# A MULTISCALE ANALYTICAL MODEL TO ASSESS FRACTURE TOUGHNESS IMPROVEMENTS DUE TO PLASTIC SHEAR BANDS

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## Abstract

*In this paper a multiscale model is provided to assess the toughening improvements in nanoparticle filled polymers caused by the formation of localised plastic shear bands. The model quantifies the energy absorbed at the nanoscale and accounts for the emergence of an interphase zone surrounding the nanoparticles. It is proved that the interphase elastic properties, which are different from those of the matrix due to chemical interactions, highly affect the stress field rising around particles causing lower or higher energy dissipation at the nanoscale.*

## 1 Introduction

The subject of improving the mechanical properties of polymers by the addition of particle fillers has received a large attention throughout the last decades. However, only recently, nanotechnology has emerged providing very promising results in increasing the mechanical behaviour of polymers by the addition of nanosized fillers. This is the reason why nanocomposites have received a higher and higher interest by the scientific community, especially for the significant amelioration in terms of stiffness, strength and toughness (see amongst others, [1]).

The modelling of nanoscale damage mechanisms is far from easy and requires a different way of thinking with respect to the approaches developed for traditional composites. As a matter of facts, the handshaking of nanoscale, microscale and macroscale quantities and phenomena urges a multiscale modelling strategy [2].

Moreover, experimental observations [3,4] allow to state that different damaging mechanisms, taking place at the nanoscale, can simultaneously contribute to the overall fracture toughness of the nanocomposite. Accordingly, the best approach to predict the fracture toughness should be a “multi-mechanism” modelling strategy, in which each contribution is appropriately determined and weighted according to the specific case (accounting for the type, morphology and functionalisation of the nanofiller and for the loading conditions) [2].

Towards this direction, the present authors have recently developed a hierarchical multi-scale model to assess the fracture thoughness improvements due to the debonding of nanoparticles and the plastic yielding of nanovoids [5-7].

As a further step, in the present paper, we address the multiscale modelling of the toughness improvement due to shear banding around nanoparticles.

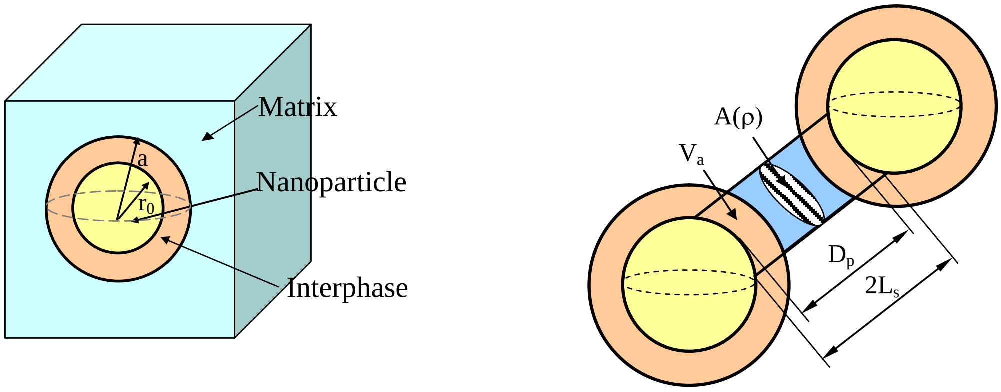
The main aims can be briefly summarised as follows:

-to quantify the toughness improvement due to the shear banding around nanoaparticles. Shear bands are supposed to be initiated by the stress concentrations around the periphery of the nanoparticles;
-to show that the formation of local shear bands is a highly dissipative mechanism, causing a high fracture toughness improvement at low nanofiller content;
-to prove that nanocomposite toughening may be strongly affected by the size of nanoparticles and by surface treatments. In particular, the effect of functionalisation is accounted for through the properties and the size of the interphase.

## 2. Multiscale strategy to analyse shear band emergence around nanoparticles

### *2.1 Description of the nanoscale system*

Within the frame of a hierarchical multiscale model, the analysis has to be carried out at different length scales. Each of these can be addressed separately, inputs being provided by the solution of the previous model (at the smaller scale).
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.* [8]. 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, $\mathbf{a/r_0}$.



a) b)

**Figure 1.** a) description of the system under analysis at the nanoscale and b) the relevant geometrical quantities used to describe the localised shear banding around a nanoparticle.

Unfortunately, the lack of precise data about the law of variation of the interphase properties across its thickness urges to assume, according to [8-10], 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 Figures 1a and 1b, is constituted by:

- a spherical nanoparticle of radius $\boldsymbol{r_0}$;
- 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 $\boldsymbol{r_0}$;
- four plastic strips departing from the nanoparticle periphery the diameter of which scales with the square root distance from the crack tip.

The properties required by the analysis can be computed by means of numerical simulations carried out within the frame of MD, as done in [9, 10], 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.

### *2.2 Application of the multiscale approach*

The system at the macro-scale is constituted of a cracked nano-modified matrix (Figure 2). Under the hypothesis of plane strain conditions, with reference to the coordinate system shown in Figure 2, the hydrostatic stress field is:

$$\sigma_h = \frac{\sigma_x + \sigma_y + \sigma_z}{3} = \frac{2(1+\nu_0)\,K_I}{3\sqrt{2\pi\rho}}\cos\frac{\phi}{2} \tag{1}$$

while the equivalent macroscopic von Mises stress is:

$$\sigma_{vM} = \frac{K_I}{\sqrt{4\pi\rho}}\cos\frac{\phi}{2}\sqrt{2\,(1-2\nu_0)^2 + 3(1-\cos\phi)} \tag{2}$$

where $K_I$ and $\nu$ are the Stress Intensity Factor of local stress fields and the Poisson's ratio of the nanocomposite, respectively.

Within a multiscale approach to the problem, the crack macroscale stress field can be regarded as the average value of the microscale stresses over a Representative Volume Element (RVE). The bridge with the nanoscale can finally be established by means of the *Average Stress Theorem* and the Mori-Tanaka approach.

Then, the maximum von Mises and hydrostatic stresses arising around the nanoparticle can be approximated by:

$$\begin{aligned}\sigma_{vM,n} &= H_{vM}\sigma_{vM} = H_{vM}\frac{K_I}{\sqrt{4\pi\pi}}\cos\frac{\phi}{2}\sqrt{2\,(1-2\nu_0)^2 + 3(1\text{-}\cos\phi)} \\ \sigma_{h,n} &= H_h\sigma_h = H_h\frac{2(1+\nu_0)\,K_I}{3\sqrt{2\pi\pi}}\cos\frac{\phi}{2}\end{aligned} \tag{3 a,b}$$

where $H_h$ is the hydrostatic part the global stress concentration tensor and, under the hypothesis of a rigid nanoparticle, it can be found in [8]. Differently, $H_{vM}$ is the deviatoric component of the global stress concentration tensor and it can be determined, in closed form, by the superposition of a recent solution proposed by the present authors [11].

We assume here that whenever the stress field around a nanoparticle is high enough, it causes local shear yielding, with the formation of less or more pronounced plastic shear bands. The region of material containing all the nanoparticles subjected to shear yielding is denoted as Shear Banding Region (SBR). The shear bands are modelled as of four plastic strips departing from the nanoparticle periphery. As we will argue better later, the size of these strips depends on the distance from the crack tip (see figure 1b).

The extension of the SBR can be determined by applying the modified von Mises yielding criterion, which explicitly takes into account the level of the hydrostatic stress [12]:

$$\sigma_{vM,n} + \sqrt{3}\mu\sigma_{h,n} = \sigma_{Ya,c}\left(1-\mu/\sqrt{3}\right) \tag{4}$$

where $\sigma_{Ya,c}$ is the interphase yield stress under compression and $\mu$ is a dimensionless pressure coefficient.

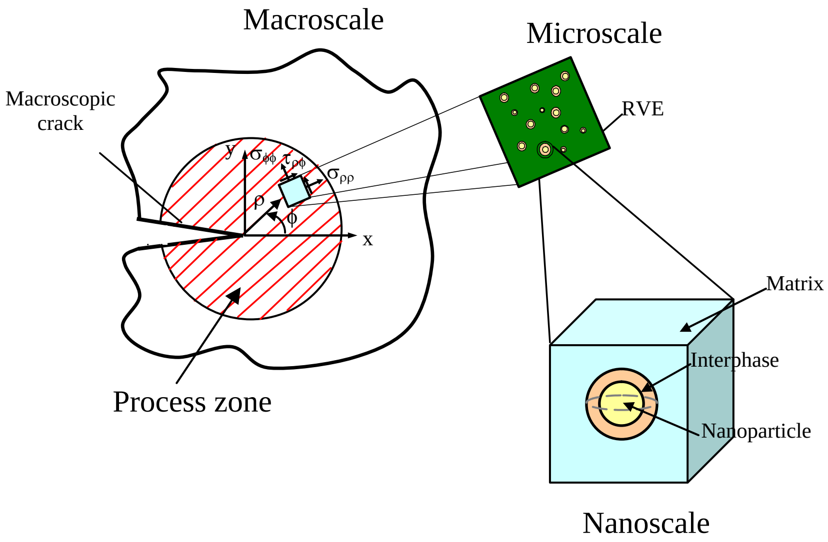


**Figure 2.** Description of the multiscale system under analysis.

Substituting Eq. (4) and solving by $\rho$ the region of the material subjected to shear banding (SBR) can be found in closed form. In this work an average value for the extension of the damage zone, regarded as representative of the overall damage behaviour, has been used. Such an average value can be defined as:

$$\bar{\rho}_{SB} = \frac{1}{2\pi}\int_{-\pi}^{+\pi} \rho_{SB}(\varphi)\, d\varphi = \frac{1}{4\pi}\left[\frac{K_I}{\sigma_{Ya,c}\left(1-\mu/\sqrt{3}\right)}\right]^2 I_{SB} \tag{5}$$

where:

$$I_{SB} = \frac{1}{2\pi}\int_{-\pi}^{+\pi}\left[H_{vM}\sqrt{2\,(1-2\nu_0)^2+3(1-\cos\phi)}+\sqrt{8/3}\mu H_h\left(1+\nu_0\right)\right]^2 \cos^2\frac{\phi}{2}\, d\phi \tag{6}$$

The analytical solution for $I_{SB}$ and $\bar{\rho}_{SB}$ can be found in a recent work by the present authors [13].

Accordingly, in the following, we will approximate the actual SBR with a circle, centred at the crack tip and having a radius equal to $\bar{\rho}_{SB}$. 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:

$$u_{SB} = U_{SB} \times \frac{3f_{p0}}{4\pi r_0^3} \tag{7}$$

where $f_{p0}$ is the volume fraction of nanoparticles. Finally, the fracture toughness enhancement due to shear band formation can be determined, according [4] as:

$$\Delta G_P = 2 \times \int_0^{\bar{\rho}_{SB}} u_P \;\, d\rho \tag{8}$$

The problem of determining the overall fracture toughness enhancement is, in this way, reconverted into finding the energy produced at the nanoscale by shear banding.

## 3. Modelling of toughness improvements due to shear bands

In agreement with previous works [3,4], the phenomenon of localized shear banding can be modeled using a very simple network according to which the local stress concentration around each nanoparticle gives rise to four shear bands, departing from the nanoparticle surface. The cross sectional area of the single shear band soundly scales with the diametrical cross sectional of the nanoparticle as:

$$A(\rho) = f(\rho)\,\pi r_0^2 \tag{9}$$

In this expression, $f(\rho)$, of which the values must fall within the range (0,1), is an appropriate function of the distance from the crack tip. For the sake of simplicity, in this work we will assume the following expression:

$$f(\rho) = 1 - \sqrt{\rho/\rho_{SB}} \tag{10}$$

where the square root law has been chosen to agree with the square root singularity.
With reference to Figure 1b, the length of the of the shear band can then be estimated as:

$$L_s = r_0 + \frac{D_p}{2} - r_0\sqrt{1 - f(\rho)} \tag{11}$$

where $D_p$ is the interparticle distance. Under the hypothesis of a cubic array for the nanoparticle distribution, which is the most feasible at low nanofiller volume fractions, $D_p$ can be estimated as:

$$D_p = \left[\left(\frac{4\pi}{3f_p}\right)^{\frac{1}{3}} - 2\right] r_0 \tag{12}$$

Starting from these geometrical quantities, the volume of material subjected to shear yileding can be found. It is worth noting (see figure 1b) that in this paper it has been considered the presence of an interphase zone between the nanoparticle and the matrix, thought of a zone of matrix of altered chemistry. Then the shear band departing from the nanoparticle boundary develops partly in the interphase zone and partly in the un-altered matrix. If we assume, for the sake of simplicity, that the matrix and the interphase yield according to a perfectly plastic law, we can disregard the elastic part of the stress-strain curve, and determine the strain energy density related to shear banding as:

$$u_{SB} = f(\rho)\tau_{ym}V_m\gamma_{fm} + f(\rho)\,\tau_{ya}V_a\gamma_{fa} = u_m + u_a \tag{13}$$

where $V_m$ and $V_a$ denote the volume of shear yielded material within the matrix and the interphase respectively for each nanoparticle and can be found in [13], $\tau_{ym}$ and $\tau_{ya}$ are the shear yielding stress of the matrix and of the interphase, while $\gamma_{fm}$ and $\gamma_{fa}$ are the shear fracture strain of the matrix and of the interphase, respectively. Substituting Eq. (13) into Eq. (7) and then into Eq. (8) results in:

$$\Delta G_{SB} = 2\int_0^{\bar{\rho}_{SB}} u_{SB}\, d\rho = \bar{\rho}_{SB}\ f_p\ \Gamma \tag{14}$$

where:

$$\Gamma = f\left(\tau_{ym}, \gamma_{fm}, \tau_{ya}, \gamma_{fa}, a/r_0\right) \tag{15}$$

is a function of the system mechanical and geometrical properties [13] and $\bar{\rho}_{SB}$ is given by Eq. (5). Further accounting for that:

$$G_I = K_I^2\left(1-\nu_0{}^2\right)/E_0 \tag{16}$$

the fracture toughness improvement turns finally out to be:

$$\Delta G_{SB} = G_{Ic} f_p \times \left( I_{SB}\, \frac{1}{4\pi\sigma_{ya}^2 (1-\mu/\sqrt{3})^2}\, \frac{E_0}{1-\nu_0^2} \times \Gamma \right) = f_p \times \psi_{SB} \times G_{Ic} \tag{17}$$

where $\psi_{SB}$ quantifies the energy dissipation at the nanoscale by localised shear banding:

$$\psi_{SB} = \left( I_{SB}\, \frac{1}{4\pi\sigma_{ya}^2 (1-\mu/\sqrt{3})^2}\, \frac{E_0}{1-\nu_0^2} \times \Gamma \right) \tag{18}$$

Since, according to [4,7] the overall fracture toughness can be written as:

$$G_{Ic} = G_{Im} + \Delta G_{SB} \tag{19}$$

being $G_m$ the fracture toughness of the pure (unloaded) matrix, the fracture toughness improvement can also be written in the following normalised form [13]:

$$\frac{\Delta G_{SB}}{G_{Im}} = \frac{f_p \times \psi_{SB}}{1 - f_p \times \psi_{SB}} \tag{20}$$

## 4. Results and discussion

In the present work, a general multi-scale approach has been proposed for the damage analysis at the nanoscale induced by 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.

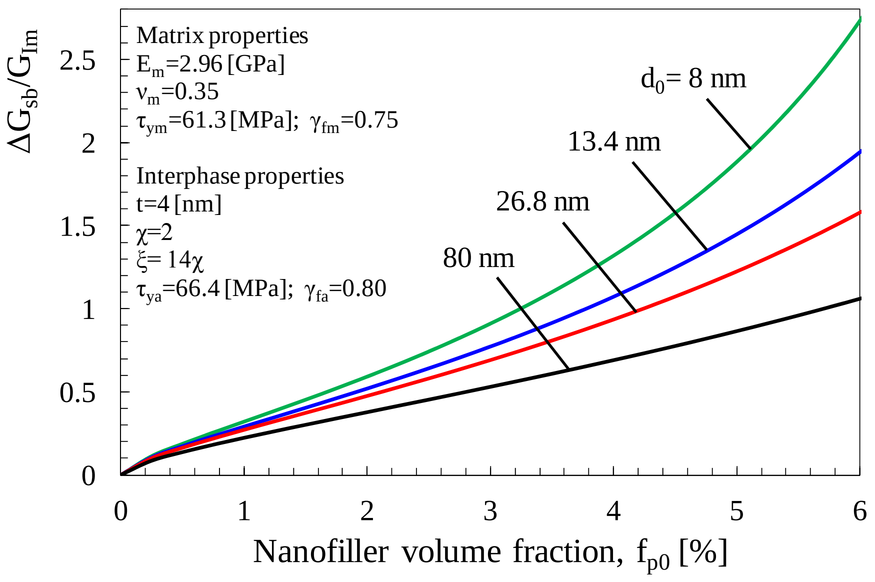


**Figure 3.** Normalised fracture toughness increment as a function of the nanofiller volume fraction. Stiffer interphase. Different nanoparticle radii.

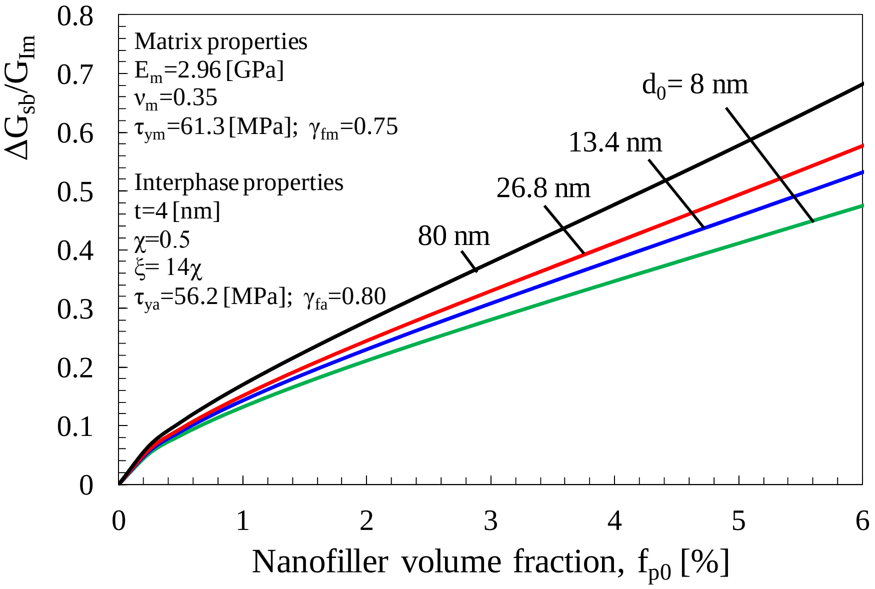


**Figure 4.** Normalised fracture toughness increment as a function of the nanofiller volume fraction. Softer interphase. Different nanoparticle radii.

In order to highlight, through examples, the most relevant features of the solution the following properties have been adopted for the matrix, according to the suggestion in Refs. [3-4]: $\tau_{ym}$=61.3 MPa, $\gamma_{fm}$=0.75, $E_m$=2.96 GPa, $\nu_m$=0.35. Conversely, the properties of the interphase have been changed in order to analyze their effect on the final solution.

The analytical model developed in this work indicates that the fracture toughness improvements of nanoparticle reinforced polymers is mainly affected by two important parameters: elastic properties of the interphase (related to the surface functionalization of nanoparticles) and the nanofiller size. Figures 3 and 4 show the effect of the particle size on the fracture toughness improvements, such an effect being different depending whether the interface is stiffer or softer than the matrix. In Figure 3, the case of an interphase stiffer than the matrix is presented. The toughness increase becomes more than 200% and it is higher for smaller nanoparticles. Different, for the case of a softer interphase, figure 4 shows that the increase is smaller with respect to the previous case and greater nanoparticle radii lead to higher fracture toughness.

## Conclusions

An analysis has been provided for the toughening of nanoparticle filled polymers caused by the emergence of localised plastic shear bands, initiated by the stress concentrations around silica nanoparticles. The model stems from the quantification of the energy absorbed at the nanoscale 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. It is proved that the interphase elastic properties highly affect the stress raising around particles, causing lower or higher energy dissipation at the nanoscale. Moreover it is proved that the particle size effects may be different depending on the elastic properties of the interphase.

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