

FRACTURE TOUGHNESS ENHANCEMENTS IN NANOCOMPOSITES: A MULTISCALE MODEL

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Abstract

The high fracture toughness improvements exhibited by nanofilled polymers is commonly thought of as due to the large amount of energy dissipated at the nanoscale. In the present work, a multiscale modelling strategy to assess the nanocomposite toughening is presented. The model accounts for the emergence of an interphase with mechanical properties different from those of the matrix.

1 Introduction

Thanks to their hierarchical structure encompassing different time and length scales, nanocomposites are endowed with properties that are not just a synergistic combination of those pertinent to bulk constituents, rather, a set of new ones coming from the exploitation of matter at its molecular state. Together with their outstanding properties, one of the most interesting features concerned with the addition of nanofillers is that they offer exceptional improvements at much lower concentrations than traditional (micro-sized) fillers assisting in the achievement of high-level performances across various engineering applications.

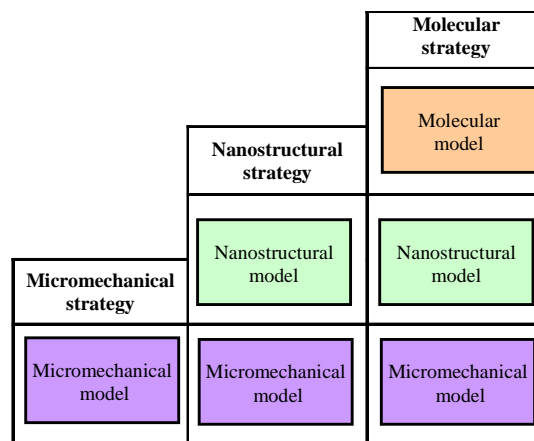


Figure 1. The concept of the “Three Stage Strategy” (TSS): building of modelling strategies from basic models.

A successful engineering application of nanocomposites requires models capable of accounting for their inherent hierarchical structure which encompasses the nano and the macro length-scales. An effective modelling should take into account the characteristic phenomena of each length-scale and bridge their effects from the smaller scale to the macroscale.

Within this aim the present authors [1] pointed out that in the most general case three main stages should be addressed in nanocomposite modeling (each stage to be tackled with the aid of a dedicated model) so that multiscale modelling strategies can be classified into three main groups, according to how many and which of the mentioned models are used within the strategy (see figure 1). This concept has been named “the three stage strategy” (TSS) concept. It is further acknowledged that the high fracture toughness improvements exhibited by nanofilled polymers are strictly related to the large amount of energy dissipated by the different damaging mechanisms taking place at the nanoscale. This is the reason for the increasing attention paid in the recent literature to identify nanocomposite damaging mechanisms and to quantify, through models, the related energy dissipation. In principle there might be different damaging mechanisms taking place simultaneously at the nanoscale contributing to the overall fracture toughness of the nanocomposite, so that the nanocomposite fracture toughness can be written as $G_{Ic} = G_{Im} + \sum_i \Delta G_i$, where G_{Im} is the

fracture toughness of the unloaded matrix and ΔG_i is the fracture toughness improvement due to the i-th damaging mechanism. Then, as pointed out recently by the present authors [1-5], the most effective approach to predict the nanocomposite toughness should be a “multi-mechanism” modelling strategy, in which each ΔG_i contribution is appropriately determined and weighted according to the specific case (accounting for the type, the morphology and the functionalisation of the nanofiller as well as of the loading conditions).

To this end the present authors have recently developed some multiscale models to describe the the fracture toughness improvements, ΔG_i , related to some toughening mechanisms typical of nanoparticle loaded polymer resins, such as nanoparticle debonding [2] plastic yielding of nanovoids [3,4] and plastic shear bands [5].

The aim of the present work is two-fold:

- First to briefly describe the multiscale models to be used to assess the fracture toughness enhancement due the single toughening mechanism arising in nanoparticle reinforced polymers;
- Second to estimate the overall fracture toughness improvements due to nanomodification, integrating all the above mentioned contributions, and to compare the predicted values with some experimental data taken from the literature.

2. Modelling of the fracture toughness of a nanocomposite

2.1 Description of the system adopted for the analysis

Different from traditional microsized composites, in nanoscale materials and structures, the surface effects become significant due to the high surface/volume ratio.

The significant effect of the elastic properties of the interphase on the critical debonding stress around nanoparticles has been recently shown by Zappalorto *et al.* [6]. This solution proves that since different functionalizers lead to different elastic properties of the interphase, the debonding stress is affected by the surface treatment depending on the interphase radius to the nanoparticle radius ratio, a/r_0 .

Unfortunately, the lack of precise data about the law of variation of the interphase properties across its thickness [7] urges to assume that a through-the-thickness average is representative

of the overall property distribution within the interphase. Consequently, the interphase is supposed to be homogeneous and isotropic.

The system under investigation at the nanoscale, shown in Figure 1, is constituted by:

- a spherical nanoparticle (nanovoid) of radius r_0 ;
- a shell-shaped interphase of external radius a and uniform properties;
- a volume of matrix of which the size are much greater than a and r_0 .

The properties required by the analysis can be computed by means of numerical simulations carried out within the frame of MD, as done in [8, 9], which provide, as outputs, the radial extension of the interphase as well as the elastic properties averaged through the thickness. Alternatively, for a specific system, they could be fitted *a posteriori* on the basis of some experimental results.

The system at the macro-scale is constituted, instead, of a cracked nano-modified matrix, while the multiscale strategy used for the analysis is shown in figure 2.

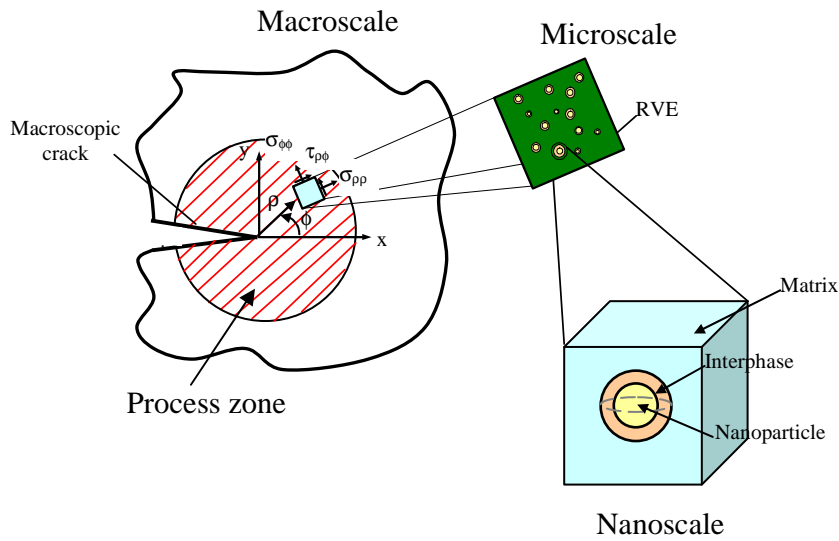


Figure 2. Description of the multiscale system under analysis.

It is assumed that the macroscopic stress fields due to the crack gives rise to a process zone containing all the nanoparticles subjected to damage, thus promoting energy dissipation at the nanoscale, and resulting, in turn, in an overall fracture toughness improvements of the nanocomposite.

Denoting with U_{SB} the energy produced at the nanoscale, according to the adopted multiscale system, the strain energy density in a RVE (microscale) can be calculated as:

$$u_{SB} = U_{SB} \times \frac{3f_{p0}}{4\pi r_0^3} \quad (1)$$

where f_{p0} is the volume fraction of nanoparticles. Finally, the fracture toughness enhancement due to the single damage mechanism can be determined, according [10, 11] as:

$$\Delta G_P = 2 \times \int_0^{\bar{p}_{SB}} u_P \, dp \quad (2)$$

2.2 Modelling of the fracture toughness enhancements due to the different damaging mechanisms

It is acknowledged (Hsieh *et al.* [10]) that the two dominant mechanisms responsible of toughening improvements for polymers reinforced by rigid nanoparticles (such as silica or alumina nanoparticles) are the localised shear banding of the polymer and particle debonding followed by subsequent plastic void growth. These two mechanisms have been recently considered separately.

2.2.1 Fracture toughness enhancement due to the plastic yielding of nanovoids

Recently Zappalorto *et al.* [2-4] assumed that in a damaged region close to the crack tip (Debonding Region, DBR) the high level of the crack-induced hydrostatic stress promotes debonding of nanoparticles and creates a number of nanovoids of the same diameter of the nanoparticles. Whenever the stress field around a nanovoid is high enough it might cause local yielding of the nanovoids which has been proven to be a high energy dissipation process. Through a multiscale analysis of the process they finally provided the following expression for the fracture toughness enhancement link to this mechanism: [3-4]:

$$\Delta G_{py} = G_{Ic} f_{p0} \left\{ \frac{4}{9\pi C_h} \cdot \frac{E_o}{E_m} \frac{(1+v_o)(1+v_m)}{1-v_o} \frac{\sigma_{Ym}}{\sigma_{cr}} \left(\frac{a}{r_0} \right)^{3 \times \left(1 - \frac{\sigma_{Ya}}{\sigma_{Ym}} \right)} e^{\left(3C_h \frac{\sigma_{cr}}{\sigma_{Ym}} - 1 \right)} \right\} = f_{p0} \times \Psi_p \times G_{Ic} \quad (3)$$

where σ_{cr} is the critical debonding stress [2-4, 6], E_o and v_o are the elastic properties of the nanocomposite, C_h is the reciprocal of the hydrostatic part of the global stress concentration tensor:

$$\sigma_{cr} \cong \sqrt{\frac{4\gamma}{r_0} \frac{E_m}{1+v_m}} \sqrt{\frac{\chi(4+\xi) - \xi(\chi-1)(r_0/a)^3}{4+\xi+4(\chi-1)(r_0/a)^3}} \quad C_h = \frac{\xi+4-4 \cdot (1-\chi)(r_0/a)^3}{(\xi+4\chi) \left(\frac{3(1-v_m)}{1+v_m} \right)} \quad (4)$$

being E_m and v_m the elastic modulus and Poisson's ratio of the matrix, K_m and K_a the bulk moduli of the matrix and the interphase, G_m and G_a are the shear elastic moduli of the matrix, the interphase, $\chi = G_a / G_m$, $\xi = 3K_a / G_m$, σ_{Ym} and σ_{Ya} the yield stress of the matrix and the interphase.

2.2.2 Fracture toughness enhancement due to localised shear banding

Recently Salviato *et al.* [5] assumed that in a damaged region close to the crack tip (Shear Banding Region, SBR) the stress concentrations around nanoparticles promotes local shear yielding, with the formation of less or more pronounced plastic shear bands. The shear bands are modelled as of four plastic strips departing from the nanoparticle periphery, the size of these strips depending also on the distance from the crack tip [5].

Through a multiscale analysis of the process Salviato *et al.* finally provided the following expression for the fracture toughness enhancement link to this mechanism [5]:

$$\Delta G_{SB} = G_{Ic} f_{p0} \times \left(\frac{I_{SB}}{4\pi\sigma_{ya}^2 (1-\mu/\sqrt{3})^2} \frac{E_o}{1-\nu_o^2} \times \Gamma \right) = f_p \times \psi_{SB} \times G_{Ic} \quad (5)$$

where μ is a dimensionless pressure coefficient, σ_{ya} is the yielding stress under compression loading of the interphase, function Γ quantifies the energy produced at the nanoscale and I_{SB} accounts for the hydrostatic and the deviatoric parts of the global stress concentration tensor around nanoparticles.

2.2.3 Overall fracture toughness of the nanocomposites

The nanocomposite fracture toughness can be written as:

$$G_{Ic} = G_{Im} + \sum_i \Delta G_i \quad (6)$$

where G_{Im} is the fracture toughness of the unloaded matrix and ΔG_i is the fracture toughness improvement due to the i -th damaging mechanism.

Substituting Eq. (3) and Eq. (5) into Eq. (6) one obtains the overall fracture toughness of the nanocomposite as a function of G_{Im} :

$$G_{Ic} = \frac{G_{Im}}{1 - f_p (\psi_{SB} + \psi_p)} \quad (7)$$

3. Comparison with some experimental data

In the present work, a general multi-scale approach has been proposed for the damage analysis induced by plastic yielding of nanovoids and shear banding around nanoparticles. It has been assumed that the nanofiller is uniformly dispersed and distributed within the volume, agglomeration being neglected at present. The effect of an interphase zone surrounding the nanoparticle, characterised by mechanical properties different from those of the matrix, is explicitly considered.

In Figure 3 the fracture toughness values predicted by Eq. (7) are compared to the fracture data from specimens made of a DGEBA epoxy nanomodified by silica nanoparticle of 10 nm of radius [10]. The properties of the matrix necessary for the theoretical prediction were reported in the original work [10]. The interphase elastic properties and thickness have been determined, instead, by fitting the experimental data on the nanocomposite Young modulus for low weight contents. Other data, such as the compressive strength of the interphase has been supposed to be sufficiently close to those of the matrix polymer. Figures 3 makes it evident that predicted values well agree with the experimental results.

Figure 4 shows a comparison between the fracture toughness values predicted by Eq. (7) the fracture data from specimens made of a DGEBA epoxy resin nanomodified by silica nanoparticles with a radius of 15 nm [12] for. As done before, the material properties necessary to the analytical predictions which were not provided in the original work have been partially determined by fitting the elastic properties of the nanocomposite and partially inferred. Figure 4 documents that also for the second studied system the agreement between theoretical predictions and experimental results is very satisfactory.

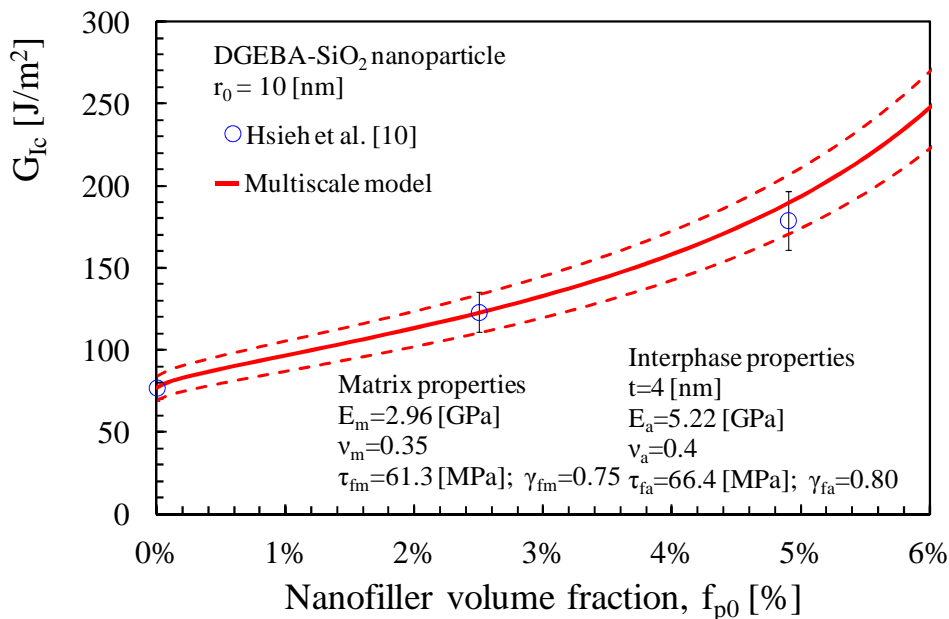


Figure 3. Comparison of the model (solid line) to experimental data taken from [10]. Matrix properties are given by the authors. Interphase properties have been obtained by fitting, *a posteriori*, with the overall elastic properties of the nanocomposite.

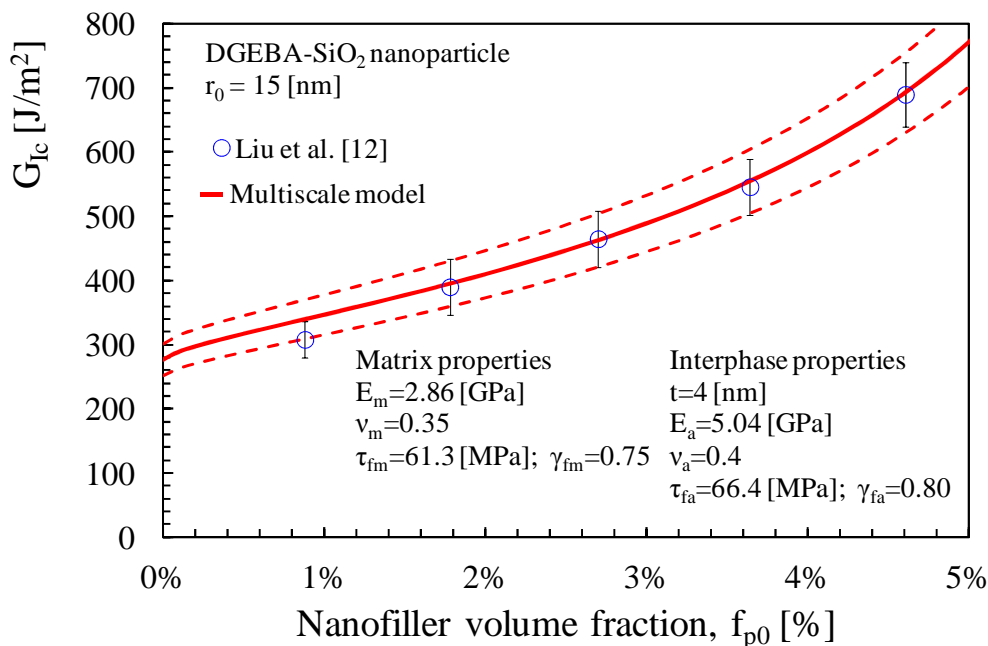


Figure 4. Comparison of the model (solid line) to experimental data taken from [12]. Matrix properties are given by the authors. Interphase properties have been obtained by fitting, *a posteriori*, with the overall elastic properties of the nanocomposite.

It is finally worth mentioning that, as a basic assumption of the present work, the nanofiller is supposed to be uniformly dispersed and distributed, neglecting the high tendency to agglomerate exhibited by nanoparticles beyond a certain value of the volume fraction. This assumption hampers the application of the model to high nanofiller volume fractions.

Conclusions

In the present work a multi-scale multi-mechanism modelling strategy has been provided for the prediction of toughness increments caused by the emergence of plastic yielding and localised plastic shear bands in nanoparticle filled resins. The model stems from the quantification of the energy absorbed at the lower scale and 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. The model has been compared to some experimental data collected from the literature, showing good agreements.

Acknowledgements

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