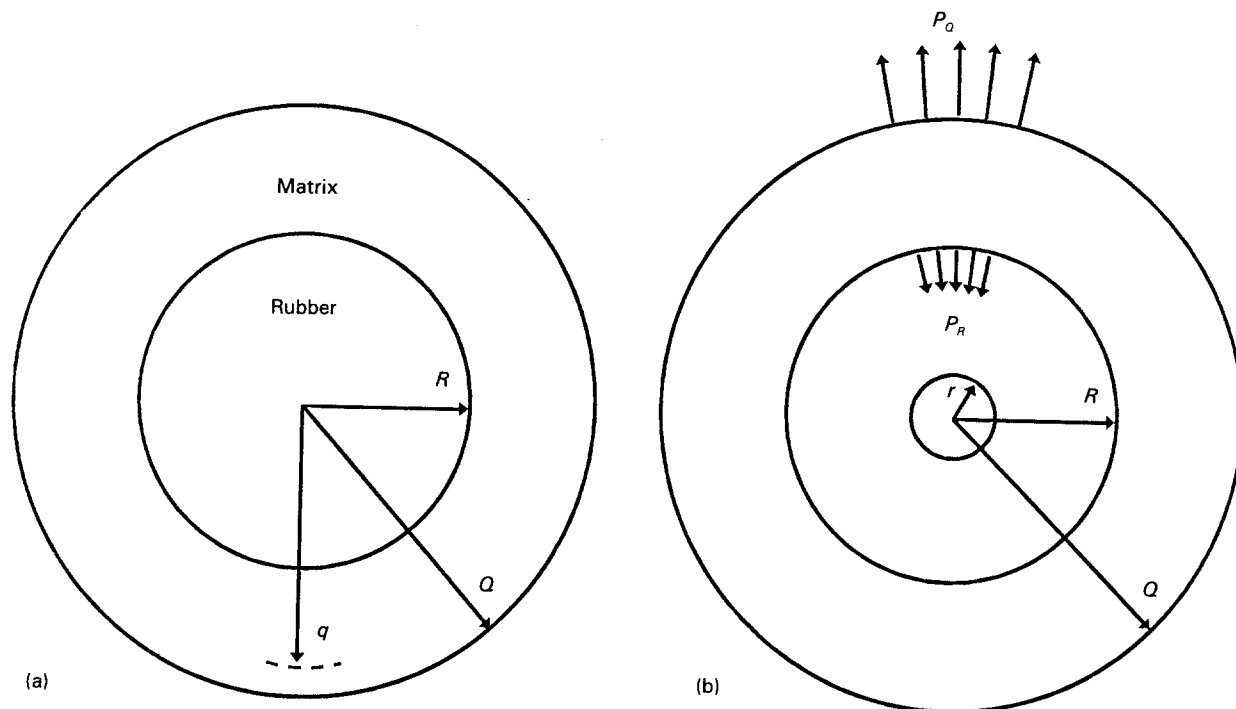


Figure 1 Composite spherical element used in the model: (a) before and (b) after cavitation, showing normal stresses acting on inner and outer surfaces of matrix shell. Radii chosen to give $\Delta V_R = 1.4\%$ and $\phi = 0.185$.

Because of the weak van der Waals attractions between neighbouring chains in an organic polymer, these dilatational strains may be sufficient to produce cohesive failure in the rubber, subsequent expansion of a void nucleus being aided by the mobility of the rubber molecules. The conditions under which cavitation occurs are explored in this paper.

As small applied shear strains are unlikely to affect void formation in the rubber, the analysis concentrates purely upon the response of a toughened polymer to imposed volume strains. Calculations are therefore based upon the elastic behaviour of a spherical shell under uniformly distributed internal and external tensile stresses P_R and P_Q acting normally to the surfaces, as illustrated in Fig. 1b. This is a standard problem in mechanics, which is addressed, for example, by Reismann and Pawlik [23]. The radial displacement $x(q)$ within the matrix at a distance q from the centre of the sphere is given by:

$$x(q) = \frac{(P_R R^3 - P_Q Q^3)q}{3K_m(R^3 - Q^3)} + \frac{(P_R - P_Q)R^3 Q^3}{4G_m(R^3 - Q^3)q^2} \quad (1)$$

Before cavitation, shear stresses within the rubber particle are zero and the only stress acting on the rubber is a mean stress, which is also the stress P_R acting normally at the particle-matrix interface. This generates a volume strain ΔV_r in the rubber:

$$P_R = K_r \Delta V_r = K_r \left(\frac{4\pi R^2 dR}{V_r} \right) = \frac{3K_r x(R)}{R} \quad (2)$$

where V_r is the volume of the rubber particle.

2.1. Energy of cavitated rubber particle

For convenience of calculation, the void is assumed to be a sphere of radius r formed at the centre of the

rubber particle. Immediately before cavitation ($r = 0$) the strain energy $U_r(0)$ of the particle is given by:

$$U_r(0) = \frac{4}{3} \pi R^3 W_r^*(0) = \frac{2}{3} \pi R^3 K_r [\Delta V_r(0)]^2 \quad (3)$$

where $W_r^*(0)$ and $\Delta V_r(0)$ are the stored energy density and volume strain within the rubber phase immediately before cavitation respectively. Usually, both the radius R and volume strain ΔV_R of the rubber particle (here taken to include both the rubber phase itself and the void) will increase during cavitation. In relation to the rubber particle, the volume fraction of the void cavity is r^3/R^3 , and the resulting volume strain within the cavitated rubber phase is $(\Delta V_R - r^3/R^3)$ where in general $\Delta V_R \neq \Delta V_r(0)$.

The formation of a cavity introduces two additional contributions to the energy of the rubber particle: a surface energy term $4\pi r^2 \Gamma$, where Γ is the surface energy of the rubber; and the shear strain energy, $\int W_{rs}^* dV$, required to stretch the rubber and allow the cavity to expand. The total energy $U_r(r)$ of the cavitated particle is then given by:

$$U_r(r) = \frac{2}{3} \pi R^3 K_r \left(\Delta V_R - \frac{r^3}{R^3} \right)^2 + 4\pi r^2 \Gamma + \int W_{rs}^* dV \quad (4)$$

A typical value of Γ for a hydrocarbon elastomer is 0.03 J m^{-2} [24].

The shear strain energy density term W_{rs}^* can be evaluated using standard rubber-like elasticity theory, and is given in abbreviated form by [20]:

$$U_{rs}(r) = 2\pi r^3 G_r F(\lambda_f) \quad (5)$$

where λ_f is the extension ratio of the rubber at failure in equi-biaxial tension. Numerical integration shows that with $\Delta V_R = \Delta V_r(0)$ the function $F(\lambda_f)$ typically increases from 0.7 to 1.3 over the range of λ_f values

from 2 to 6. Reported values of λ_f for vulcanized natural rubber in equi-biaxial tension are between 3.5 and 4.0 [25]. In the original analysis, $F(\lambda_f)$ includes the irreversible work done in stretching material in the centre of the particle beyond λ_f , to give a broken membrane around the cavity. This irreversible work term is relatively small when the radial strain $x(R)/R$ at the particle–matrix interface is small.

With the inclusion of terms representing the work done in stretching the rubber membrane around the growing void, the final expression for the energy of a cavitated particle becomes:

$$U_r(r) = \frac{2}{3} \pi R^3 K_r \left(\Delta V_R - \frac{r^3}{R^3} \right)^2 + 4\pi r^2 \Gamma + 2\pi r^3 G_r F(\lambda_f) \quad (6)$$

or, dividing by the volume of the rubber particle, V_R :

$$\frac{U_r(r)}{V_R} = \frac{K_r}{2} \left(\Delta V_R - \frac{r^3}{R^3} \right)^2 + \frac{3\Gamma}{R} \frac{r^2}{R^2} + \frac{3G_r F(\lambda_f)}{2} \frac{r^3}{R^3} \quad (7)$$

Equation 7 relates the energy density of the particle directly to the normalized radius r/R , emphasizing the point that only the term in Γ is affected by the absolute size of the particle: the surface work term becomes more important as the particle size is reduced.

As noted earlier, the mean stress (negative pressure) acting within the rubber phase is the product of its bulk modulus and its volume strain. After cavitation, this is given by $K_r(\Delta V_R - r^3/R^3)$. The area over which this stress acts is $\pi(R^2 - r^2)$. In addition, there are surface forces acting over a line of length $2\pi r$, and biaxial stretching forces f_{rs} within the rubber membranes surrounding the void. The total force, f_r , acting on the current cross-section of the rubber particle, πR^2 , is given by:

$$f_r = f_{rs} + 2\pi r \Gamma + \pi(R^2 - r^2) K_r \left(\Delta V_R - \frac{r^3}{R^3} \right) \quad (8)$$

By applying the equation for equi-biaxial stretching of a rubber shell, following the method given in [20], it can be shown that f_{rs} is:

$$f_{rs} = 2\pi G_r r^2 \int_{\lambda=\frac{R}{R_0}}^{\lambda_f} \frac{(\lambda^3 - \lambda^{-3})}{(\lambda^3 - \rho)^{\frac{5}{3}}} d\lambda \quad (9)$$

The normal stress acting on the particle–matrix boundary is then given by:

$$P_R = P_r = \frac{f_r}{\pi R^2} = \frac{f_{rs}}{\pi R^2} + \frac{2r\Gamma}{R^2} + K_r \left(1 - \frac{r^2}{R^2} \right) \times \left(\frac{R^3 - R_0^3}{R_0^3} - \frac{r^3}{R_0^3} \right) \quad (10)$$

where R_0 is the radius of the unstressed particle. Under the conditions relevant to particle cavitation, where void sizes and overall strains are small, the two leading terms are also small, and the stress P_R is determined largely by the term in K_r .

2.2. Energy of Matrix Shell

Equation 1 may be simplified by substituting the rubber volume fraction ϕ for R^3/Q^3 , to give:

$$\frac{x(q)}{q} = \frac{P_Q - \phi P_R}{3K_m(1 - \phi)} + \frac{(P_Q - P_R)R^3}{4G_m(1 - \phi)q^3} \quad (11)$$

The volume strain ΔV_Q in the complete particle-shell element is then obtained by setting $q = Q$:

$$\Delta V_Q = \frac{3x(Q)}{Q} = \frac{P_Q - \phi P_R}{K_m(1 - \phi)} + \frac{3(P_Q - P_R)\phi}{4G_m(1 - \phi)} \quad (12)$$

Similarly, the volume strain ΔV_R in the particle can be related to the stresses acting on the matrix shell by setting $q = R$ in Equation 11:

$$\Delta V_R = \frac{3x(R)}{R} = \frac{P_Q - \phi P_R}{K_m(1 - \phi)} + \frac{3(P_Q - P_R)}{4G_m(1 - \phi)} \quad (13)$$

As noted earlier, ΔV_R is the volume strain in the rubber particle, which includes everything within a sphere of radius R . Before cavitation, this is equal to ΔV_r , the volume strain in the rubber phase. However, after cavitation $\Delta V_R = \Delta V_r + r^3/R^3$.

It is important to note that an apparently large void may represent only a very small volume fraction of the particle or composite element, and that within the elastic strain region under discussion the overall effect of cavitation on the radii Q and R is extremely small. Fig. 1 is drawn with $r = 0.24R$ and $R/Q = 0.57$, which corresponds to a particle volume strain $r^3/R^3 = 1.4\%$ and a particle volume fraction $\phi = 0.185$. With these dimensions, an increase of less than 0.1% in Q would be more than enough to compensate for the volume occupied by the void.

3. Predictions of the model

The foregoing set of equations provides a basis for calculating the energy of the composite element as a function of void size r under a range of loading conditions. Three standard conditions are discussed below: fixed volume strain in the particle, fixed volume strain in the combined element and fixed applied stress P_Q .

3.1. Volume strain of rubber particle constant

The behaviour of the rubber particle during cavitation is most easily understood by holding the volume strain ΔV_R constant so that no further work is done by the matrix and all energy changes take place within the particle. This condition is unlikely to arise in practice, but it simplifies the calculations by relating the energy of the rubber particle, $U_r(r)$, directly to the void radius r through Equations 6 and 7, and thus provides a straightforward basis for discussing the effects of each parameter in the equation upon void formation.

The predictions of the model are illustrated below in a series of examples, in which ΔV_R , R , G_r and Γ are each varied in turn. The bulk modulus of rubbers is relatively insensitive to chain structure and testing conditions and is therefore treated as a constant: the chosen value of $K_r = 2000$ MPa is for polybutadiene [26]; the function $F(\lambda_f)$ is taken as 1.0

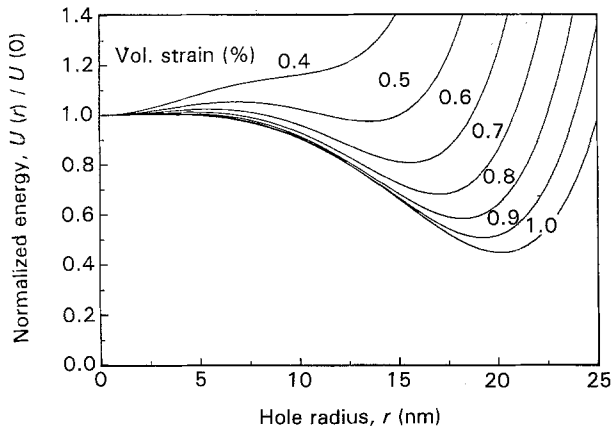


Figure 2 Normalized energy of rubber particle as a function of void radius, for a series of volume strains ΔV_R in the rubber particle. Calculated using Equation 6 with $R = 0.1 \mu\text{m}$, $G_r = 0.4 \text{ MPa}$, $K_r = 2 \text{ GPa}$, $\Gamma = 0.03 \text{ J m}^{-2}$, $F(\lambda_r) = 1$. Fixed ΔV_R during cavitation.

throughout. Other quantities used in the calculations are listed in the figure captions.

Fig. 2 shows the relationship between the normalized energy $U_r(r)/U_r(0)$ and void radius r for a fixed particle radius of $0.1 \mu\text{m}$ at a series of fixed volume strains ΔV_R . For the higher volume strains, energy falls rapidly with void size, reaching a minimum which corresponds approximately to $(r/R)^3 = \Delta V_R$, so that ΔV_R , the volumetric strain energy stored in the rubber phase, decreases (approximately) to zero. Beyond the minimum, the energy rises again, essentially because at fixed ΔV_R a further increase in void size can be achieved only by compressing the rubber against the surrounding matrix. This situation could, in principle, arise if the stored energy were released suddenly, so that the material surrounding the growing void acquired enough kinetic energy to go through a number of damped radial oscillations before reaching equilibrium.

The important point to note from Fig. 2 is that the energy minimum becomes more shallow as the applied volume strain ΔV_R is reduced, until eventually it is impossible to form a void without increasing the energy of the particle above that of the void-free state. This provides a convenient criterion for cavitation: the particle must be able to reach a lower energy on forming a void.

The critical volume strain for cavitation is a function of particle size R . Fig. 3 shows the relationship between $U_r(r)/U_r(0)$ and r/R for a series of fixed particle sizes, all at a fixed ΔV_R of 0.4% . As R decreases the surface energy term becomes increasingly important, with the result that the energy minimum becomes shallower and moves to lower r/R . In other words, equilibrium is reached well before the stored strain energy can fall to zero. Eventually, a critical particle size is reached, below which cavitation cannot occur at the specified volume strain. To calculate the critical conditions for void formation, $\partial U_r/\partial r$ was obtained from Equation 7 and set equal to zero. The normalized energy $U_r(r)/U_r(0)$ was then set equal to 1.0 and the two resulting equations were solved for r/R and R . The analysis shows that there is an inverse

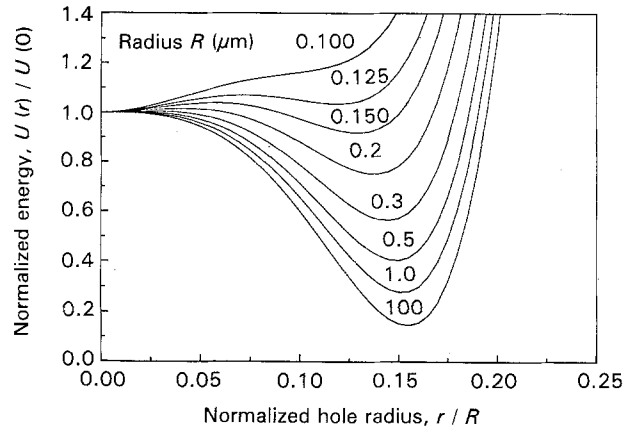


Figure 3 Normalized energy of rubber particle calculated using Equation 7 for a series of particle sizes, $\Delta V_R = 0.4\%$. Other conditions as Fig. 2.

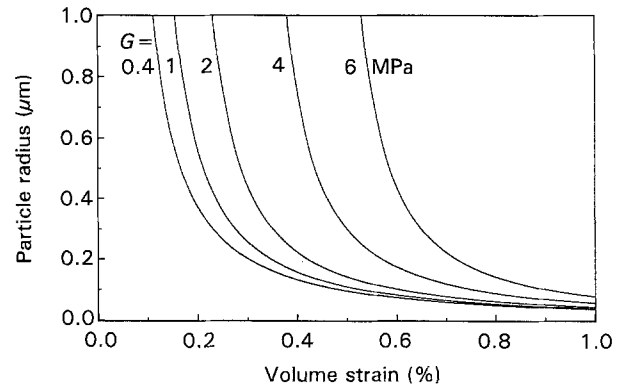


Figure 4 Critical particle radius at cavitation for rubbers with various shear moduli G_r . Calculated using Equation 6. Other conditions as Fig. 2.

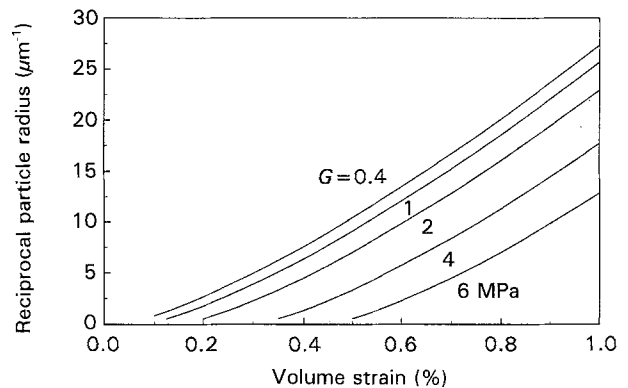


Figure 5 Data from Fig. 4 replotted as R^{-1} versus volume strain.

relationship between critical particle radius and volume strain at cavitation, as illustrated in Figs 4 and 5. The plot of R^{-1} versus ΔV_R is particularly helpful in identifying critical combinations of particle size and volume strain.

The relationship is strongly dependent upon G_r , the shear modulus of the rubber phase. Unlike K_r , G_r is subject to very wide variations with time, temperature and degree of cross-linking. Typically, G_r increases by more than three orders of magnitude as the rubber is cooled through its glass transition. Above T_g , similar changes occur with increasing strain rate. The shear

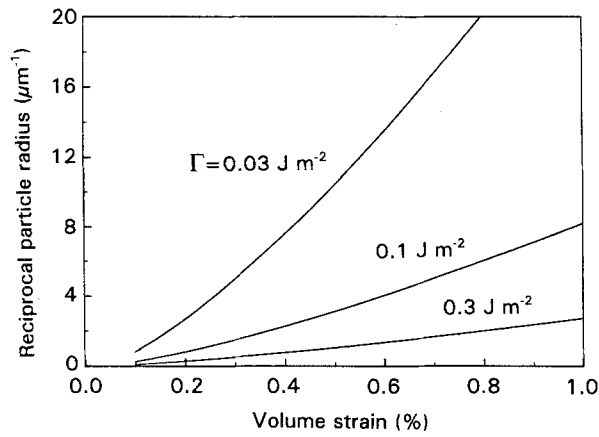


Figure 6 Effect of volume strain on critical R^{-1} for different Γ values. Other conditions as Fig. 2.

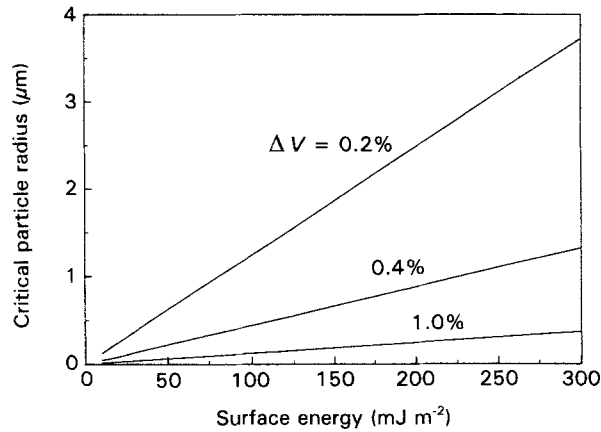


Figure 7 Relationship between critical particle radius and surface energy Γ of rubber. Other conditions as Fig. 2.

moduli of elastomers are also raised substantially by chemical cross-linking or by partial crystallization. Figs 4 and 5 show that much smaller changes in G_r than those occurring at T_g have a dramatic effect on cavitation behaviour: increased resistance to stretching of the rubber membranes surrounding the void nucleus can result in the complete suppression of hole formation.

The failure behaviour of the rubber, represented by $F(\lambda_f)$, is also subject to wide variations. In the foregoing discussion $F(\lambda_f)$ was assigned a typical value of 1.0 [20] and G_r was varied. However, since G_r and $F(\lambda_f)$ appear only as products throughout the analysis, this procedure has exactly the same effect as fixing G_r and varying $F(\lambda_f)$: the results given in Figs 4 and 5 therefore apply to stated values of $G_r F(\lambda_f)$ and not simply of G_r .

Fig. 6 shows the effect of varying surface energy Γ . The curve for $\Gamma = 0.03 \text{ J m}^{-2}$ corresponds to that for $G_r = 0.4 \text{ MPa}$ in Fig. 5. van der Waals surface energies of hydrocarbon rubbers are not intrinsically subject to wide variations, but it can be argued that Γ should include an additional contribution due to breaking of chemical bonds during cavitation. This approach was adopted by Kramer [27] in his analysis of crazing in glassy polymers: bond rupture was estimated to increase Γ from 0.040 to 0.087 J m^{-2} in polystyrene, which is uncross-linked. In rubbers with high

degrees of cross-linking, bond rupture could raise Γ substantially. Fig. 7 shows the proportionality between critical particle radius and Γ predicted by the model, further emphasizing the importance of surface energy in controlling cavitation.

3.2. Volume strain of rubber particle variable

The results given above reflect the general way in which cavitation is affected by the properties of the rubber particle and illustrate the main features of the model. However, they tend to overestimate critical particle sizes and volume strains because they make no allowance for the energy input from the matrix as the void forms and the stresses at the particle-matrix interface relax. The amount of energy available depends upon the precise loading conditions.

Stresses and strains in the combined particle-shell element in its initial state, before cavitation, may be obtained from Equations 2, 12, and 13. From Equations 2 and 13:

$$\frac{P_R}{K_r} = \frac{P_Q - \phi P_R}{K_m(1 - \phi)} + \frac{3(P_Q - P_R)}{4G_m(1 - \phi)} \quad (14)$$

which on rearranging gives:

$$P_R = P_Q \left[\frac{K_r(4G_m + 3K_m)}{4G_m(K_r - K_m)\phi + K_m(4G_m + 3K_r)} \right] = P_Q \zeta \quad (15)$$

The term ζ becomes zero when the rubber particle is replaced with a void, which is equivalent to setting $K_r = 0$. Substitution for P_R in Equation 12 gives the following expression for K_e , the bulk modulus of the (non-cavitated) combined particle-matrix element:

$$K_e = \frac{dP_Q}{d(\Delta V_Q)} = \frac{4G_m K_m(1 - \phi)}{4(1 - \zeta\phi)G_m + 3K_m\phi(1 - \zeta)} \quad (16)$$

Then:

$$\frac{U_e(0)}{V_Q} = \frac{P_Q^2}{2K_e} = \frac{K_e(\Delta V_Q)^2}{2} \quad (17)$$

where V_Q is the volume of the element.

In order to calculate energy changes in the combined element during cavitation it is necessary to define boundary conditions. A relationship can then be obtained between the radial displacement of the particle-matrix boundary, $x(R)$, and void radius r . This must be consistent with the condition that the forces acting across the particle-matrix boundary are in equilibrium, i.e. that the same value of P_R satisfies Equations 10, 12 and 13. The total energy of the combined element can then be determined as a function of r .

The results given below are based on two standard boundary conditions: a fixed volume strain ΔV_Q and a fixed applied stress P_Q . If P_Q is fixed then substitution into Equation 13 enables P_R to be calculated for a series of chosen radial strains $x(R)$. If ΔV_Q is fixed then Equations 12 and 13 together provide a pair of simultaneous equations in P_Q and P_R for each value of $x(R)$. In either case, the relationship between P_R and $x(R)$ (and hence ΔV_R) is obtained. The results can

then be applied to Equation 10 to find corresponding values of r . The equations thus yield a set of stresses and strains at radial distances r , R and Q , from which the energies of both cavitated rubber particle and matrix shell can be calculated.

Once the volume strain of either the rubber particle or the combined element is fixed the system becomes isolated from the surroundings and all further energy changes are internal. As shown in Figs 2 and 3, when the volume strain in the particle is held constant during cavitation, it is convenient to express results obtained using the model in terms of the normalized energy $U_r(r)/U_r(0)$. Similarly, when the volume strain ΔV_Q is held constant the energy of the combined element can be normalized as $U_e(r)/U_e(0)$, where U_e is the sum of energies in particle and matrix. However, when P_Q is held constant work is done by the surroundings during cavitation of the rubber and the system is no longer a closed one. Under these conditions the choice of an initial energy that can be used to normalize the data is less obvious.

In the present study the problem has been resolved by defining a maximum potential energy, $U_p(0)$, which is reached by the surroundings immediately before cavitation, and is therefore a function of the initial volume strain in the rubber at cavitation, $\Delta V_R(0)$. The energy $U_p(0)$ is taken as $4\pi Q^2 P_Q \Delta x_Q(\max)$, where $\Delta x_Q(\max)$ is the maximum possible radial deflection of the shell's outer surface on reducing the stress at the particle-matrix boundary from $P_R(0)$ to zero. In general, P_R does not vanish when the rubber cavitates but remains positive in accordance with Equation 10. The total energy of the system at a given void radius r , for the case that P_Q is held constant, is then given in normalized form by:

$$\frac{U_T(r)}{U_T(0)} = \frac{U_r(r) + U_m(r) + U_p(r)}{U_r(0) + U_m(0) + U_p(0)} \quad (18)$$

Fig. 8 compares curves of normalized energy $U_T(r)/U_T(0)$ against reduced void size r/R for the three loading conditions: fixed ΔV_R , fixed ΔV_Q , and fixed P_Q . The three sets of curves are similar in shape but as expected show progressively smaller critical volume strains $\Delta V_r(0)$ at cavitation as the amount of energy supplied to the particle by the matrix and surroundings increases. This point is further emphasized in

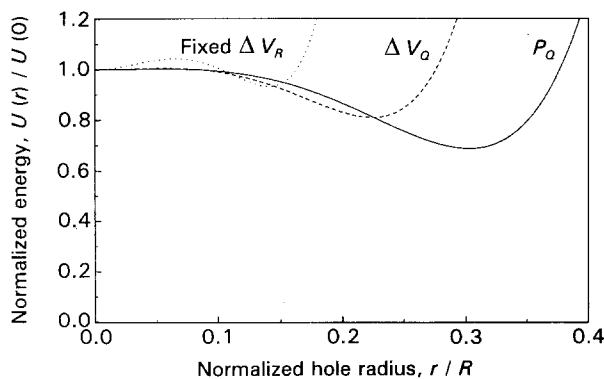


Figure 8 Reduced energy $U_T(r)/U_T(0)$ as a function of void size calculated on the basis of: (a) fixed ΔV_R ; (b) fixed ΔV_Q ; (c) fixed P_Q during cavitation. $\phi = 0.15$, $G_m = 1.2$ GPa, $K_m = 3.4$ GPa.

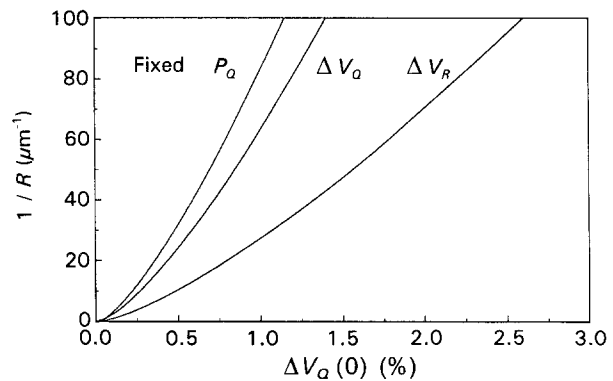


Figure 9 Plots of critical particle size R versus initial volume strain in rubber particle $\Delta V_Q(0)$ calculated for: (a) fixed ΔV_R ; (b) fixed ΔV_Q ; (c) fixed P_Q during cavitation.

Fig. 9, which compares curves of critical particle size against initial volume strain in the rubber particle under the three different loading conditions.

4. Discussion

The model outlined in a previous paper, and developed in the present study, provides, for the first time, a quantitative basis for discussion of cavitation in rubber-toughened plastics. It thus offers the possibility of resolving a number of problems that have arisen in interpreting the fracture behaviour of these materials. By emphasizing the way in which volume strain, particle size and material properties interact in determining whether the rubber will cavitate, the model identifies key features of the toughening mechanism.

Cavitation in itself cannot be regarded as an important energy-absorbing process. Indeed, it has been shown that it can result from comparatively small energy interchanges taking place within the rubber particles. Furthermore, it does not immediately produce a major increase in volume: most of the calculations in this paper are based on the assumption that the volume strain of either the rubber particle or the particle-matrix combination is constant; even when the matrix shell is allowed to expand by a volume equal to that of a typical stable void the overall effect on volume strain is only ca. 0.2%. The real importance of cavitation is that it reduces the resistance of the polymer to volumetric expansion in response to dilatational applied stress fields which occur, especially, at crack tips. This aspect of cavitation is discussed elsewhere [20]. Under appropriate conditions it may also provide free surfaces for craze initiation.

If the matrix polymer has a low yield stress, large-scale plastic deformation may take place before the volume strain is high enough to cause cavitation of the rubber particles. On the other hand, if the yield stress is very high, fracture will probably intervene before the benefits of cavitation are seen in the form of an enlarged plastic zone. It follows that cavitation should be most effective when the material is near a brittle-ductile transition, so that it can have the effect of shifting the transition to lower temperatures, higher strain rates or larger specimen thicknesses.

Particle size is clearly critical under some conditions. The model shows that very small particles, with diameters below ca. 0.1 μm , are likely to be effective only in situations where the polymer can reach high stresses without either yielding or breaking. In this context, the work of Gaymans *et al.* [28] on the Izod impact strength of toughened nylon 6 is particularly interesting. They showed that the brittle-tough transition temperature T_{BT} shifted downwards on reducing particle diameter over the range 1.6–0.2 μm , an effect that appears to be related to inter-particle spacing. Within this range the upper level of impact strength achieved above T_{BT} is independent of particle diameter. However, if particle sizes are reduced further, the trend is reversed: T_{BT} moves upwards and the maximum impact strength observed falls linearly with increasing diameter. These results are consistent with a critical particle size at cavitation in toughened nylon, as required by the model. Another paper from the same research group [29] shows an upward shift in T_{BT} with increasing modulus of the rubber particles, again as required by the model. Further evidence in support of the model has been obtained in experiments on toughened urethane-methacrylate resins [19], which will be the subject of a separate paper.

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