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Detachment of an elastic matrix from a rigid spherical inclusion

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An approximate theoretical treatment is given for detachment of an elastomer from a rigid spherical inclusion by a tensile stress applied to the elastomeric matrix. The inclusion is assumed to have an initially-debonded patch on its surface and the conditions for growth of the patch are derived from fracture energy considerations. Catastrophic debonding is predicted to occur at a critical applied stress when the initial debond is small. The strain energy dissipated as a result of this detachment, and hence the mechanical hysteresis, are also evaluated. When a reasonable value is adopted for Young's modulus E of the elastomeric matrix, it is found that detachment from small inclusions, of less than about 0.1 mm in diameter, will not occur, even when the level of adhesion is relatively low. Instead, rupture of the matrix near the inclusion becomes the preferred mode of failure at an applied stress given approximately by $E/2$. For still smaller inclusions, of less than about 1 μm in diameter, rupture of the matrix becomes increasingly difficult, due to the increasing importance of a surface energy term. These considerations account for the general features of reinforcement of elastomers. Small-particle fillers become effectively bonded to the matrix, whereas larger inclusions induce fracture near them, or become detached from the matrix, at applied stress that can be calculated from the particle diameter, the strength of adhesion, and the elasticity of the matrix material.

1. Introduction

Elastomers are often filled with high loadings of relatively rigid particulate materials in order to stiffen and strengthen them. These effects depend strongly upon the particle size of the filler and upon the degree of bonding between the elastomer and the filler [1]. When the particle size is small, less than about 1 μm, even a moderate degree of interaction between the elastomeric matrix and the filler seems to be sufficient to produce a surprisingly high level of reinforcement. When the particle size is relatively large, the matrix seems to be easily detached from the filler particles at relatively low tensile stresses and the level of reinforcement is correspondingly low [1].

The tensile stress at which an elastic matrix will become detached from a rigid spherical inclusion is derived here on simple theoretical grounds. Only low concentrations of filler are considered, such that the strain fields around each particle do not interact to a significant degree, and the matrix itself is treated as a linearly-elastic material, with Young's modulus E. Detachment is assumed to start at an already-debonded region, present initially on the surface of the particle. It is assumed to take place by growth of this debonded region when the elastic strain energy thereby released in the matrix is greater than the energy required for further debonding. This is a straightforward application of Griffith's fracture criterion [2]. It leads to a prediction of catastrophic debonding when the initially-debonded region is small in size. Moreover, the amount of strain energy lost from the system as a result of debonding can be readily evaluated from the difference between the strain energy levels before and after debonding has taken place. An estimate can be made in this way of the additional mechanical hysteresis due to detachment of the matrix from the filler.

A somewhat similar analysis has recently been put forward, dealing with the conditions for

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detachment from a spherical inclusion under a triaxial tension [3]. That study differs from the present analysis in two important respects. The process of detachment was assumed to take place simultaneously at all points on the spherical surface, rather than progressively from an initially debonded region. Secondly, the strain energy released by dilation of the matrix after detachment has taken place was considered to be wholly expended in the detachment process itself, in the form of bond fracture energy. In contrast, the analysis developed here, although rather approximate in nature, treats the debonding process as a continuous one, starting from the hypothetical initially-debonded region on the surface of the inclusion. It leads to the prediction of both stable and unstable (i.e. catastrophic) modes of growth of the debond, depending upon the size of the initial debond relative to the size of the inclusion.

In a final section, other modes of failure are considered. It is shown that detachment from small inclusions is improbable, even when the level of adhesion is low and that fracture of the matrix itself in the vicinity of the inclusion becomes increasingly difficult as the size of the inclusion is reduced. These conclusions explain, at least in part, the reinforcing action of small particles.

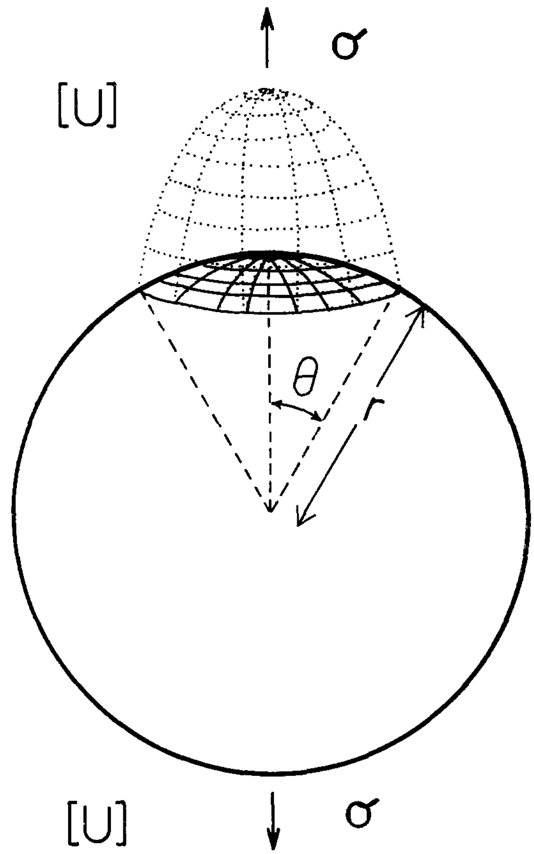

Figure 1 Sketch of a single inclusion showing debonded area and associated volume ΔV effectively free from stress.

2. Theoretical considerations

2.1. Critical stress for detachment

A single spherical inclusion within an elastic matrix is shown schematically in Fig. 1. A small circular area on the surface of the inclusion is assumed to be debonded from the matrix initially. Growth of this debonded patch will take place when the tensile stress σ applied to the specimen at its distant edges reaches a critical value, denoted σ_a. A relation for this critical stress is now derived by means of an approximate energy analysis.

For simplicity, the initially-debonded patch is assumed to be located on the surface of the inclusion in the direction of the applied stress, Fig. 1. Other locations would result in higher values of the critical stress, as will be shown later, so that this assumption leads to minimum values for σ_a. The stress field set up in the material is divided conceptually into two regions, as shown in Fig. 1: a far-field region where the strain energy density U is assumed to be unaffected by the presence of the debonded area, and a region in the immediate vicinity of the debonded zone, shown shaded in Fig. 1, within which the strain energy density is assumed to be effectively zero because the debonded zone cannot transmit a tensile stress to the matrix. A similar assumption was made by Rivlin and Thomas in their analysis of an edge crack in a homogeneous elastic solid [4].

The volume ΔV of the unstressed region will be given by

$$\Delta V = k(r \sin\theta)^3 \qquad (1)$$

on general dimensional grounds, where $r\theta$ is the radius of the circular debonded zone and k is a dimensionless quantity evaluated later. The area A of the debonded zone is $2\pi r^2(1-\cos\theta)$. The loss ΔW in elastic strain energy when the debonded zone increases in area by ΔA is then given by

$$\Delta W = U\left(\frac{\partial(\Delta V)}{\partial\theta}\right)\left(\frac{\partial\theta}{\partial A}\right)\Delta A$$

$$= (3k/4\pi)(Ur \sin 2\theta)\Delta A. \qquad (2)$$

In accordance with Griffith's fracture criterion, it is assumed that the debonded area will grow if this reduction in stored strain energy is equal to, or greater than, the energy required for debonding, namely $G_a \Delta A$, where G_a is the bond fracture energy per unit of bonded surface. The criterion for debonding thus becomes

$$U \geqslant 4\pi G_a / 3kr \sin 2\theta. \qquad (3)$$

In terms of the applied tensile stress σ, U is given by $\sigma^2/2E$ where E is Young's modulus for the composite material. The applied stress σ_a necessary to cause debonding is therefore given by

$$\sigma_a^2 = 8\pi G_a E / 3kr \sin 2\theta. \qquad (4)$$

In order to obtain a value for the numerical quantity k, this result is now specialized to the case when θ is small and the debonded zone becomes a small circular region of radius $a = r\theta$. Mossakovskii and Rybka have treated the corresponding case of the detachment of an elastic half-space from a rigid plate when a circular debond of radius a is located at the interface [5]. They deduced that

$$\sigma_a^2 = 2\pi G_a E / 3a. \qquad (5)$$

On comparing Equations 4 and 5, taking θ to be small, a value of 2 is obtained for the numerical parameter k.

It is clear from Equation 4 that the tensile stress for detachment is quite large both when the radius $r\theta$ of the initial debond is small, and also when the debonded region is large, when $\theta \simeq 90°$. It passes through a minimum value when $\theta = 45°$, i.e. for inclusions which are debonded initially over a substantial fraction of their surface. This minimum value of σ_a is given by

$$\sigma_{a_{min}}^2 = 4\pi G_a E / 3r. \qquad (6)$$

It is similar in magnitude to the stress causing detachment of an elastic material from a rigid substrate, initiated by a debond of radius r (Equation 5). It is also similar to that deduced for detachment from a spherical inclusion of radius r under a triaxial tension σ_t [3],

$$\sigma_t^2 = 8 G_a E / 3r.$$

It represents (in the present instance) the lowest stress at which detachment would occur under the most favourable circumstances, i.e. when a relatively large debond is present at the inclusion surface initially, and it is located in a particularly favourable way with respect to the direction of the applied tension. Under all other circumstances the debonding stress will be higher than that given by Equation 6. Indeed, when the size of the initial debond, represented by the angle θ, is small, it is clear from Equation 4 that debonding will take place in a catastrophic way because the stress required to maintain the debonding process decreases as θ increases. Once the applied stress and stored elastic energy reach their critical levels, then the debond will grow abruptly until $\sin 2\theta$ attains its original value again. If θ is small to start with, then debonding will take place until $\theta \simeq 90°$, i.e. until debonding is virtually complete.

2.2. Energy dissipated in debonding

The loss of stored elastic energy as a result of this abrupt debonding can be evaluated by means of Equation 1. The unstressed zone will increase from its small initial size to a final volume of approximately $2r^3$, when k is given the value of 2 deduced earlier. Thus, the decrease in strain energy is approximately $2Ur^3$. If it is assumed, as seems likely, that detachment occurs simultaneously at both poles of the inclusion, then the decrease in strain energy for each inclusion becomes $4Ur^3$. The number n of inclusions per unit volume of the filled material is given by

$$n = 3c/4\pi r^3$$

where c is the volume fraction of the composite material occupied by inclusions. Thus, the total reduction in strain energy density caused by debonding is obtained as

$$\Delta U / U_0 = 3c/\pi, \qquad (7)$$

where U_0 denotes the input strain energy up to the point of detachment. The ratio $\Delta U/U_0$, referred to hereafter as the mechanical hysteresis ratio H, is therefore predicted to be independent of particle size and proportional to the volume fraction c of particles in the composite.

It should be noted that Equation 7 is based upon two special assumptions, which will only hold under quite restricted circumstances. The first is that the stress fields around each particle are assumed not to interact significantly. This implies that the particles are separated by distances comparable to, or greater than, their diameters, and this in turn implies that their volume fraction

c is small, not more than about 10 per cent. The second assumption is that small debonded areas are present initially on the particle surface, and that they are favourably located with respect to the applied stress direction. This implies that there are, in fact, many small debonded areas per particle. Those suitably positioned with respect to the applied stress will presumably act as nuclei for the detachment process.

3. Other modes of failure

The mechanism of detachment treated in the preceding section is likely to be valid only for relatively large particles, weakly bonded to the matrix, and different mechanisms of detachment will operate under other circumstances. For example, when the level of adhesion between the matrix and the inclusion is sufficiently high, the elastomeric matrix will undergo cavitation in the vicinity of the particle [6]. In this case, the matrix does not detach from the particle directly, but instead it undergoes internal rupture near the particle surface, nucleated by a small precursor void present within the elastomeric matrix. The void is torn open by triaxial tensions generated in the neighbourhood of the particle. The condition for this mode of failure to occur is that the applied tensile stress must reach a critical value, given by [6, 7]

$$\sigma_f \simeq (E+P)/2, \qquad (8)$$

where P denotes the ambient pressure (usually atmospheric pressure and hence small in comparison with E).

On comparing the minimum value of the critical stress for detachment, Equation 6, with the predictions of Equation 8 for the cavitation stress σ_f, it can be seen that detachment will not take place if

$$G_a/r > 3E/16\pi \qquad (9)$$

because the detachment stress σ_a then exceeds the stress σ_f for cavitation. When E is given a value of 3 MPa, characteristic of rubbery solids, and G_a a value of $10\,J\,m^{-2}$, representing a relatively weakly bonded interface [8], then Equation 9 predicts that detachment will not take place for particles having a diameter of less than about 0.1 mm. Instead, the matrix will abruptly tear open near the particle at the applied stress given by Equation 8.

Although this failure process is quite different from the detachment mechanism considered earlier, nevertheless the mechanical hysteresis ratio H will still be given by Equation 7, to a good approximation, because the assumptions on which that equation was based are still valid. The cavities form abruptly and grow to a size that relieves the high stresses set up in the vicinity of the particle surface in the same way as the abrupt growth of a debond on the particle surface. Indeed, the cavities often tear towards the particle surface as they develop and bring about debonding in this way [6]. The initial failure stress, however, is quite different and depends only upon Young's modulus E (Equation 8).

If the precursor voids within the elastomeric matrix are even smaller, less than about 100 nm in diameter, then the critical applied stress σ_f will no longer be given by Equation 8. Instead, an additional constraint on the expansion of a void becomes significant, arising from its own surface energy. This additional term, given by $2\gamma/a$ where γ denotes the surface energy of the matrix and a denotes the radius of the void, becomes large when the radius a is small. Thus, the applied stress must overcome both the elastic resistance to expansion, represented by E in Equation 8, and a large surface energy contribution as well [9].

From simple dimensional considerations it is clear that no large precursor voids can be located within the immediate vicinity of a small inclusion. Indeed, it seems reasonable to assume that the largest void that can exist near to an inclusion will be about one order of magnitude smaller in size than the inclusion itself. Thus, cavitation stresses for particles of less than about 1 μm in diameter are likely to be considerably larger than those predicted by Equation 8, due to the large surface energy contribution in these cases. Moreover, the smaller the particle, the larger is the stress required to create a cavity in its vicinity by tearing open a precursor void.

It can be concluded that an elastomeric matrix will not detach from small particles, less than about 0.1 mm in size, by debonding, even when the level of adhesion is low. Furthermore, the process of local cavitation in the matrix, leading to the same effects as detachment, will become increasingly difficult as the particle size is further reduced. Rigid inclusions of less than about 1 μm in size are likely to be effectively bonded to the matrix in all circumstances and thus act as reinforcing fillers, in accord with experience [1].

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