Composites Science and Technology 72 (2011) 49–55

Contents lists available at SciVerse ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

# Influence of the interphase zone on the nanoparticle debonding stress

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ARTICLE INFO

*Article history:*
Received 1 January 2011
Received in revised form 15 September 2011
Accepted 27 September 2011
Available online 2 October 2011

*Keywords:*
A. Nano particles
B. Debonding
B. Interphase
B. Interfacial strength

ABSTRACT

One of the most appealing features concerned with nanomodification of polymeric resins for structural applications is the perspective of obtaining high toughness even at low nanofiller volume fractions. Such performances are related to the energy dissipated through the damage mechanisms taking place at the nanoscale. Among these, nanoparticle debonding could take an important role either as a mechanism itself or as a trigger for phenomena like plastic void growth or matrix shear yielding. In the present work, a model for the hydrostatic tension related to debonding is presented. The model accounts for some important issues inherently related to the nanoscale with particular reference to the emergence of an interphase surrounding the nanoparticle. Results can be useful in view of a multi-scale modelling of the problem.

## 1. Introduction

In the recent literature great attention has been paid to nanoscale reinforcements to significantly increase polymer stiffness, strength and toughness with low reinforcement concentrations (see, among the others, [1–6]). The improvement of polymer toughness broadens the nanocomposite field of standalone applications and makes the use of nanocomposite systems as matrices for fibre reinforced composites a smart solution. As a matter of facts, nanomodified polymers can be the basis for the further development of a new class of composites through which all the benefits coming from nanosized materials together with all those concerned with the addition of micrometric size fibres can be synergistically exploited.

The understanding of the relation between the nanostructure and the overall mechanical behaviour of nanocomposites plays an important role in the development of such materials. This need has given rise in the literature to a large number of modelling strategies. Thostenson and Chou [7] proposed a model for an epoxy matrix reinforced by aligned multi-walled carbon nanotubes (MWCNTs), where the actual filler nanostructure is accounted for by introducing a solid effective fibre through an iso-strain condition.

Independently, Luo and Daniel [8] studied the prediction of elastic properties of polymer layered silicate (PLS) nanocomposites. They accounted for the nanoclay morphology by a three-phase Mori-Tanaka model (matrix, exfoliated clays and cluster of intercalated clays) and for the actual nanofiller orientation and grade of exfoliation.

Recently, molecular modelling strategies based on discrete computational modelling techniques have also been used to investigate nanocomposite systems [9–13].

Different from the above mentioned works, which are focused on the assessment of elastic properties and disregard strengthening and toughening mechanisms, a study on the effects of nanoparticles on fracture properties of epoxy resins has been carried out by Wetzel et al. [14]. Together with a comprehensive experimental analysis, the authors studied the effects of various fracture mechanisms, such as crack deflection and crack pinning, by means of some micromechanical models. A similar approach has been later used by Johnsen et al. [15] and Zhao et al. [16].

A study on the energy dissipation due to the interfacial debonding of nanoparticles has been done by Chen et al. [17]. By means of an energy analysis of the process, these authors derived a simple size-dependent formulation for the debonding stress 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.

More recently Lauke [18] analysed the energy dissipation phenomena by considering, besides particle debonding, voiding and subsequent yielding of the polymer. The conclusions drawn by Lauke are different depending on the used debonding criterion (critical stress or critical energy). The same author also provided the theoretical basis for a test to determine the interfacial adhesion strength between a coated particle and a polymer matrix material [19].

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doi:10.1016/j.compscitech.2011.09.016

Williams [20] 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.

All the works mentioned above are founded on the definition of a criterion for discriminating debonding. This particular problem was initially investigated by Nicholson [21], who considered a rigid spherical inclusion embedded in and completely adhered to a much larger sphere of matrix. Assuming that the adhesive bond was weak and the matrix sphere is subjected to a uniform fixed radial stress on its outer surface, Nicholson found a criterion for detachment. The case of a rigid spherical inclusion under a tensile stress applied to the elastomeric matrix was analysed by Gent [22]. Here the inclusion is assumed to have an initially-debonded patch on its surface and the conditions for growth of the patch are derived from fracture energy considerations.

In the previous works, the existence of only two different phases (i.e the particle and the matrix) is assumed. Although this sounds reasonable at the microscale, it does not hold valid for nanosized reinforcements. In this case the molecular structure of the polymer matrix is significantly altered at the particle/matrix interface and this perturbed region is comparable in size with that of the nanoparticle [10,13]. In the present paper particular attention is paid to the interphase zone surrounding the nanoparticle, which, due to inter and supra-molecular interactions, might be characterised by chemical and physical properties different from those of the constituents. The aim of the present study is to determine a closed form expression for the critical debonding stress accounting for the existence of an interphase zone of different properties between the nanoparticle and the matrix. In more details:

- the problem is formulated and solved by considering a nanoparticle of radius $\boldsymbol{r}_0$ surrounded by a shell-shaped interphase of radius **a**;
- the expression for the critical debonding stress is determined within the frame of the Finite Fracture Mechanics (FFM) approach. Stress and displacement fields at incipient debonding and after debonding has taken place are determined by using the Cauchy Continuum Theory;
- the solution makes explicit the role played by the properties and the size of the interphase zone.

## 2. Description of the system under analysis

Different from traditional microsized composites, in nanoscale materials and structures, the surface effects become significant [23–25], due to the high surface/volume ratio. Then, as stated by Ajayan et al. [25], when dealing with polymer nanocomposites it is extremely important to analytically describe the presence of an interphase and to be able to correctly estimate properties accounting for the interfacial region [25].

Unfortunately, the data available so far in the literature about the interphase zone are not enough to precisely formulate the law of variation of its properties across the thickness, as well as its size. Those parameters varies from case to case [26]. For example, Odegard et al. [10], by using molecular dynamics (MD) simulations, studied a system made of silica nanoparticles and a polyimide matrix reporting the existence of an interphase zone whose size was comparable with that of nanoparticles and the elastic properties lower than those of the matrix. Different results have been obtained by Yu et al. [13]; these authors, studying systems made of epoxy resins, found an interphase zone stiffer than the matrix.

For the sake of simplicity, in this work we assume that, even if there might be a gradual transition of the interphase properties across its thickness to the bulk ones, a through-the-thickness average is representative of the overall property distribution (according to [10,13]). Consequently, the interphase is supposed to be homogeneous and isotropic. Thus the system under investigation, shown in Fig. 1, is constituted by:

- a spherical nanoparticle of radius $\boldsymbol{r}_0$;
- a shell-shaped interphase of external radius **a** and uniform properties;
- a matrix of radius $\boldsymbol{b}$ loaded by a hydrostatic stress *S*.

The properties required by the analysis can be computed by means of numerical simulations carried out within the frame of MD as done in [10,13]; such method provides, as outputs, the radial extension of the interphase as well as the elastic properties averaged through the interphase thickness.

The interphase extension might also be measured through the experimental approach proposed by Zammarano et al. [27] even though it needs to be validated for nanofillers different from those considered by the authors.

## 3. An energy approach to the problem

According to the Finite Fracture Mechanics (FFM) approach [28], the debonding of a nanoparticle can be assessed by imposing the following energy and stress conditions:

$$-\frac{\delta U}{\delta A} \geqslant \gamma \quad \text{and} \quad \sigma \geqslant \sigma_c \tag{1a-b}$$

where $\sigma_c$ is the normal interfacial strength, $\delta U$ is the change in potential energy, $\delta A$ is the newly created debonded surface and $\gamma$ is the interfacial fracture energy.

With the aim to determine the critical debonding stress from Eq. (1a), it is possible to make use of the following equilibrium equation, involving the energy states of the system during the debonding process:

$$\delta W = \delta K + \delta U^{m+a} + \delta U^{p} + 4\gamma\pi r_0^2 \tag{2a}$$

where $\delta W$ is the work done by external forces, $\delta K$ is the variation in the kinetic energy, $\delta U$ is the variation in the elastic energy stored in the matrix and interphase ($\delta U^{m+a}$) and in the nanoparticle ($\delta U^{p}$) and $\boldsymbol{r}_0$ is the nanoparticle radius.

Since the initial state is static, $\delta K$ is always positive and Eq. (2a) can be also rewritten as:

$$\delta W \leqslant \delta U^{m+a} + \delta U^{p} + 4\gamma\pi r_0^2 \tag{2b}$$

The term $\delta W$ in Eq. (2b) can be expressed as:

$$\delta W = S \times \delta u^{m}(b) \times 4\pi b^2 \tag{3}$$

where $\boldsymbol{b} \gg \boldsymbol{r}_0$ represents the matrix radius, $\delta \mathrm{u}^{m}$ is the variation in the matrix displacement field from the initial condition (incipient

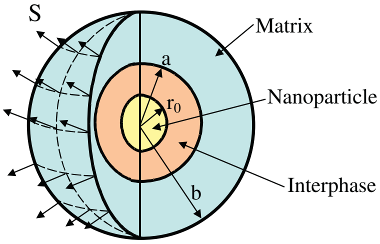

**Fig. 1.** Description of the system under analysis: nanoparticle of radius $\boldsymbol{r}_0$ embedded in an interphase region or radius **a**. Bulk material of radius **b** subjected to a hydrostatic stress *S*.