A multiscale model to describe nanocomposite fracture toughness enhancement by the plastic yielding of nanovoids

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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 due to plastic yielding of nanovoids is presented. The model accounts for the emergence of an interphase with mechanical properties different from those of the matrix.

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1. Introduction

The recent advances in nanotechnology go towards the production of multi-functional materials through the designing of structures at the nanometer scale. One of the most interesting features concerned with nanocomposites is that they offer exceptional improvements at very low filler concentrations, thus assisting in the achievement of high-level performances across various engineering applications. It is 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 [1–12]. An initial study on the energy dissipation due to the interfacial debonding of nanoparticles has been done by Chen et al. [2]. 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 this mechanism. 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. The analysis carried out by Chen et al. [2] has been later extended by Zappalorto et al. [3] 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 matrix, due to inter and supra-molecular interactions taking place at the nanoscale. On parallel tracks, the effects of surface elastic constants on the debonding stress of nanoparticles have been investigated by Salviato et al. [4] who showed that the range of the nanoparticle radii where those effects are significant is limited to the nanoscale. Lauke [5] analysed the energy dissipation phenomena by considering, besides particle debonding, voiding and subsequent yielding of the polymer. Williams [6] re-analysed in detail the toughening of particle filled polymers assuming that plastic void growth around debonded or cavitated particles is the dominant mechanism for energy dissipation. Williams [6] further noted that, even if the debonding process is generally considered to absorb little energy, it is essential to reduce the constraint at the crack tip and, in turn, to allow the epoxy polymer to deform plastically via a void-growth mechanism. A similar result was found also by the present authors in some preliminary analyses [7,8]. Hsieh et al. [9,10] studied the fracture toughness improvements resulting from nanomodification of epoxy resins with silica nanoparticles. Based on experimental observations, they identified two dominant mechanisms responsible of toughening improvements, namely localised shear banding of the polymer (thought of as initiated by the stress concentrations around the periphery of the nanoparticles) and particle debonding followed by subsequent plastic void growth. Conversely, other mechanisms such as crack pinning, crack deflection and immobilised polymer around the particles were not observed. Then, with the aim to predict the fracture toughness improvements resulting

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from nanomodification, they adapted a previous model due to Huang and Kinloch [13] for rubber modified epoxy polymers. Such a solution, 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. Starting from these experimental observations, it is possible to state that 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 ith damaging mechanism. Then, as pointed out recently by these authors [14], 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).

Some preliminary analyses in this direction have already been reported in Refs. [7,8]. Those analyses are completed and extended in the present paper, where the multiscale modelling of the toughness improvement due to plastic yielding around nanovoids is addressed.

As a basic hypothesis, it is assumed that debonding of nanoparticles takes place and creates a number of nanovoids of the same diameter of the nanoparticles, which subsequently encounter plastic deformation. This hypothesis is supported by the experimental observations by Hsieh et al. [9,10]. The major novelty of the present paper, with respect to those above mentioned dealing with the same subject [5,6,9,10], 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. As shown by Zappalorto et al. [3], the interphase properties, which may be 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 prove that nanoparticle debonding can be regarded to absorb little energy, being instead essential to allow the local plastic yielding of the epoxy polymer;
– to quantify the toughness improvement due to the plastic yielding of nanovoids, thought of as nucleated by debonded nanoparticles;
– to show that plastic yielding of nanovoids 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 implicitly considered through the properties and the size of the interphase.

The analysis will be carried out considering two different elastic–plastic laws to describe the material behaviour, namely an elastic power hardening law and an elastic perfectly-plastic law. The latter is thought of as a simplified assumption to be used in the absence of detailed information about the hardening behaviour of the matrix and 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 first part of a more general multiscale model including the contributions of other mechanisms.

As a further step of the activity in this direction, the present authors are also going to develop a multiscale modelling of the polymer shear banding [15].

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

2.1. General concepts

A successful engineering application of nanocomposites requires models capable of accounting for their inherent hierarchical structure which encompasses the nano and the macrolength-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 [14]. For this reason, in the present analysis, we deal with three different length scales, macro-, micro- and nano-, each of them being characterised by mechanical quantities which are, by a conceptual point of view, different. Accordingly, we will use terms like "macroscale stress" and "microscale stress". Thus, in order to avoid misunderstandings it is worth giving the correct definitions for the quantities used at each scale, as well as to briefly discuss the link between them.

The macro-scale system and the macro-scale quantities: the macroscale system is thought of as an amount of material over which all the mechanical quantities (such as stresses and strains) are regarded as averaged values [16] and they are supposed to be representative of the overall material behaviour. Within this scale, it is assumed that the material is homogeneously and continuously distributed over its volume "*so that the smallest element cut from the body possesses the same specific physical properties as the body*" [17]. So long as the geometrical dimensions defining the form of the body are very large in comparison with the dimensions relevant at the smaller scales (such as the size of a single nanofiller), the assumption of homogeneity can be used with great accuracy. In addition, if the nanofiller is randomly oriented and uniformly distributed, the material can also be treated as isotropic.

The macroscale system accounts for the loading conditions and the presence of material defects (like macroscopic cracks) and all the governing equations are dependent only on macroscopic averaged quantities.

The micro-scale system and the micro-scale quantities: the microscale system is thought of as being sufficiently small to be regarded, mathematically, as an infinitesimal volume of the macroscale one. At the same time it has to be, by definition, large enough to be statistically representative of the properties of the material system. The latter hypothesis is supposed to hold valid as far as the nanofiller is uniformly distributed and dispersed over the volume. Within this scale, all the mechanical properties are supposed to be pointwise values [16]. The micro-scale system is often regarded as a *Representative Volume Element* (RVE).

The nano-scale system: 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).

It is finally worth mentioning that the definitions above given are not necessarily limited to the analysis of nanostructured materials, but they have a more general validity and they can be applied to any system and application interested by three length scales (a large-scale, a medium-scale and a small-scale) fulfilling the requirement that the "large-scale" is much larger than the "medium-scale", which, in turn, is much larger than "small-scale".

2.2. Relationship between stresses and strains in the different systems

Let consider a general boundary value problem in statics; the macro-scale stress or strain, σ or ε, can be regarded as a general function of material coordinates $\{\sigma, \varepsilon\} = \{f_1(X_1, X_2, X_3), f_2(X_1, X_2, X_3)\}$.

According to [16,18,19], functions f_i, which are supposed to satisfy the governing equations of statics at the macroscale, can