Composites Science and Technology 83 (2013) 27–31

Contents lists available at SciVerse ScienceDirect

Composites Science and Technology

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

Nanocomposite toughness from a pull-out mechanism

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ARTICLE INFO

Article history:
Received 29 December 2011
Received in revised form 13 March 2013
Accepted 23 April 2013
Available online 28 April 2013

Keywords:
A. Carbon nanotubes
A. Nanocomposites
B. Interfacial strength
B. Fracture toughness

ABSTRACT

We quantify nanocomposite toughness through a reanalysis for nanotubes of the Cottrell–Kelly–Tyson (CKT) model, of the definition of critical length, and of the energy dissipation model for pull-out. The effect of the hollow cylindrical geometry of nanotubes is discussed, followed by an examination of proper ways to compare energy dissipation at the nano and micro levels.

1. Introduction

There is increasing evidence in the literature for significant improvements in structural toughness of composites due to the use of nano-scale reinforcement [1–4]. Particularly relevant and central is the relationship between nanotube–matrix interfacial adhesion, which is not easy to measure directly, and nanocomposite toughness. It is possible to detach a nanotube from a polymer matrix and thereby measure interfacial adhesion either using a drag-out configuration [5], nano pull-out tests [6–9], and Raman tests [10]. Indirect tests on macrocomposites are also possible [11], and numerical simulations are available as well [12].

An additional parameter, the cylindrical structure of nanotubes, is playing a role that has seemingly been neglected so far in the literature, even though this structural aspect quantitatively affects the definitions of tube critical length (tubes with length above the critical length will preferentially break rather than pull-out of a matrix, whereas they will all pull-out rather than break if their length is below the critical length) and pull-out energy. We propose in the present paper to quantify nanocomposite toughness through re-examination for nanotubes of the Cottrell–Kelly–Tyson (CKT) model, of the critical length definition, and of the energy dissipation model for pull-out [13–17] by including the effect of the hollow cylindrical geometry of nanotubes. We then further discuss appropriate ways to compare energy dissipation at the nano and micro levels along the lines of our previous work [2,4].

2. The CKT model revisited

One of the experimentally most difficult problems in nanocomposite physics concerns the assessment of the extent and efficiency of stress transfer through the interface between nanotubes and polymers. The importance of this parameter rests on two facts: (i) efficient stress transfer from matrix to nanotube is necessary to take advantage of the very high Young's modulus and strength of carbon nanotubes in nanocomposites; and (ii) toughness is undeniably dependent on the nature of the tube-polymer interface but this dependence is not necessarily identical to the classical micro-fiber case, as will be clarified later. Regarding point (i), the much larger (exposed surface)/volume ratio of NTs (surface/volume = 2/radius, which is two orders of magnitude larger for NTs than for a traditional 10 μm fiber) implies that much larger interfacial areas are available for stress transfer. Classically the matrix–fiber stress transfer mechanism is relatively well described by models such as the CKT model [13–17], which will be adapted here for nano-composites. Much additional insight (regarding stress profiles and interfacial stress transfer ability) is traditionally provided by micro-Raman spectroscopy [10]. The interfacial chemistry in single CNT-polymer systems is quite well understood and its implications on interfacial adhesion have been experimentally studied by Barber et al. [5–8] and more recently by Tsuda et al. [9]. These experimental studies are currently the only ones available in the literature. Regarding point (ii) above, the classical pull-out energy dissipation model is re-examined here for hollow nanotubes, using a modified definition of the critical length.

Indeed, a straightforward correction can be made to the CKT scheme to account for the hollowness of the reinforcing nanotube

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http://dx.doi.org/10.1016/j.compscitech.2013.04.017

(or of a fiber, for that matter). Referring to Fig. 1, assuming that the force gradient between both edges of a differential element (BA) results in interfacial shear along the element, a force balance expression for the tube-polymer system may be expanded [18] from the classical version proposed for a fiber–polymer system [13–15] as follows:

$$F_{shear\ over\ AB} = F_{tension\ at\ edge\ A} - F_{tension\ at\ edge\ B}$$

or

$$\tau_{NT}(\pi D_{NT})dx = (\sigma_{NT} + d\sigma_{NT})\left(\frac{\pi D_{NT}^2 - \pi d_{NT}^2}{4}\right) - \sigma_{NT}\left(\frac{\pi D_{NT}^2 - \pi d_{NT}^2}{4}\right)$$

where τ_{NT} is the nanotube–polymer interfacial shear strength, σ_{NT} is the tensile strength of a nanotube segment of length dx, and d_{NT} and D_{NT} are the inner and outer tube diameters, respectively. Integration of this equation provides an expression for the interfacial shear strength between a hollow tube whose length is equal to the critical length ℓ_c [13–16] and the surrounding polymer:

$$\tau_{NT} = \sigma_{NT}(\ell_c)\left[0.5\left(\frac{\ell_c}{D_{NT}}\right)^{-1}\left(1 - \frac{d_{NT}^2}{D_{NT}^2}\right)\right] \quad (1)$$

where ℓ_c/D_{NT} is the critical aspect ratio of the nanotube and d_{NT}/D_{NT} is its diameter ratio. The classical CKT model for full cylinders (fibers) is recovered when $d_{NT} = 0$. The wall thickness ($=(D_{NT} - d_{NT})/2$) of single-wall nanotubes (SWNTs) may be equated to the spacing between neighboring walls, thus 0.34 nm.

3. Critical length of embedded nanotubes

The inversion of Eq. (1) provides an expression for the critical length of an embedded cylindrical fiber or tube:

$$\ell_c = \frac{D_{NT}\sigma_{NT}(\ell_c)}{2\tau_{NT}}\left(1 - \frac{d_{NT}^2}{D_{NT}^2}\right) \quad (2)$$

which represents a simple extension of the classical definition of the critical length of full fibers. The important point is that the critical length is now a function of the size of the hollow core: for a given external diameter, the critical length turns increasingly smaller for larger cores. This is shown in Fig. 2a for a (hypothetical) hollow carbon fiber and in Fig. 2b for nanotubes. In the former case the decrease is continuous (because a fiber wall can take any value of thickness) whereas in the latter it is discontinuous since the nanotube wall thickness only takes discontinuous (one could use the term 'quantized') values that are integer multiples of a single wall thickness.

4. The pulling out of nanotubes from a matrix

We shall assume that the fracture toughness of polymer-based composites is most often dominated by the fiber pull-out mechanism [13–17], as there is much experimental evidence for this in the literature, although other processes such as fiber debonding are occasionally significant too. Fundamental work on the toughness of short fiber composites was performed by many researchers, and developed extensively in the group of Lauke in Dresden [19–24].

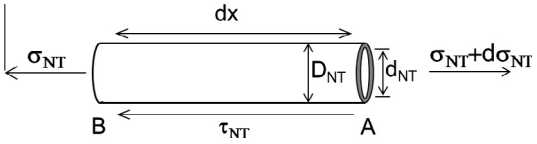

Fig. 1. Stresses acting on a differential element of a hollow tube or fiber.

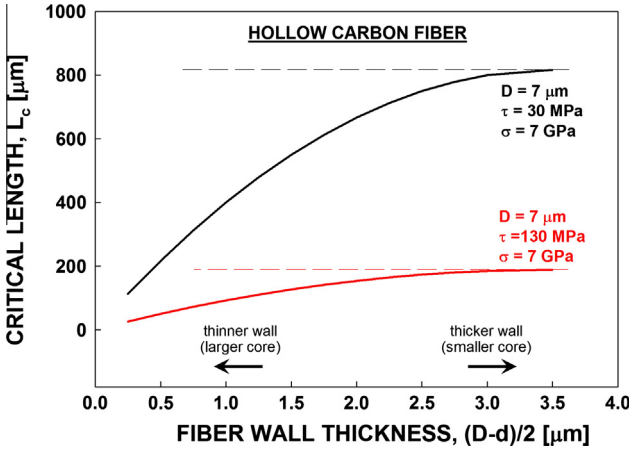

Fig. 2a. The critical length of a (hypothetical) hollow carbon fiber as a function of the fiber wall thickness, for weak and strong interfacial adhesion (30 and 130 MPa, respectively). Dashed lines refer to the critical length of full fibers calculated from the classical CKT model. See Eq. (2) in the text.

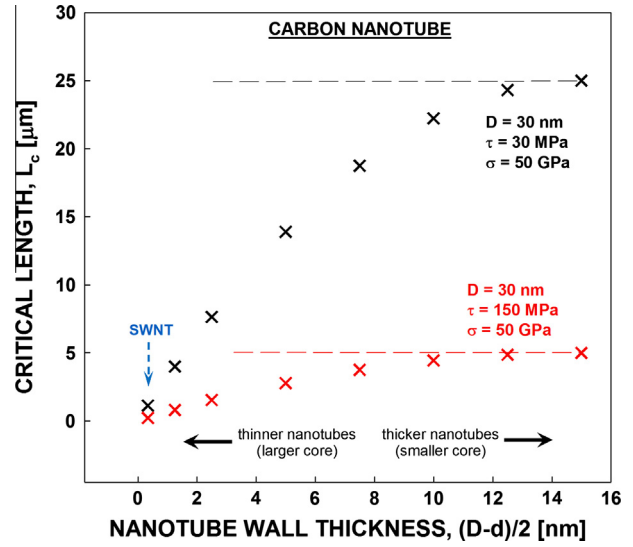

Fig. 2b. The critical length of a nanotube as a function of wall thickness, for weak and strong interfacial adhesion (30 and 150 MPa, respectively). Dashed lines refer to the critical length of a hypothetical full nanotube as calculated from the classical CKT model. A typical nanotube is currently barely a few microns long at most, thus generally shorter than the critical length even when the interface adhesion is relatively high.

We avoid here the complexities of the energy calculations arising from all fracture mode contributions (for details, see for example extensive surveys in Refs. [17,23]), and focus exclusively on the pull-out mode. We reformulate the pull-out energy model bearing in mind that the critical length is now also dependent on the tube hollow core size (or wall thickness) and not just on the outside diameter as for a full fiber.

Referring to Fig. 3, with $R_{NT} = D_{NT}/2$, an axial force $F = 2\pi R_{NT} x \tau_i$ (acting on the tube and resisted by shear, τ_i, along the tube-matrix interface) is required to pull the nanotube out of the matrix. As pull-out proceeds the pull-out length x decreases progressively from its original length, $x = \ell_{emb}$, and so does the applied force F.

If as commonly assumed the interfacial shear stress remains constant during pull-out, the work of pull-out for a single tube is:

$$W_{PO} = \int_0^{\ell_{emb}} F dx = \pi R_{NT} \ell_{emb}^2 \tau_i \quad (3)$$