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Plastic Yielding Around Nanovoids

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Abstract

Nanocomposites hierarchical structure, ranging from nano to macro length-scales, urges to account for the characteristic phenomena of the different involved length-scales and to bridge their effects up to the macroscale. This makes the assessment of nanocomposite mechanical properties a challenging task.

In the present work, a model to assess the nanocomposite toughening due to plastic yielding of nanovoids is presented. The model accounts for the emergence of an interphase, created by the inter- and supra-molecular interactions arising at the nanoscale, with mechanical properties different from those of the matrix.

Keywords: polymer nanocomposites; nanoparticles; multiscale modelling; plastic void; debonding region (DBR); interphase.

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1. Introduction

The outstanding physical and mechanical properties of nanocomposites are commonly thought of as due to the so called “nano-effect”, a consequence of the hierarchical structure of this kind of materials. Indeed, a uniform dispersion of nanoreinforcements not only gives rise to an enormous interfacial area per unit volume (*SSA*) [1] but also causes the formation of an interphase “layer” whose properties can be very different from those of the constituents [2, 3]. In the recent literature there is a large amount of data reporting improvements of stiffness, strength and toughness in nano-reinforced polymers (see amongst others, Wetzel *et al.* [4] and Zhao *et al.* [5]). However, a successful engineering application of this class of materials requires, beyond experimental analyses, models capable of accounting for their inherent hierarchical structure, which encompasses the nano and the macro length-scales.

If, by the one hand, modelling molecular interactions between nanofillers and the matrix would require a discrete approach, the introduction of such an atomistic model up to macro length-scales is limited by

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the impracticability of accounting for more than some hundred millions of atoms. This fact gives rise to the need of a multiscale modelling, each dominant mechanism being studied by means of the best suited approach with reference to the given length scales.

In principle, toughness improvements at low nanofiller contents can only be explained by analysing the amount of energy dissipated by the different damaging mechanisms taking place at the nanoscale. For example Lauke [6] analysed the energy dissipation phenomena by considering particle debonding, voiding and subsequent yielding of the polymer. Williams [7] further analysed the toughening of particle filled polymers assuming that plastic void growth around debonded or cavitated particles is the dominant mechanism for energy dissipation.

However, in the authors' opinion the best suited approach should be a "multi-mechanism" modelling strategy, in which each contribution is weighted according to the specific case (accounting for the type, the morphology and the functionalisation of the nanofiller as well as of the loading condition).

As a further step toward such a multi-mechanism strategy, in the present paper we present a multiscale model with the aim to quantify the toughness improvement due to plastic yielding around nanovoids. Different from [6, 7], the present work explicitly considers the emergence of an interphase, created by the inter and supra-molecular interactions arising at the nanoscale, with mechanical properties different from those of the matrix.

2. Description of the multiscale system under analysis

Consider, initially, a macrosized crack in a nano-modified matrix (see Fig. 1a). Under the hypothesis of plane strain conditions, the hydrostatic stress component at the crack tip is:

$$\sigma_h = \frac{\sigma_x + \sigma_y + \sigma_z}{3} = \frac{2(1+\nu_o)K_I}{3\sqrt{2\pi\rho}}\cos\frac{\phi}{2} \tag{1}$$

where K_I and ν_o are the Stress Intensity Factor of local stress fields and the Poisson coefficient of the nanocomposite, respectively.

At the nanoscale, it is assumed that debonding of nanoparticles takes place, creating a number of nanovoids of the same diameter of the nanoparticles. The inter and supra-molecular interactions between nanofillers and the polymer are accounted for by embedding the nanovoid into an interphase, thought of as a zone of altered chemistry [2, 3, 8]. Such a zone is characterised by mechanical properties different from those of the matrix. The system under investigation at the nanoscale, neglecting for the time being nanofiller agglomeration, is shown in Fig. 1a and is constituted by a spherical void of initial radius $\mathbf{r_0}$, a shell-shaped interphase of external radius **a** and uniform properties, and a matrix of radius **b** much greater than $\mathbf{r_0}$ and **a**, subjected to a uniform hydrostatic stress.

Within a multiscale approach to the problem, the crack macroscale stress, σ_h, can be regarded as the average of the microscale stresses over a Representative Volume Element (RVE). The bridge with the nanoscale can be established by means of the *Average Stress Theorem* and the Mori-Tanaka approach, so that the hydrostatic stress component around the nanovoid can be approximated by:

$$\sigma_n(\rho,\phi) = \frac{\sigma_h}{C_h} = \frac{1}{C_h}\frac{2(1+\nu_o)K_I}{3\sqrt{2\pi\rho}}\cos\frac{\phi}{2} \tag{2}$$

where C_h is reciprocal of the hydrostatic part of the global stress concentration factor (see [8] for further details).

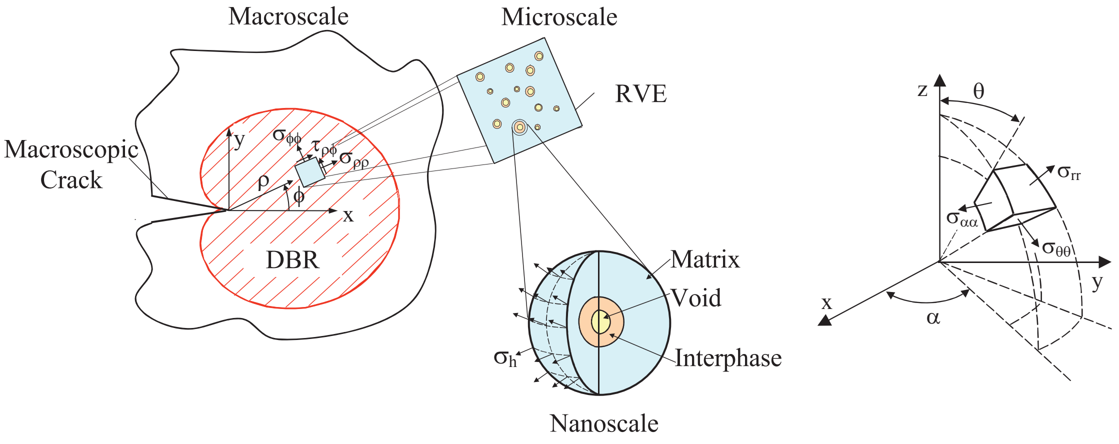
3. Preliminary analytical framework

The extension of the debonding region (DBR), meant as the region around the crack tip confining all the debonding-induced nanovoids, can be assessed by equating σ_n, Eq. (2), with the critical debonding stress σ_{cr}:

$$\sigma_{cr} = \sigma_n(\rho,\phi) = \frac{1}{C_h}\times\frac{2(1+\nu_o)K_I}{3\sqrt{2\pi\rho}}\cos\frac{\phi}{2} \tag{3}$$

where σ_{cr} can be determined in closed form [8]. Solving Eq. (3) by ρ results in:

$$\rho^*(\phi) = \frac{1}{(C_h)^2}\times\frac{2(1+\nu_o)^2 K_I^2}{9\pi\sigma_{cr}^2}\cos^2\left(\frac{\phi}{2}\right) = A\times\cos^2\left(\frac{\phi}{2}\right) \tag{4}$$



(a) (b)

Figure 1. (a) Description of the multiscale system under analysis. (b) Spherical coordinate system and stress components used to describe the stress field around nanovoids.

Whenever the stress field around a nanovoid is high enough to cause local yielding, denoting by R_P the extension of the plastic zone, two different conditions are possible:

- The entire interphase and a part of the matrix are yielded ($R_P>a$);
- Only a part of the interphase is yielded ($R_P<a$).

For the sake of simplicity, in this work we consider only the first condition, while a more comprehensive analysis is carried out in [9].

With reference to the coordinate system shown in Fig. 1b, invoking the Tresca yield criterion and assuming the matrix obeys an elastic-perfectly plastic behaviour, the yielding condition and the equilibrium equations for $r<R_P$ result in the following system:

$$\sigma_{eq} = \sigma_{\theta\theta} - \sigma_{rr} = \sigma_{Ym} \qquad \frac{\partial\sigma_{rr}}{\partial r} + \frac{2\sigma_{rr} - \sigma_{\theta\theta} - \sigma_{\alpha\alpha}}{r} = \frac{\partial\sigma_{rr}}{\partial r} + 2\times\frac{\sigma_{rr} - \sigma_{\theta\theta}}{r} = 0 \tag{5}$$

where σ_{Ym} is the matrix yield stress. The solution for σ_{rr}, satisfying Eq. (5), is:

$$\sigma_{rr}^{(pl)} = 2\sigma_{Ym} \times \mathrm{Ln}\left\{ (r/a) \times (a/r_0)^{\sigma_{Ya}/\sigma_{Ym}} \right\} \tag{6}$$

where σ_{Ya} is the yield stress of the interphase.

Whenever $r>R_P$, the matrix behaves elastically and stress and displacement fields can be described by the following equations [8]:

$$\sigma_{rr}^{(el)} = E_m\left[\frac{A_m}{1-2\nu_m} - 2\frac{B_m}{r^3(1+\nu_m)}\right] \qquad \sigma_{\theta\theta}^{(el)} = E_m\left[\frac{A_m}{1-2\nu_m} + \frac{B_m}{r^3(1+\nu_m)}\right] \qquad u^{(el)} = A_m r + \frac{B_m}{r^2} \tag{7}$$

where E_m and ν_m are the matrix Young modulus and Poisson coefficient. Unknown constants can be determined by applying the following boundary conditions:

$$\left.\sigma_{rr}^{(el)}\right|_{r=b} = \sigma_h, \qquad \left.\sigma_{eq}^{(pl)}\right|_{r=R_P} = \sigma_{\theta\theta}^{(el)} - \sigma_{rr}^{(el)} = \sigma_{Ym}, \qquad \left.\sigma_{rr}^{(el)}\right|_{r=R_P} = \left.\sigma_{rr}^{(pl)}\right|_{r=R_P} \tag{8}$$

Solving the system in Eq. (8), the plastic radius R_P and the displacement increase between the yielded and the un-yielded states, evaluated at r=b, turn out to be:

$$R_P = a \times \left(\frac{r_0}{a}\right)^{\frac{\sigma_{Ya}}{\sigma_{Ym}}} \times e^{\left(\frac{\sigma_h}{2\sigma_{Ym}} - \frac{1}{3}\right)} \qquad \Delta u \cong \frac{(1+\nu_m)\sigma_{Ym}}{3E_m} \times \frac{a^3}{b^2}\left(\frac{r_0}{a}\right)^{3\times\frac{\sigma_{Ya}}{\sigma_{Ym}}} e^{\left(\frac{3\sigma_h}{2\sigma_{Ym}} - 1\right)} \tag{9}$$

4. Plastic yielding contribution to the nanocomposite toughness

The energy produced at the nanoscale by plastic yielding of a single nanovoid is:

$$U_P = F \times \Delta u = 4\pi\sigma_h \times \frac{(1+\nu_m)\sigma_{Ym}}{3E_m} \times a^3 \times \left(\frac{r_0}{a}\right)^{3\times\frac{\sigma_{Ya}}{\sigma_{Ym}}} e^{\left(\frac{3\sigma_h}{2\sigma_{Ym}} - 1\right)} \tag{10}$$

Accordingly, the strain energy density in a RVE (microscale) can be calculated as:

$$u_P = U_P \times \frac{3f_{p0}}{4\pi r_0^3} = F \times \Delta u \times \frac{3f_{p0}}{4\pi r_0^3} = f_{p0} \times \frac{(1+\nu_m)\,\sigma_{Ym}\sigma_h}{E_m} \times \left(\frac{a}{r_0}\right)^{3\times\left(1-\frac{\sigma_{Ya}}{\sigma_{Ym}}\right)} \times e^{\left(\frac{3\sigma_h}{2\sigma_{Ym}} - 1\right)} \tag{11}$$

Finally the macroscale increment in terms of Strain Energy Release Rate can be estimated by [10, 11]:

$$\Delta G_P = 2 \times \int_0^{\rho^*(\phi=\pi/2)} u_P \; d\rho \tag{12}$$

Solving Eq. (12) is far from easy, since u_p has a complex dependence on ρ. We can overcome this problem by substituting σ_h with the following mean value:

$$\overline{\sigma_h} = \frac{1}{\rho^*(\phi = \pi/2)} \times \int_0^{\rho^*(\phi=\pi/2)} \sigma_h \, d\rho = 2 \times C_h \sigma_{cr} \tag{13}$$

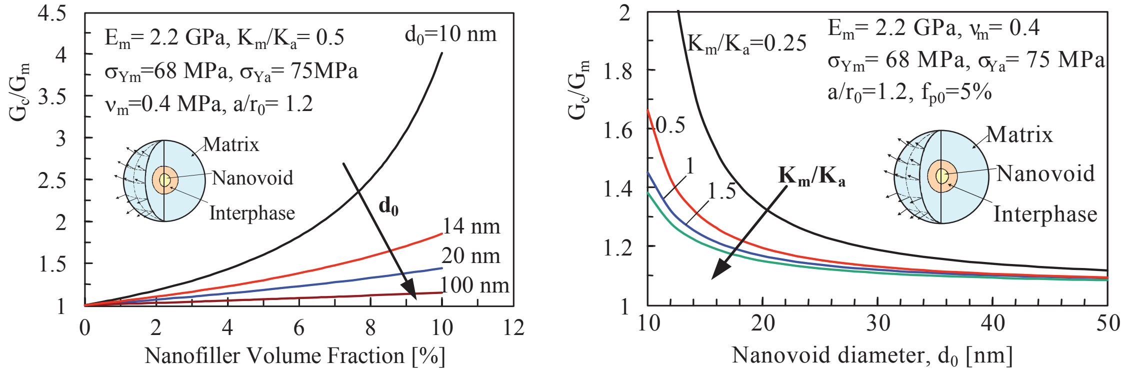
This simplified procedure is rather close to that used by Lauke [6]. Substituting Eq. (11), with $\sigma_h = \overline{\sigma_h}$, into Eq. (12) and noting that $G = K_I^2 / E_o \times \left(1 - {\nu_o}^2\right)$, the toughness improvement due to plastic yielding becomes:

$$\Delta G_P = G_c \times f_{p0} \times \left[\frac{4(1+\nu_0)(1+\nu_m)}{9\pi(1-\nu_0)} \frac{E_0}{E_m} \times \frac{\sigma_{Ym}}{C_h \sigma_{cr}} \left(\frac{a}{r_0}\right)^{3\times\left(1-\frac{\sigma_{Ya}}{\sigma_{Ym}}\right)} \times e^{\left(\frac{3C_h\sigma_{cr}}{\sigma_{Ym}}-1\right)} \right] = f_{p0} \times \psi_P \times G_c \tag{14}$$

where ψ_P is the term in square brackets.

Finally, assuming $G_c = G_m + \Delta G_P$, being G_m the matrix fracture toughness, the nanocomposite fracture toughness turns out to be:

$$G_c = \frac{G_m}{1 - f_{p0} \times \psi_P} \tag{15}$$



(a) (b)

Fig. 2. (a) Plots of G_c/G_m according to Eq. (15) versus the nanofiller volume fraction; nanovoid of different diameter, d_0. (b) Plots of G_c/G_m according to Eq. (15) versus the nanovoid diameter: different interphase properties. K_m and K_a are the bulk moduli of the matrix and of the interphase, respectively.

5. Example of application

Examples of application of the analytical results obtained in previous sections are shown in Figs. 2. In particular fig. 2a shows the toughness improvement due to plastic yielding, G_c/G_m, versus the nanofiller volume fraction, f_{p0}, as predicted by Eq. (15). The great influence exerted by the nanovoid diameter, d_0, is evident, the ratio G_c/G_m rapidly decreasing as d_0 increases.

Differently, Fig. 2b shows the substantial effect of the interphase properties on the fracture toughness improvement. Then, as different functionalizers lead to different properties of the interphase, nanocomposite toughening may be strongly affected by surface treatments. This result is extremely important for the engineering practice and will be further analysed in [9].

It is finally worth noting that in this work debonding has been thought of as a necessary condition for the highly dissipative plastic yielding contribution to take place.

6. Conclusions

The present work provides a model to assess the toughness improvement due to plastic yielding around nanovoids, thought of as nucleated by debonding of nanoparticles.

Neglecting, for the time being, possible effects of nanofiller agglomeration, the inter- and supra-molecular interactions between nanofillers and the polymer are accounted for by introducing an interphase embedding the nanovoid, with mechanical properties different from those of the matrix. It has been shown that plastic yielding is a highly dissipative mechanism, causing a high fracture toughness improvement at low nanofiller content. Finally it has been shown that nanocomposite toughening may be strongly affected by size of nanoparticle and surface treatments.

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