

THE EFFECT OF SURFACE STRESSES ON THE CRITICAL DEBONDING STRESS AROUND NANOPARTICLES

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Abstract. With the aid of an energy analysis and the surface elasticity theory, this work provides a closed form solution for the critical debonding stress of a rigid nanoparticle embedded in an elastic matrix subjected to a remote hydrostatic stress. It is proved that the debonding stress depends on the particle radius, the matrix elastic properties and the fracture energy per unit surface. The solution allows quantifying the effects of surface elastic constants, also showing that the smaller the particle size the more significant those effects are.

Keywords: nanocomposites, debonding, surface elasticity

1. Introduction

In traditional composites, some mechanical properties are dominated by the fibres and some others are instead controlled by the matrix. Since the matrix mechanical stiffness properties are low, much attention, in the recent literature, has been paid to nanoscale reinforcements to significantly increase polymer stiffness, strength and toughness with low reinforcement concentrations (see, among the others, Wetzels *et al.*, 2003, Wichmann *et al.*, 2006, Cortes *et al.*, 2010, Ayatollahi *et al.*, 2011). Accordingly, an interest in the subject of the filler size effect at the nano meter scale has been arisen.

The nanoparticle size effect on the energy dissipation due to the interfacial debonding has been studied by Chen *et al.* (2007) by means of an energy analysis of the process. These authors derived a simple size-dependent formulation for the debonding stress, which was later used to compute the energy dissipation due to interfacial debonding. The size distribution of particles was thought of as obeying a logarithmic normal distribution and the Weibull distribution function was used to describe the probability of debonding at the interface.

Lauke (2008) analysed the energy dissipation phenomena by considering, besides particle debonding, voiding and subsequent yielding of the polymer. The conclusions drawn by Lauke were different depending on the used debonding criterion (critical stress or critical energy).

Recently, Williams (2010) analysed toughening of particle-filled polymers assuming that plastic void growth around debonded, or cavitated, particles is the dominant mechanism for energy dissipation.

However, all the models mentioned above neglect certain important aspects of nanosized materials. As the filler size is decreased to the nanoscale the intra- and supra-molecular interactions lead to the emergence of an interphase whose properties differ from those of both the constituents and whose thickness may be comparable to the to particles size. Sevostianov and Kachanov (2006, 2007) showed that the effect of the interphase on the overall properties may be substantial, the controlling parameters being the ratio of the interphase thickness to the particle size and the variability of the properties across the interface thickness.

Another issue that could be increasingly important, as the particle size is decreased, is the emergence of surface stresses. The analytical framework to account for this issue was developed by Gurtin and Murdoch (1975, 1978).

In the present work, the effects of surface stresses on debonding of nanoparticles are investigated by means of an energy analysis of the problem, reformulated according to the surface elasticity theory. The aims of the work can be summarised as follows:

- to provide a closed form solution for the critical debonding stress of a rigid nanoparticle embedded in an elastic matrix, subjected to a remote hydrostatic stress;
- to prove that the debonding stress depends on the particle radius, the matrix elastic properties and the fracture energy per unit surface;
- to quantify the effects of surface elastic constants on the debonding stress, also showing that the smaller the particle size the more significant those effects are.

2. Analytical framework and results

In the absence of a pre-existing defect, the debonding of a nanoparticle requires, simultaneously, that the normal stress acting on the interface is higher than the normal interfacial strength, σ_c , and that the energy released during the process is greater than the fracture energy:

$$\sigma \geq \sigma_c \quad -\frac{\delta U}{\delta S} \geq \gamma \quad (1a-b)$$

where δU is the change in potential energy, δS is the newly created debonding surface and γ is the fracture energy per unit surface. This is in agreement with the criterion for crack nucleation proposed by Leguillon (2002).

Let us assume the nanoparticle, which is embedded within a matrix of radius b

much greater than r_0 , is loaded by a remote hydrostatic stress (Figure 1a) and that the debonding takes place all around the nanoparticle. Then the following equation for the potential energy holds:

$$\delta U = \delta U^p + \delta U^m = -\frac{1}{2} \sigma_{cr} \delta S \left[\delta u^p(r_0) + \delta u^m(r_0) \right] \tag{2}$$

where σ_{cr} is the normal stress at the nanoparticle at incipient debonding conditions, δu^p and δu^m are the change in the radial displacement field around the nanoparticle/matrix interface from the initial condition, incipient debonding, to the final condition, post debonding, (the superscripts p and m refer to the nanoparticle and the matrix, respectively). Eq. (2) allows the energy condition given by Eq. (1b) to be rewritten as a stress condition.

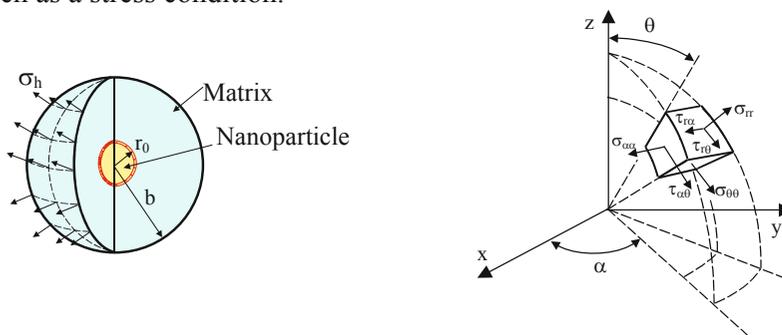


Figure 1. (a): Nanoparticle of radius r_0 embedded in an elastic matrix subjected to an hydrostatic stress σ_h . (b) Spherical coordinates system is used.

It is worth noting that, when dealing with surface elasticity theory, the term γ accounts for the energy spent to create a new surface at constant strain as well as for that spent to deform the already created surfaces (Müller and Saúl, 2004).

Due to the spherical symmetry of the problem, only the radial displacement, u , is nonzero and, in the absence of body forces, it obeys to the Euler equation:

$$\frac{d^2 u}{dr^2} + \frac{2}{r} \frac{du}{dr} - \frac{2u}{r^2} = 0 \tag{3}$$

so that

$$u^k = A_k r + \frac{B_k}{r^2} \quad \sigma_{rr}^k = 3K_k A_k - 4 \frac{B_k G_k}{r^3} \quad \text{with } k=m, p \tag{4}$$

where K_k and G_k are the bulk and the shear moduli, respectively. Within the framework of surface elasticity, the boundary conditions of the problem are different from those of the traditional continuum theory. Indeed, on the surface, the following equilibrium equations can be stated (Sharma *et al.*, 2003):

$$\begin{aligned}\sigma_{rr}^m - \sigma_{rr}^p &= \frac{\sigma_{\varphi\varphi}^s + \sigma_{\vartheta\vartheta}^s}{r} \\ \tau_{r\varphi}^m - \tau_{r\varphi}^p &= - \left(\frac{1}{r} \frac{\partial \sigma_{\varphi\varphi}^s}{\partial \varphi} + \frac{1}{r \sin \varphi} \frac{\partial \tau_{\varphi\vartheta}^s}{\partial \vartheta} + \frac{\sigma_{\varphi\varphi}^s - \sigma_{\vartheta\vartheta}^s}{r} \cot \varphi \right) \\ \tau_{r\vartheta}^m - \tau_{r\vartheta}^p &= - \left(\frac{1}{r} \frac{\partial \tau_{\varphi\vartheta}^s}{\partial \varphi} + \frac{1}{r \sin \varphi} \frac{\partial \sigma_{\vartheta\vartheta}^s}{\partial \vartheta} + \frac{2\tau_{\varphi\vartheta}^s}{r} \cot \varphi \right)\end{aligned}\quad (5a-c)$$

where $\tau_{\varphi\vartheta}^s$, $\sigma_{\vartheta\vartheta}^s$ and $\sigma_{\varphi\varphi}^s$ are the surface stress components.

Assuming a non-sliding condition, the strain field is continuous throughout the surface and, due to the spherical symmetry of the problem, no surface shear strains are present. Then, the surface stresses can be linked to strain components through the following equation (Sharma *et al.*, 2003):

$$\sigma_{\beta\alpha}^s = 2\mu^s \delta_{\beta\gamma} \varepsilon_{\gamma\alpha} + \lambda^s \varepsilon_{\gamma\gamma} \delta_{\beta\alpha} \quad (6)$$

Accordingly, Eqs. (5) simplify in:

$$\sigma_{rr}^{(m)} - \sigma_{rr}^{(i)} = \frac{2}{r} K_s \varepsilon \quad \tau_{r\varphi}^{(m)} - \tau_{r\varphi}^{(i)} = 0 \quad \tau_{r\vartheta}^{(m)} - \tau_{r\vartheta}^{(i)} = 0 \quad (7)$$

where $K_s = 2(\lambda_s + \mu_s)$ is the surface elastic modulus.

Then, the boundary conditions of the problem can be written as:

$$\sigma_r^p \Big|_{r=r_0} = \sigma_{cr} \quad \sigma_r^m \Big|_{r=r_0} = \sigma_{cr} + \frac{2}{r_0} K_s^- \varepsilon \quad u^p \Big|_{r=r_0} = u^m \Big|_{r=r_0} \quad (8a-c)$$

for incipient debonding and

$$\sigma_r^m \Big|_{r=r_0} = \frac{2}{r_0} K_s^+ \varepsilon \quad \sigma_r^m \Big|_{r=b} = \sigma_h \quad (9a-b)$$

for post debonding. Whenever the nanoparticle can be regarded as far stiffer than the matrix (as in the case of a metal oxide or silica nanoparticle embedded in an epoxy matrix) the following equations hold:

$$\delta u^p \ll \delta u^m \quad \delta u^m = \frac{\sigma_{cr}}{2K_s^+ / r_0 + 4G_m} r_0 \quad (10a-b)$$

$$\gamma = \Gamma + \frac{K_s^+}{r_0} \frac{\sigma_{cr}^2}{(2K_s^+ / r_0 + 4G_m)^2} \quad (11)$$

where the effects of residual stresses have been neglected.

Substitution of Eqs. (10) and Eq. (11) into Eq. (2), and then into Eq. (1-b), results into the following expression for the critical debonding stress:

$$\sigma_{cr} = \zeta \sqrt{\frac{\gamma}{2r_0 G_m}} \quad (12)$$

where $\zeta = 2(K_s^+ / r_0 + 2G_m)$ is a parameter which depends on the matrix elastic properties, the surface elastic properties and the nanoparticle radius. It should be noted that, when the nanoparticle radius is sufficiently high ($r_0 \gg K_s^+ / 2G_m$) the solution tends to the equation:

$$\sigma_{cr,0} = 2\sqrt{2\Gamma G_m / r_0} \quad (13)$$

Eq. (13) only depends on the energy per unit surface fracture Γ , the matrix elastic properties and the nanoparticle radius and matches the solution previously obtained by Chen *et al.* (2007), disregarding surface effects.

It is finally interesting to verify the range of the nanoparticle size where the effect of surface stresses is significant. To this end, figure 2 shows the critical debonding stress given by Eq. (12) normalised with respect to $\sigma_{cr,0}$, Eq. (13), which neglects surface stresses, considering different values of the surface elastic modulus K_s^+ .

Results are obtained considering a stiff nanoparticle embedded in an epoxy matrix. It is evident that the range of the nanoparticle radii where the effect of surface stresses is significant is very limited, approximately up to 10 nm. As it can be seen, within this range, the influence exerted by the surface elastic modulus is very high. Different, for larger nanoparticles the influence of the surface elastic modulus becomes negligible, and all the curves asymptotically tend to the value given by Eq. (13).

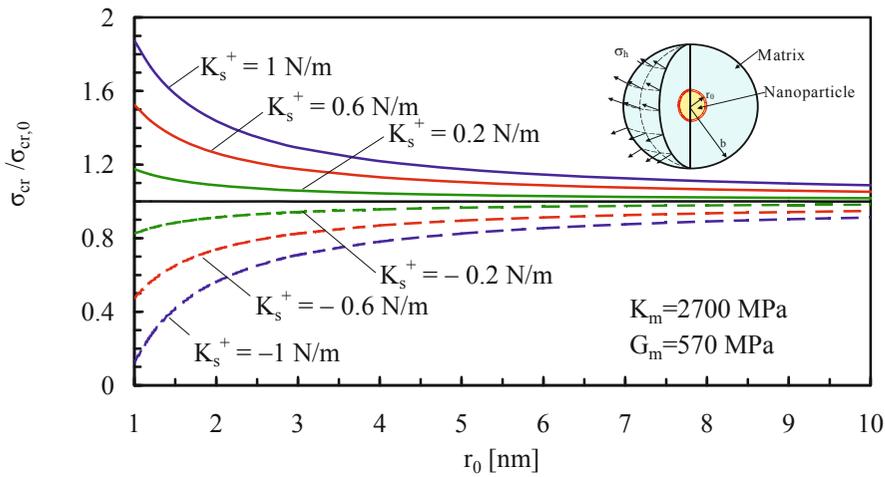


Figure 2. Normalised debonding stress versus the nanoparticle radius, r_0 , according to Eq. (12). Different values of the surface elastic modulus K_s^+ .

3. Conclusions

In the present work a new closed form solution for the critical debonding stress of a rigid nanoparticle embedded in an elastic matrix subjected to a remote hydrostatic stress has been determined. The solution has been obtained by using, in combination, an energy analysis and the surface elasticity theory. Results highlight that the critical debonding stress is an explicit function of the particle size, the matrix elastic properties and the fracture energy per unit surface. It is also proved that the smaller the particle size the more significant the effects of surface elastic constants are.

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