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On the micromechanics of composites containing spherical inclusions

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Exact solutions for the stress distribution inside a spherical inclusion embedded in an otherwise homogeneous matrix are obtained. Such expressions provide a framework for discussing the load carrying capacity of rubber inclusions and the effect of interfacial bonding on the toughness of such filled systems. Parametric studies of the influence of constituent stiffness ratios on the resultant stress patterns in the inclusion and matrix have been conducted. Results indicate that chemical bonding between the particle and matrix is not necessary for soft inclusions, but is essential for rigid inclusions.

1. Introduction

The toughness of many glassy polymers can be enhanced by the addition of spherical fillers with limited sacrifice in other physical properties of the resultant composites. The toughening mechanisms in elastomeric filled polymers include rubber tearing [1], matrix cold drawing [2] and provision of multiple yield sites [3]. Rigid inclusions, such as glass beads, have been used to increase the fracture toughness of epoxies by a crack-pinning mechanism [4].

The role of interfacial bonding in toughening of glassy polymers has not been elucidated clearly. Since the 1960s the bulk, suspension, and emulsion polymerization processes have become standard methods for the manufacture of high-impact polystyrene (HIPS), acrylonitrile-butadiene-styrene (ABS) and related polymers [5]. These processes consist of grafting rubber particles to a glassy matrix. In the 1970s developments in block copolymerization technology offered another route to polymer blends. The block copolymer introduced into the interfacial region has properties superior to grafted HIPS [6]. A quantitative study of the effects of interfacial bonding on rubber-toughened nylon 6 has been performed by Wu [7]. He has demonstrated that van der Waals' adhesion is sufficient for rubber-toughening of composites. In 1986, Nauman [8] patented a novel compositional quenching process to manufacture polymer blends. Subsequent studies [9] have shown that the toughness of numerous brittle polymers such as styrene-acrylonitrile copolymer (SAN), epoxies, polyimides and polyphenylene ether have been improved without interfacial bonding between the modifier and base resins.

The application of continuum mechanics to particulate composites originates from Goodier's stress analysis around an elastic inclusion in an otherwise uniform matrix [10]. Experimental studies by Wang *et al.* [11, 12] have confirmed the adequacy of Goodier's formulae. Using different craze initiation criteria to analyse the location of craze initiation for both soft and hard particle inclusions, Wang *et al.* concluded that locations predicted by the strain energy criteria and principle strain criteria agreed best with the test data. Extended studies applying Goodier's analysis to determine the stress state in a three-phase composite containing particles with a core-shell morphology can be found in the literature [13, 14]. However, an incorrect application of boundary conditions at the core/shell interface in [13] resulted in an invalid stress distribution in both core and shell regions. A simplified finite-element analysis has been performed by Broutman and Panizza [15] to study the stress interference of multiple particles. The results indicated that the single-particle model is valid for composites containing particles up to 10% by volume. However, most studies have concentrated on the stress distribution and yield mechanisms in the matrix and a complete stress analysis inside the particle has not yet been reported.

The objective of this paper is to investigate the effect of interfacial bond strength on the post-yield behaviour of particulate reinforced polymers. Stress functions have been constructed using spherical harmonic functions. The parametric coefficients have been determined from boundary conditions at the interface. This technique provides a concise description of the stress distribution both inside and outside the spherical inclusion.

2. Solution of general case

The analysis of the stress distribution inside a spherical inclusion has been based on the model shown in Fig. 1, which consists of a single particle embedded in an otherwise uniform matrix, which is subject to remote uniaxial tension. Physical properties, such as shear modulus (G) and Poisson's ratio (μ), are distinguished by subscript 1 for the matrix and 2 for the inclusion. Both materials are assumed to be homogeneous, isotropic and linearly elastic. Further,

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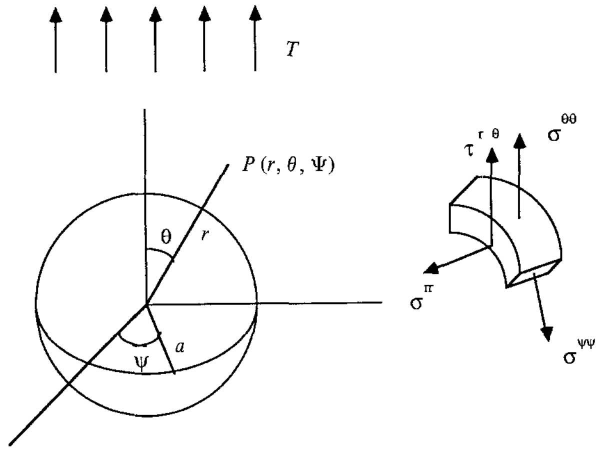

Figure 1 Elementary model of composites containing spherical inclusion.

perfect adhesion between the particle and the matrix is assumed. It will be demonstrated that such assumptions are valid, even for rubbery inclusions in a glassy polymer.

The theoretical basis for the three-dimensional solution of this general problem using harmonic functions was established by Love [16]. The physical meaning of these harmonic functions and general formulae for displacement and stress determination can be found in Goodier's study [10]. The displacement and stress fields for the matrix and the particle in spherical coordinates have been derived using three independent harmonic functions individually for the two materials. The selection of the specific spherical harmonic functions is dictated by the boundary conditions.

Following Goodier [10], the harmonic functions for the matrix are

$$\phi_{-1} = \left[\frac{A}{r}\right] \tag{1}$$

$$\phi_{-3} = 2\left[\frac{B}{r^3}(3\cos^2\theta - 1)\right] \tag{2}$$

$$\omega_{-3} = \frac{2}{3}\left[\frac{C}{r^3}(3\cos^2\theta - 1)\right] \tag{3}$$

For the particle:

$$\phi_2 = [Fr^2(3\cos^2\theta - 1)] \tag{4}$$

$$\omega_2 = \frac{7 - 4\mu_2}{3}[Dr^2(3\cos^2\theta - 1)] \tag{5}$$

$$\omega_0 = \frac{5 - 4\mu_2}{2(1 - 2\mu_2)}[H] \tag{6}$$

The expressions in the square brackets are spherical harmonics of degree n (refer to [17] for a general discussion). A, B, C, D, F and H are arbitrary constants which will be determined later. The other constants multiplying the spherical harmonic functions were selected so that the displacement and stress fields could be directly compared with Goodier's results.

The stresses and displacements induced by the spherical inclusion can be derived using the well known equations (see Appendix). For the matrix:

$$u_1^{rr} = \frac{A}{r^2} - \frac{3B}{r^4} + \frac{5 - 4\mu_1}{3(1 - 2\mu_1)}\frac{C}{r^2} + \left(-\frac{9B}{r^4} + \frac{5 - 4\mu_1}{1 - 2\mu_1}\frac{C}{r^2}\right)\cos 2\theta \tag{7}$$

$$u_1^{\theta\theta} = -\left(\frac{2C}{r^2} + \frac{6B}{r^4}\right)\sin 2\theta \tag{8}$$

$$\sigma_1^{rr} = 2G_1\left[\frac{2A}{r^3} + \frac{12B}{r^5} + \frac{-2(5 - \mu_1)}{3(1 - 2\mu_1)}\frac{C}{r^3} + \left(\frac{36B}{r^5} + \frac{-2(5 - \mu_1)}{1 - 2\mu_1}\frac{C}{r^3}\right)\cos 2\theta\right] \tag{9}$$

$$\tau_1^{r\theta} = 2G_1\left[-\frac{2(1 + \mu_1)}{1 - 2\mu_1}\frac{C}{r^3} + \frac{24B}{r^5}\right]\sin 2\theta \tag{10}$$

$$\sigma_1^{\theta\theta} = 2G_1\left[\frac{-A}{r^3} - \frac{3B}{r^5} + \frac{5C}{3r^3} + \left(-\frac{21B}{r^5} + \frac{C}{r^3}\right)\cos 2\theta\right] \tag{11}$$

$$\sigma_1^{\psi\psi} = 2G_1\left[\frac{-A}{r^3} - \frac{9B}{r^5} - \frac{C}{3r^3} + \left(-\frac{15B}{r^5} + \frac{3C}{r^3}\right)\cos 2\theta\right] \tag{12}$$

For the inclusion:

$$u_2^{rr} = Hr + Fr + 2\mu_2 Dr^3 + (3Fr + 6\mu_2 Dr^3)\cos 2\theta \tag{13}$$

$$u_2^{\theta\theta} = -[3Fr + (7 - 4\mu_2)Dr^3]\sin 2\theta \tag{14}$$

$$\sigma_2^{rr} = 2G_2\left[\frac{1 + \mu_2}{1 - 2\mu_2}H + F - \mu_2 Dr^2 + (3F - 3\mu_2 Dr^2)\cos 2\theta\right] \tag{15}$$

$$\tau_2^{r\theta} = -2G_2[3F + (7 + 2\mu_2)Dr^2]\sin 2\theta \tag{16}$$

$$\sigma_2^{\theta\theta} = 2G_2\left[\frac{1 + \mu_2}{1 - 2\mu_2}H + F - 5\mu_2 Dr^2 - (3F + 7(2 + \mu_2)Dr^2)\cos 2\theta\right] \tag{17}$$

$$\sigma_2^{\psi\psi} = 2G_2\left[\frac{1 + \mu_2}{1 - 2\mu_2}H - 2F - (7 + \mu_2)Dr^2 - (7 + 11\mu_2)Dr^2\cos 2\theta\right] \tag{18}$$

where u is displacement; σ^{rr}, $\sigma^{\theta\theta}$ and $\sigma^{\psi\psi}$ are radial, hoop and meridian stresses; τ is shear stress; r is the radius from the centre of the inclusion; and the superscripts represent the tensorial notation (Fig. 1).

It can be shown that these expressions satisfy the following equations of equilibrium free from body force:

$$\frac{\partial\Delta}{\partial r} + \frac{1 - 2\mu}{1 - \mu}\frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}(\bar{\omega}_\psi\sin\theta) = 0 \tag{19}$$

$$\frac{\partial\Delta}{\partial\theta} - \frac{1 - 2\mu}{1 - \mu}\frac{1}{\sin\theta}\frac{\partial}{\partial r}(r\bar{\omega}_\psi\sin\theta) = 0 \tag{20}$$

where

$$\Delta = \frac{1}{r^2}\frac{\delta}{\delta r}(r^2 u^{rr}) + \frac{1}{r\sin\theta}\frac{\delta}{\delta\theta}(u^{\theta\theta}\sin\theta)$$

$$\bar{\omega}_\psi = \frac{1}{2r}\left[\frac{\partial u^{rr}}{\partial\theta} - \frac{\partial}{\partial r}(ru^{\theta\theta})\right]$$

since $u^{\psi\psi} = 0$, $u^{rr} = u^{rr}(r, \theta)$ and $u^{\theta\theta} = u^{\theta\theta}(r, \theta)$.

When an elastic solid is subject to uniform tension, the displacements and the stresses (in spherical coordinates) at any radius a are:

$$u^{rr} = \frac{Ta}{4G_1}\left[\frac{1-\mu_1}{1+\mu_1} + \cos 2\theta\right] \quad (21)$$

$$u^{\theta\theta} = -\frac{Ta}{4G_1}\sin 2\theta \quad (22)$$

$$\sigma^{rr} = \frac{T}{2}(1 + \cos 2\theta) \quad (23)$$

$$\tau^{r\theta} = -\frac{T}{2}\sin 2\theta \quad (24)$$

where T is the remote uniaxial tension. The six constants A, B, C, D, F and H can be evaluated from the boundary conditions. At the interface ($r = a$), u^{rr}, $u^{\theta\theta}$, σ^{rr} and $\tau^{r\theta}$ must be continuous. The displacements and stresses outside the inclusion are obtained by adding Equations 7 to 10 to Equations 21 to 24, respectively, and the displacements and stresses inside the inclusion are taken as Equations 13 to 16. Equating displacements and stresses at the common boundary $r = a$ and rearranging the terms with and without cos 2θ, which varies as θ changes, six simultaneous equations were obtained:

$$-\frac{A}{a^2} - \frac{3B}{a^4} + \frac{5-4\mu_1}{3(1-2\mu_1)}\frac{C}{a^2} + \frac{Ta}{4G_1}\frac{1-\mu_1}{1+\mu_1} = Ha + Fa + 2\mu_2 Da^3 \quad (25)$$

$$-\frac{9B}{a^4} + \frac{5-4\mu_1}{1-2\mu_1}\frac{C}{a^2} + \frac{Ta}{4G_1} = 3Fa + 6\mu_2 Da^3 \quad (26)$$

$$\left(\frac{2C}{a^2} + \frac{6B}{a^4}\right) + \frac{Ta}{4G_1} = [3Fa + (7 - 4\mu_2)Da^3] \quad (27)$$

$$2G_1\left[\frac{2A}{a^3} + \frac{12B}{a^5} + \frac{-2(5-\mu_1)}{3(1-2\mu_1)}\frac{C}{a^3}\right] + \frac{T}{2} = 2G_2\left[\frac{1+\mu_2}{1-2\mu_2}H + F - \mu_2 Da^2\right] \quad (28)$$

$$2G_1\left(\frac{36B}{a^5} + \frac{-2(5-\mu_1)}{1-2\mu_1}\frac{C}{a^3}\right) + \frac{T}{2} = 2G_2[3F - 3\mu_2 Da^2] \quad (29)$$

$$2G_1\left[-\frac{2(1+\mu_1)}{1-2\mu_1}\frac{C}{a^3} + \frac{24B}{a^5}\right] - \frac{T}{2} = -2G_2[3F + (7 + 2\mu_2)Da^2] \quad (30)$$

The six constants then can be evaluated analytically using a Macsyma symbolic manipulation program performed on a SUN Workstation 3/60:

$$\frac{A}{a^3} = -\frac{T}{6G_1(1+\mu_1)} \times \frac{G_1(1-2\mu_2)(1+\mu_1) - G_2(1-2\mu_1)(1+\mu_2)}{2G_1(1-2\mu_2) + G_2(1+\mu_2)} \quad (31)$$

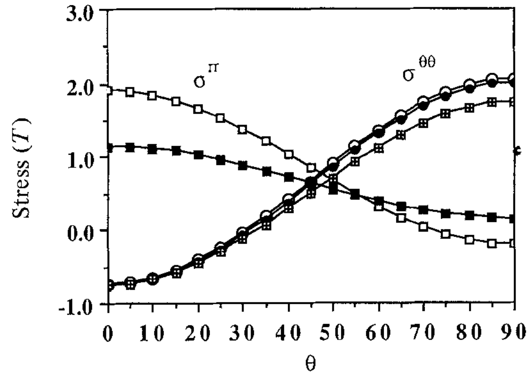

Figure 2 Stress concentrations outside the inclusion of different materials.

$$\frac{B}{a^5} = \frac{T}{8G_1}\frac{G_1 - G_2}{G_1(7-5\mu_1) + G_2(8-10\mu_1)} \quad (32)$$

$$\frac{C}{a^3} = \frac{5T}{8G_1}\frac{(G_1 - G_2)(1-2\mu_1)}{G_1(7-5\mu_1) + G_2(8-10\mu_1)} \quad (33)$$

$$F = \frac{5T}{4}\frac{1-\mu_1}{G_1(7-5\mu_1) + G_2(8-10\mu_1)} \quad (34)$$

$$D = 0 \quad (35)$$

$$H = \frac{T(1-\mu_1)}{2(1+\mu_1)}\frac{(1-2\mu_2)}{G_1(2-4\mu_2) + G_2(1+\mu_2)} \quad (36)$$

Note that the stress function inside the particle is not a function of radius because $D = 0$.

3. Stress distribution and adhesion requirements

3.1. Stress distribution

The stress state around the particle affects not only the initiation of crazing or shear yielding, but also influences the post-yield behaviour (such as debonding and rubber tearing). Poisson's ratios and stiffness ratios in this study are presented in Table I. These parameters resemble glass bead, soft rubber, hard rubber, and rubber with rigid occlusion. All stresses have been normalized to the applied stress, T. The resultant stress distributions around the interface are expressed graphically for convenience of comparison.

Figure 2 presents typical stress concentration profiles outside the inclusion for different G_1/G_2 ratios. The matrix yields either near the pole for rigid inclusions or at the equator for soft inclusions [11, 12]. Figure 3 shows a typical stress distribution inside the rigid inclusion. Note that the radial and shear hoop stresses are symmetrical and have a maximum value of approximately 1.9 at $\theta = 0$ and $\theta = \pi/2$, respectively. The principal stress distributions are shown in Fig. 4.

TABLE I Parameters of material properties

	Poisson's ratio	Stiffness ratio (G_1/G_2)
Matrix	0.33	
Rigid inclusion	0.28	0.01
Soft inclusion (1)	0.48	1000
Soft inclusion (2)	0.48	100
Soft inclusion (3)	0.48	10
Soft inclusion (4)	0.48	1

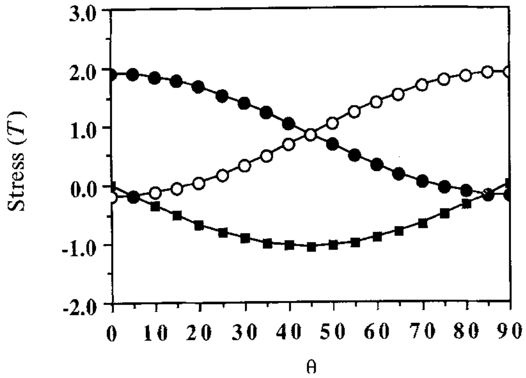

Figure 3 Stress distribution inside rigid inclusion.

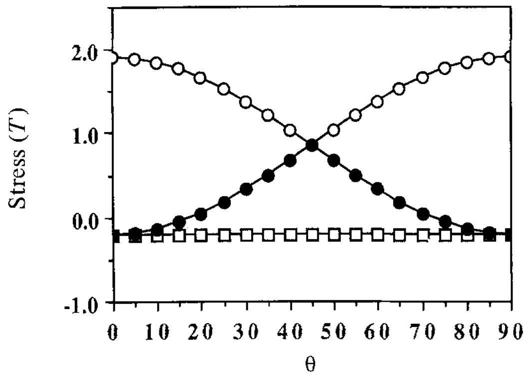

Figure 4 Principal stresses of rigid inclusion.

The stress distributions inside the soft inclusion are presented in Figs 5a–d for inclusion is under hydrostatic tension, with small deviations between the radial, hoop and meridian stress. Also, the shear stress is very small. Therefore, the assumption of elastic properties for the soft inclusion is preserved. As the stiffness ratio decreases, the stress difference between radial, hoop and meridian stress increases. The stress level is also seen to increase.

3.2. Adhesion and inclusion failure analysis

Adhesive failure includes debonding and molecular pullout from the matrix. The debonding failure is presumed active when the continuous stress at the interface (σ^{rr} or $\tau^{r\theta}$) exceeds the bond strength of the material [13]. However, rubber particles are known to withstand high hydrostatic tensile and compressive stresses. To account for this, failure should be presumed to occur when molecular pullout takes place in conjunction with either the Tresica or von Mises criteria. The Tresica criterion is:

$$2\tau_{max} = \max[\sigma_1, \sigma_2, \sigma_3] - \min[\sigma_1, \sigma_2, \sigma_3] \tag{37}$$

and the von Mises criterion, which is equivalent to constant distortional strain energy [18], is:

$$\tau_{oct} = \frac{1}{3}\sqrt{(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2} \tag{38}$$

where τ_{max} and τ_{oct} are material constants, the critical shear stress and yield stress respectively. σ_1, σ_2 and σ_3 are principal stresses, which may be written as:

$$\sigma_1 = \frac{1}{2}(\sigma^{rr} + \sigma^{\theta\theta}) + \frac{1}{2}\sqrt{(\sigma^{rr} - \sigma^{\theta\theta})^2 + 4(\tau^{r\theta})^2} \tag{39}$$

$$\sigma_2 = \frac{1}{2}(\sigma^{rr} + \sigma^{\theta\theta}) - \frac{1}{2}\sqrt{(\sigma^{rr} - \sigma^{\theta\theta})^2 + 4(\tau^{r\theta})^2} \tag{40}$$

and

$$\sigma_3 = \sigma^{\psi\psi} \tag{41}$$

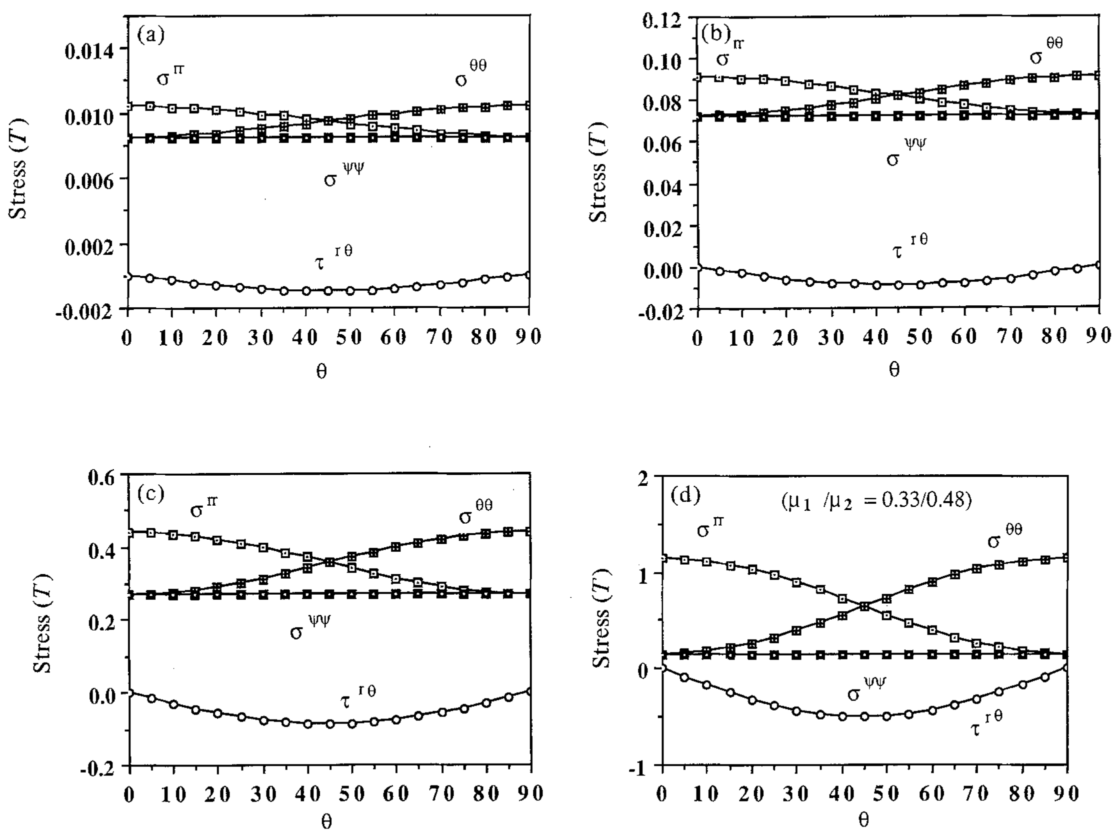

Figure 5 Stress distributions inside different inclusions. G_1/G_2 = (a) 1000; (b) 100; (c) 10; (d) 1.

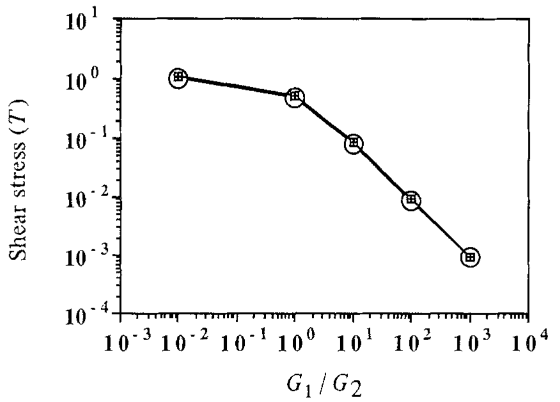

Figure 6 Maximum shear sresses of different inclusions. ○, τ_{oct}; ■, τ_{max}.

Figure 6 shows that τ_{max} and τ_{oct} decay rapidly as stiffness ratio increases. The bond strength of C–C bonds and the weakest van der Waals force (London force) are $370\,kJ\,mol^{-1}$ and $5\,kJ\,mol^{-1}$, respectively [19]. The yield strength of the matrix is less than the C–C bond strength. Therefore the low shear stress state in the soft inclusion, approximately one thousandth the applied stress for $G_1/G_2 = 1000$, ensures the integrity of rubber and matrix even as the crack propagates. This phenomenon has been observed in a rubber-toughened nylon system [7], in which the matrix yields extensively and no debonding or rubber tearing occurs. At the other extreme, interfacial bonding is essential for glass-bead toughened epoxies [20, 21] and polyesters [22] due to the high stress state across the interfacial region. The adhesion requirement for rubber particles containing matrix occlusions lies between these two cases.

4. Conclusions

A set of equations with concise constants has been obtained to calculate the stress distribution within the spherical inclusion and in the otherwise uniform matrix. The need for strong interfacial bonding depends on the stiffness ratio of the constituents. Stress calculations inside the soft inclusion reveal that van der Waals adhesion can be sufficient to relieve the high localized stresses in the matrix. Therefore the soft inclusion acts as yield initiator as well as crack arrestor. However, the adhesion between particle and matrix becomes more important as the stiffness of the inclusion increases. The rigidity also constrains the post-yield behaviour of the matrix. Even though thermally induced residual stresses were not considered in this study, the analysis should be valid for composites made by continuous solvent removing processes such as solvent casting and compositional quenching processes. The effect of particle size on the yield behaviour is not considered in this study. Finally, it is noted with emphasis that such investigations are crucial for a proper understanding of toughening mechanisms in composites.

Appendix

The displacement and stress fields from spherical harmonic functions, ϕ_n and ω_n, can be expressed as follows:

$$u^{rr} = \frac{\partial \phi_n}{\partial r} + r^2 \frac{\partial \omega_n}{\partial r} + \alpha_n r \omega_n \tag{A1}$$

$$u^{\theta\theta} = \frac{1}{r}\frac{\partial \phi_n}{\partial \theta} + r\frac{\partial \omega_n}{\partial \theta} \tag{A2}$$

The general formulae for the strain are:

$$e^{rr} = \frac{\partial u^{rr}}{\partial r} \tag{A3}$$

$$e^{\theta\theta} = \frac{1}{r}\frac{\partial u^{\theta\theta}}{\partial \theta} + \frac{u^{rr}}{r} \tag{A4}$$

$$e^{\psi\psi} = \Delta - e^{rr} - e^{\theta\theta} \tag{A5}$$

$$e^{r\theta} = \frac{1}{r}\frac{\partial u^{rr}}{\partial \theta} + r\frac{\partial}{\partial r}\left(\frac{u^{\theta\theta}}{r}\right) \tag{A6}$$

The general stress–strain relationships are:

$$\sigma^{rr}, \sigma^{\theta\theta}, \sigma^{\psi\psi} = 2G\left[\frac{\mu}{1-2\mu}\Delta + (e^{rr}, e^{\theta\theta}, e^{\psi\psi})\right] \tag{A7}$$

$$\tau^{r\theta} = Ge^{r\theta} \tag{A8}$$

where Δ is the dilation which is equal to $[2n + (3 + n)\alpha_n]\omega_n$, and the constant α_n is

$$-2\,\frac{3n + 1 - 2(2n + 1)\mu}{n + 5 - 4\mu}.$$

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