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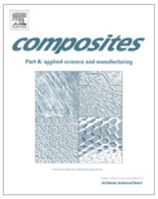

Plastic shear bands and fracture toughness improvements of nanoparticle filled polymers: A multiscale analytical model

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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, initiated by the stress concentrations around nanoparticles. The model quantifies the energy absorbed at the nanoscale and accounts for the emergence of an interphase zone around the nanoparticles. It is proved that the elastic properties of the interphase, which are different from those of the matrix, due to chemical interactions, highly affect the stress field rising around particles and the energy dissipation at the nanoscale.

1. Introduction

Throughout the last decades the subject of improving the mechanical properties of polymers by the addition of particle fillers has received a large attention. However, only recently nanotechnology has emerged providing very promising results in increasing the mechanical properties 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 which can be obtained at low nanofiller contents (see amongst others, [1,2]). It is acknowledged that the reasons for such improvements must be sough in the huge amount of energy dissipated by the numerous damaging mechanisms taking place at the nanoscale. This is the reason why, it is suggested that the best approach to address the prediction of nanocomposite toughness 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 the loading conditions) [3–7].

However, 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 where two different characteristic lengths at most (microscale and macroscale) are reasonably described by means of continuum mechanics.

When dealing with nanocomposites, the handshaking of nanoscale, microscale and macroscale quantities and phenomena urges a multiscale modelling strategy [6]. Indeed, the introduction of atomistic models, able to account for molecular interactions between nanofillers and the matrix, up to macro length-scales is limited by the impracticability of accounting for more than some hundred millions of atoms. Initial steps towards modelling strategies which account for nanostructure features, such as nano-reinforcement size and distributions, are due to Chen et al. [8]. They provided a simple size-dependent formulation for the debonding stress, later used to compute the energy dissipation due to this mechanism. The analysis carried out in [8] has been later extended by Zappalorto et al. [9] who developed a closed form expression for the critical debonding stress accounting for the existence of an interphase zone embedding the nanoparticle. Such a zone is thought of as characterised by chemical and physical properties different from those of the nanoparticle and of the matrix. On parallel tracks, the effects of surface elastic constants on the debonding stress of nanoparticles have been investigated by Salviato et al. [10] who showed that the range of the nanoparticle radii where those effects are significant is limited to the nanoscale.

Independently, Lauke [7] and Williams [11] analysed the energy dissipation phenomena by considering, besides particle debonding, voiding and subsequent yielding of the polymer. While analysing the fracture toughness improvements resulting from nanomodification of epoxy resins with silica nanoparticles, Hsieh et al. [4,5] experimentally observed two dominant mechanisms responsible of toughening improvements: localised shear banding of the polymer and particle debonding followed by subsequent plastic void growth. They also modified a previous model due to Huang and Kinloch [12] with the aim to assess the fracture toughness improvements resulting from nanomodification. Such a solution,

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which was proved to be in a very good agreement with the experimental data, requires some quantities to be set on the basis of fracture surface observations. The present authors have recently developed a hierarchical multi-scale model to assess the fracture toughness improvements due to the debonding of nanoparticles and the plastic yielding of nanovoids [13–15]. In more details, it has been shown that the energy absorbed through nanoparticle debonding is almost negligible, but debonding is a necessary condition for the subsequent plastic yielding around nanovoids created by debonded nanoparticles, such a toughening mechanism being, instead, of primary concern. The model quantifies the energy absorbed at the nanoscale and accounts for the emergence of an interphase zone around the nanoparticles [13–15]. The experimental observations carried out in [4,5] 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 nanocomposite toughness can be written as $G_{\text{Ic}} = G_{\text{Im}} + \sum_i \Delta G_{\text{i}}$, where G_{Im} is the toughness of the unloaded matrix and ΔG_{i} is the toughness improvement due to the *i*-th damaging mechanism. Then, the best 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 [6]. As a further step towards this multimechanism strategy, in the present paper we address the multiscale modelling of the toughness improvement due to shear banding around nanoparticles. The major novelty of the present paper, with respect to those above mentioned dealing with the same topic [4,5], lays on the fact that the effect of an interphase zone surrounding the nanoparticle, characterised by mechanical properties different from those of the constituents, is explicitly considered. Zappalorto et al. [9] have already demonstrated that the interphase properties (which are linked to surface functionalizers) have a significant effect on the debonding stress, especially for nanoparticle radii below 50 nm.

Briefly, the aims of the present paper can be summarised as follows:

- to quantify the toughness improvement due to the shear banding around nanoparticles. 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.

It is worth mentioning here again that the correct estimation of the fracture toughness improvement resulting from nanomodification requires the modelling of all the possible damage mechanisms taking place at the nanoscale. Accordingly this work has to be seen as a part of a more general multiscale model including the contributions of other mechanisms analysed in previous works [13–15].

2. Description of the hierarchical multiscale strategy adopted for the analysis

2.1. General concepts

Modelling of nanocomposite mechanical properties urges to deal with three different length scales, macro-, micro- and nano-, each of them being characterised by peculiar phenomena and mechanical quantities. Accordingly, we will use terms like "macroscale stress" or "microscale stress" and, in order to avoid misunderstandings it is worth giving the correct definitions for these quantities and briefly discussing the link between them.

Macro-scale: at the macroscale, the material is assumed to be homogeneously and continuously distributed "so that the smallest element cut from the body possesses the same specific physical properties as the body" [16]. In addition, under the hypothesis that the nanofiller is randomly oriented and uniformly distributed, the material can also be thought of as isotropic. All the mechanical quantities (such as stresses and strains) are regarded as averaged values [17] and supposed to be representative of the overall material behaviour.

Micro-scale: the micro-scale system is commonly described as a RVE (Representative Volume Element) and it has to be large enough to be statistically representative of the properties of the material system. Contemporaneously, whenever the nanofiller is uniformly distributed and dispersed, the microscale system can be regarded to be, within reason, sufficiently small to be an infinitesimal volume of the macro-scale one. All the microscale mechanical properties are considered here as pointwise values [17].

Nano-scale: the nanoscale system represents a single unit cell of those compounding the micro-scale system; it accounts for the material morphology (such as nanofiller type and size).

Macroscale stresses, σ, can be regarded as the average values over a RVE of the microscale stresses [17–19]:

$$\sigma = \frac{1}{V}\int_{\text{V}} \hat{\sigma} dV \tag{1a}$$

where $\hat{\sigma}$ is the micro-scale stress distributions and V is the volume of the RVE.

The handshaking between the mechanical quantities characterising the different length scales can be carried out thanks to the Mori–Tanaka theorem, which allows to disregard of the actual microscale fields by approximating stresses on the boundary of nano-inhomogeneities (nanoscale). If the considered volume fractions are small enough to avoid significant particle–particle interactions, this can be carried out taking advantage of the Global Concentration Tensors of Eshelby dilute solution, **H**, and of the mean value for the fields over the RVE which, thanks to Eq. (1a) equate the macroscale ones:

$$\sigma_{\text{n}} = \mathbf{H} : \left\{ \frac{1}{V}\int_{\text{V}} \hat{\sigma} dV \right\} = \mathbf{H} : \sigma \tag{1b}$$

The procedure just described is also summarised in the flow chart shown in Fig. 1.

2.2. Multiscale strategy to analyse shear bands around nanoparticles

2.2.1. Description of the nanoscale system

Different from traditional microsized composites, in nanoscale materials and structures the surface effects become important [20–22] 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. [9]. This solution proves that, since different functionalizers lead to different elastic properties of the interphase, the debonding stress is highly affected by the surface treatment depending on the interphase radius to the nanoparticle radius ratio, $\mathbf{a}/\boldsymbol{r_0}$.

Unfortunately, the lack of precise data about the law of variation of the interphase properties across its thickness [23] urges to assume, according to [9,24,25] that a through-the-thickness