ON THE EFFECT OF LONG CARBON NANOTUBES ON MODE I DELAMINATION TOUGHNESS OF LAMINATED COMPOSITES

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Abstract

A simple micromechanics-based model is proposed to study the effect of interlaminar long multi-walled carbon nanotubes (MWCNTs) in improving the delamination crack growth resistance of double-cantilever-beam specimens. It is assumed that the long MWCNTs （about 60μm）has been grown on the surface of the micro-fiber fabric cloth layouts, normal to the fiber lengths, resulting in a through-thickness enhancement between plies under loading. The long MWCNTs provide the bridging tractions to resist the delamination crack propagation when they are pulled out from the surrounding polymer matrix. Based on the molecular dynamics analysis and experimental measurements, a piecewise linear bridging traction law for the pull-out of long MWCNTs is proposed to evaluate the enhancement of the delamination toughness of laminated composites. An analytical approach used in stitching and z-pinning technology is then employed to parametrically study the effect of the long MWCNTs on the delamination toughness.

1 Introduction

The application of composite laminates with excellent in-plane properties has been retarded by its poor through-the-thickness properties, especially its poor delamination toughness. A considerable amount of research has been devoted to improve the damage tolerance of a laminated composite structure, either by using tougher matrices or by utilizing stitching, knitting, z-pinning, weaving or braiding to introduce through-the-thickness reinforcement into the laminates. The delamination toughness could be improved significantly by introducing through-the-thickness reinforcements at the cost of sacrificing in-plane properties, i.e., reduction in in-plane stiffness and strength, which degrades the practical performance of composite laminates [1].

Carbon Nanotubes (CNTs) has been proposed to improve the electronic, thermal and mechanical properties of engineering materials since Iijima confirmed their structures in 1991 [2]. For multi-walled CNTs, it possesses Yang’s modulus ~1TPa and fracture strength ~130GPa. Significant progress has been made both in CNTs manufacture and its applications in the last two decades [3].

Many research works have focused on applying the CNTs to reinforce the polymer composites. However, only small improvements in the bulk mechanical properties has been achieved, compared with conventional fiber-reinforced composites, due to dispersion, alignment of the CNTs within the matrix, adhesion between the CNTs and matrix, and the CNT length [3]. Nevertheless, recent advances in CNTs enable us to produce relatively reliable well-aligned and long CNTs [4], which indicate that the difficulties in manufacturing practical MWCNTs may be overcome sooner or later.

Veedu et al reported a novel scheme to use CNTs to improve the delamination toughness of laminated composites [5]. They proposed to apply interlaminar MWCNT forests into the laminates to enhance its delamination toughness. The MWCNTs were grown on the surface of micro-fiber fabric cloth layouts in its normal direction, resulting in an enhanced interlaminar properties. These nanotube-coated fabric cloths serve as building blocks for the multilayered composites, whereas the nanotube forests provide the much-needed interlaminar strength and toughness under various loading conditions. For the fabricated 3D composites with nanotube forests, Veedu et al [5] reported remarkable improvements in the interlaminar fracture toughness, hardness, in-plane mechanical properties, damping, thermoelastic behavior, and thermal and electrical conductivities, which makes these structures truly multifunctional**.**

In this paper, the interlaminar MWCNT forests are treated as stitches or z-pins at the nano scale of geometrical size for the bridging entities of MWCNTs. Similar to the stitching and z-pinning analysis, a MWCNT bridging model is proposed to predict the effect of long CNTs on mode I delamination toughness of composite laminates [6, 7]. A carbon nanotube, perpendicularly embedded in the matrix between two adjacent layers of composites, is assumed to be pulled out from the surrounding matrix under mode I opening loading, such as double cantilever beams (DCB) testing. The friction between a carbon nanotube and its surrounding matrix or between the inner tubes and the outermost tube of a multi-walled carbon nanotube [7-9] provides the bridging traction to retard the propagation of the delamination crack, which results in an enhanced delamination toughness for the laminated composites.

2 Long MWCNTs forests bridging model

Figure 1 depicts the nano manufacturing process presented in Veedu et al [5]. As shown in Figure 1, well-aligned long multi-walled CNTs can be grown perpendicularly to 2D woven fabrics of SiC using the chemical-vapour-deposition (CVD) process. The fabrics are then infiltrated by epoxy matrix and are subsequently stacked to produce laminated composites [5]. When the delamination crack front propagates along the epoxy matrix with embedded long MWCNTs forests under open loading, the long MWCNTs are loaded in axial tension due to the interaction between the outermost carbon nanotube with the surrounding epoxy matrix.

According to the experimental observation and measurement on MWCNTs pull-out behavior [7-10], two bridging mechanisms of long MWCNTs could be expected. One of the possible pull-out modes is that the whole individual MWCNTs may be pulled out from the matrix, where the friction between the outermost nano-tube and the surrounding matrix provides the bridging traction to the delamination crack. The other possible pull-out mode is that the inner carbon nanotubes are pulled out from the outermost carbon nanotube after the outermost carbon nanotube is broken under high axial tension (the interfacial friction between the outermost nanotube and its surrounding matrix due to the opening load), which is also referred to as sword-in-sheath mechanism [7, 8].

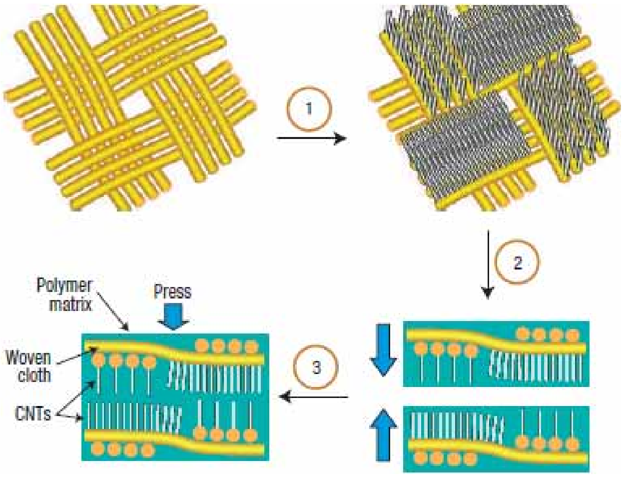


Figure 1 Schematic diagram of the steps involved in the hierarchical nano manufacturing of a 3D composite. (1) Aligned nanotubes grown on the fiber cloth. (2) Stacking of matrix-infiltrated MWCNT-grown fiber cloth. (3) 3D nano-composite plate fabrication by hand lay-up. (after [5])

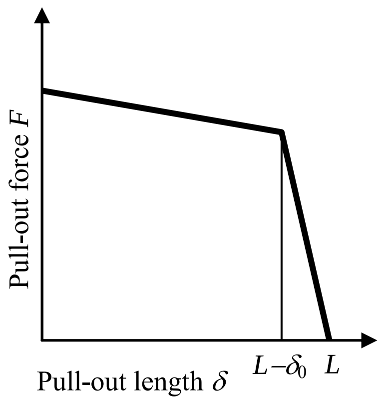


Figure 2 A simplified double-linear MWCNTs bridging law

It should be pointed out that above two bridging mechanisms are based on the observations and measurements of the pull-out test of an individual MWCNTs from its surrounding matrix. Further investigation on the pull-out behavior of long MWCNTs embedded in the adjacent layers of composites is necessary to identify the dominant bridging mechanism. For the sake of simplicity, only the later case, i.e., the sliding out of the inner nanotubes from the outermost nanotube subsequent to the breakage of the outermost nanotube, is considered in this paper. More detailed analysis of both bridging mechanisms is presented in [11].

A controlled sliding and pullout test of nested shells in individual MWCNTs conducted by Yu et al [7] indicates that the interfacial shear stress is attributed to the static and dynamic shear interaction between the CNT shells for the case of the inner nanotubes being pulled out from the outer nanotubes and the solid-solid capillary interface force due to the creation of a new shell interface area in the pullout event (surface tension effect). The measured bridging force decreases slightly (or is almost constant) during the inner CNT shell is pulled out for a longer interaction length between the CNT shells (>2μm) and drops sharply to zero when the interaction length is short (<2μm). The molecular dynamics analysis [12] suggests that tangent bridging traction in the interface between the MWCNTs and the surrounding matrix is constant during the pullout process, which correlates well with the experimental results conducted by Yu et al [7] for the case of initial contact length being 7μm. It is assumed that the MWCNTs are cylindrical with a circular cross-section. To simplify the analysis, the effect of MWCNTs abrasion or matrix crumbling during MWCNTs stretching and pull-out is neglected. The deformation in the matrix is also assumed to be negligible. Due to its high modulus and high tensile strength, the elastic stretching and tensile failure are ignored for the whole MWCNTs pull-out process. As shown in Figure 2, the bridging traction provided by an individual MWCNTs can be written as:

$$F = \begin{cases} \tau\pi d_c(L-\delta)+F_i & (L-\delta>\delta_0) \\ \dfrac{(\tau\pi d_c\delta_0+F_i)(L-\delta)}{\delta_0} & (\delta_0 \ge L-\delta \ge 0) \\ 0 & (L-\delta<0) \end{cases} \quad (1)$$

where d_c is the diameter of a MWCNTs with its length L. τ is the frictional stress on the interface between MWCNTs and its surrounding matrix. δ is the pull-out displacement of MWCNTs, which is equal to the open displacement of the two substrate beams at the location of the MWCNT. F_i is the shear interaction strength between the MWCNT and its surrounding matrix. δ_0 is the critical embedded length of a MWCNT when the sharp drop of the pull-out force starts.

The fracture-surface image of a DCB specimen shown in [5] indicates that the long WMCNTs are fully pulled out from the matrix with one end is attached to the delaminated laminate surfaces. Therefore, it is reasonable to assume that the outermost shell of the long WMCNTs is broken in the middle on the delamination crack plan and half length of the inner shells are pulled out from the either side of the MWCNTs.

It has been shown that the geometrical distribution of reinforcement entities, such as stitches, can significantly affect the enhanced delamination toughness [13]. However, it is evident that the distance between the MWCNTs is much shorter (~10-20nm), compared with that for stitches (~4-6mm). Therefore, it is reasonable to ignore the effect of the MWCNTs distribution on the enhancement in delamination toughness, and therefore the MWCNTs are assumed to be uniformly distributed in the polymer matrix. The bridging tractions provided by the MWCNTs can be written as

$$f = C_d F \quad (2)$$

where C_d is the density of the MWCNTs (number of MWCNTs per unit area).

3 Modeling of mode I delamination toughness of DCB specimen reinforced by long MWCNT forests

As shown in Figure 3, a DCB specimen is employed to study the enhanced mode I delamination toughness by long MWCNT forests. The crack propagation condition is governed by the

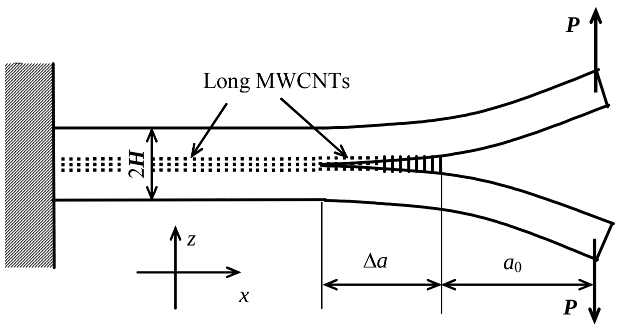


Figure 3 Double-cantilever-beams reinforced by long MWCNTs forests

equality of the net stress intensity factor K to the intrinsic fracture toughness of the composites K_{IC}. There are two contributions to K, one is the stress intensity factor due to the applied load, K_A, and the other, K_{CNT}, is due to the closure traction f acting across the crack surfaces within the bridging zone. Hence we have

$$K = K_A - K_{CNT} = K_{IC} \quad (3)$$

Then the enhanced delamination toughness K_R can be written as

$$K_{\mathrm{R}} = K_{\mathrm{IC}} + K_{\mathrm{CNT}} \tag{4}$$

It should be pointed out that the insertion of the long WMCNT forests may affect the intrinsic fracture toughness of the composites due to the stress concentration at the location of the WMCNTs. To simplify the analysis, it is assumed that the intrinsic fracture toughness of the composites is unchanged so that equation (3) and (4) can be employed to analyze the effect of the long WMCNTs forests on the fracture toughness of the composites.

According to Foote and Buchwald [14], the stress intensity factor K_I at the crack tip of a DCB specimen due to an applied load P (per unit width) at a distance t from the crack tip can be approximately calculated from:

$$K_I = C\frac{P}{\sqrt{H}} f\left(\frac{t}{H}\right) \tag{5}$$

where

$$f\left(\frac{t}{H}\right) = \sqrt{12}\left(\frac{t}{H}+0.673\right)+\sqrt{\frac{2H}{\pi t}} - \left[0.815\left(\frac{t}{H}\right)^{0.619}+0.429\right]^{-1} \tag{6}$$

and C is a correction factor, which depends on the anisotropic elastic material properties. For an orthotropic material, C is calculated from [14]:

$$C = \sqrt{E_o/E} \tag{7}$$

where E_o is the orthotropic modulus as shown in [6]. The formula for $f(t/H)$ is within 1.1% of the exact values for all values of t/H with a large un-cracked ligament.

The stress intensity factor, K_{CNT}, due to the closure traction may be computed from:

$$K_{\mathrm{CNT}}(\Delta a) = -C\int_0^{\Delta a} p(t)\frac{1}{\sqrt{H}} f\left(\frac{t}{H}\right)dt \tag{8}$$

and the equilibrium crack growth condition then becomes

$$K_{\mathrm{R}}(\Delta a) = K_{IC} + C\int_0^{\Delta a} p(t)\frac{1}{\sqrt{H}} f\left(\frac{t}{H}\right)dt \tag{9}$$

To obtain the crack growth resistance, K_{R}, the applied load corresponding to the critical stress intensity factor at the tip of the crack should firstly be iteratively determined. Then by removing all the nano-stitch elements, the stress intensity factor can be re-calculated for the same geometry and applied load, and this new value of stress intensity factor is K_{R}.

4 Numerical results and discussion

The DCB composite specimen shown in Figure 3 is analyzed. The DCB specimen has the total length 120mm, the width 20mm and the thickness $2H$ = 1.2mm.The initial crack length a is assumed to be 13mm. The MWCNTs density is assumed to be 25 μm^{-2} and the embedded MWCNTs have a length of 60μm.

The material properties of the composites and the MWCNTs are as follows:

E=23.1Mpa, τ=0.08Mpa, F_i=152nN, d_c=10nm

The critical stress intensity factor for the laminate beam is K_{IC}=2.0$MPa\sqrt{m}$ and it is assumed that this value remains constant across the whole interlaminar interface of the specimen.

It should be noted that the material properties of the composites and the MWCNTs above are taken from reference [5] and [7], respectively. Some data are based on the observation of the pictures shown in [5].

Figure 4 depicts the delamination crack growth resistance K_R initially increases from the intrinsic fracture toughness 2.0$MPa\sqrt{m}$ with crack growth due to the bridging tractions provided by the long MWCNTs forests in the crack wake and then attains an asymptotic value $K_\infty \approx 2.38$ $MPa\sqrt{m}$, which is about 19% increase in the mode I stress intensity factor. This asymptotic value is achieved because the bridging zone size is now saturated and remains constant with further crack growth.

It can be observed from Figure 4 that the delamination crack propagates about 0.9mm, which indicates that the saturated bridging zone is very short. Unlike the stitching and z-pinning technology, the MWCNTs forests are only embedded between the adjacent two laminate laminar and its length (about 60μm) is very small in the structural scale, compared to the crack open displacement. As a result, the MWCNTs are totally pulled out at a small crack open displacement. Nevertheless, the proposed analytical model can be employed to study the effect of the long WMCNTs forests on the mode I fracture toughness for the DCB geometry.

The effect of the long WMCNTs density on K_R-Δa curve is shown in Figure 5. Apparently, an increase in the WMCNTs density (from 30μm^{-2} to 90μm^{-2}) leads to a significant increase in the stress intensity factor (from $K_\infty \approx 2.38\ MPa\sqrt{m}$ to $K_\infty \approx 3.20\ MPa\sqrt{m}$). At the meantime, the length of saturated bridging zone becomes shorter with the increased WMCNTs density.

Figure 6 demonstrates the effect of the WMCNTs length (L=30, 60 and 90 μm) on K_R-Δa curves. For longer WMCNTs forests, only a slight higher bridging traction is estimated according to equation (1), which may imply that the length of WMCNTs might insignificantly affect the enhanced delamination toughness. However, to totally pull out the inner shells of WMCNTs from the outermost nanotube of longer WMCNTs, the crack open displacement at the crack front needs to be large enough, which leads to a longer saturated bridging zone. As a result, a higher stress intensity factor is predicted for the longer MWCNTs. As a parametric analysis, the asymptotic values of delamination toughness for much longer MWCNTs (up to 0.6mm) are also given in Figure 6(b). It can be seen from Figure 6(b) that the increase in the length of zone saturated bridging zone is fast for shorter MWCNTs (<0.1mm) and slows down for longer MWCNTs. On contrast, nearly linear increase in the asymptotic value of delamination toughness with the prolonging MWCNTs can also be observed from Figure 6(b). This is attributed to the increase in both the saturated bridging zone and the maximum bridging traction for individual longer MWCNTs.

6 Conclusions

A continuum mechanics approach is proposed to study the effect of the long WMCNTs forests embedded in the interlaminar matrix on the delamination toughness of laminated composites. The relationship of the pull-out displacement and pull-out force of a WMCNT based on both the molecular dynamics analysis and the experimental measurements is employed as micro bridging law. The numerical results showed that an increase in the WMCNTs density and the length of WMCNTs can lead to a higher delamination toughness of composite laminates.

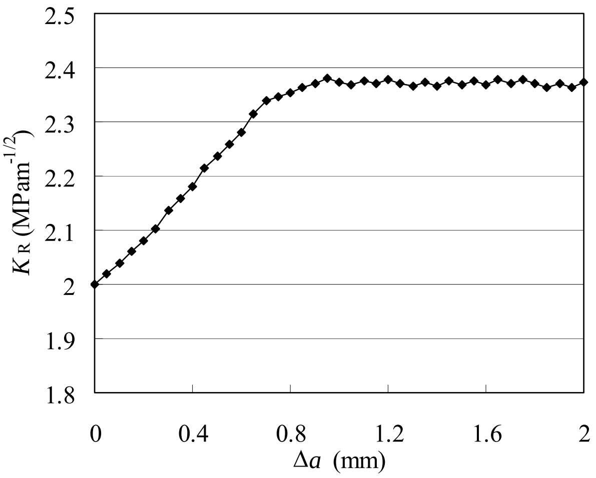
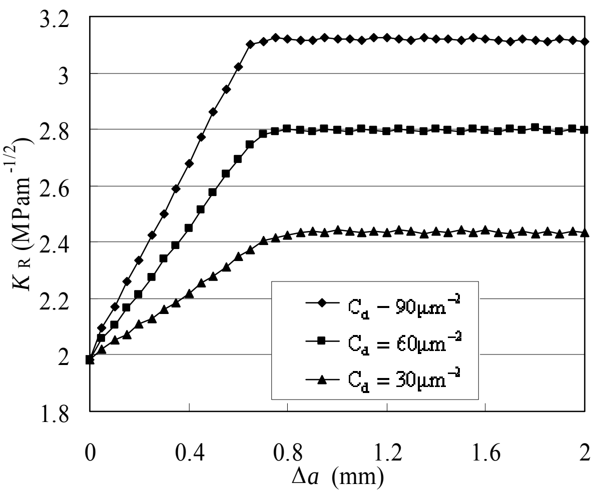
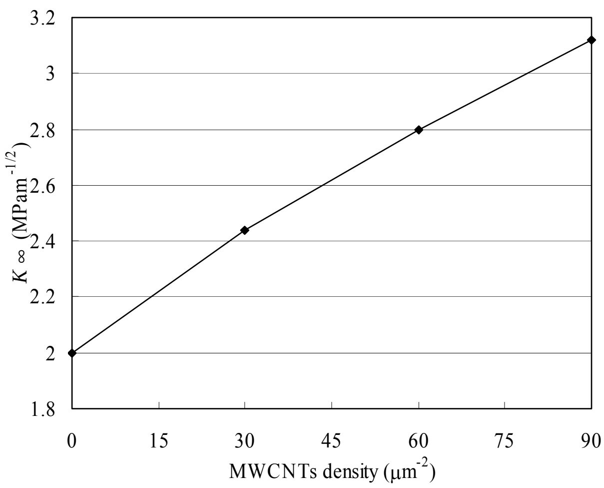


Figure 4 K_R-Δa curve for the DCB specimen

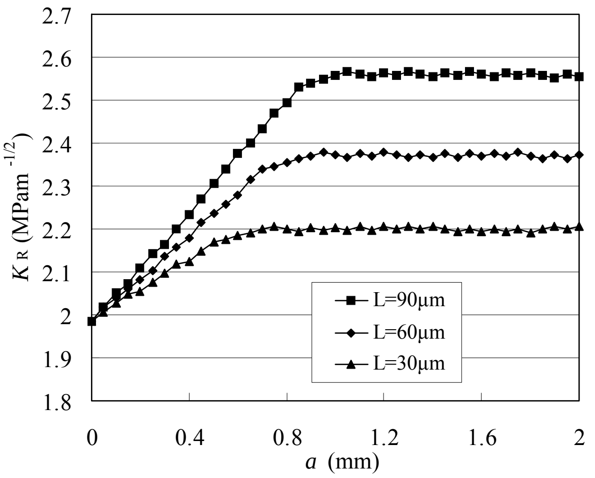


a) K_R -Δa curves for the DCB specimen with different MWCNTs density

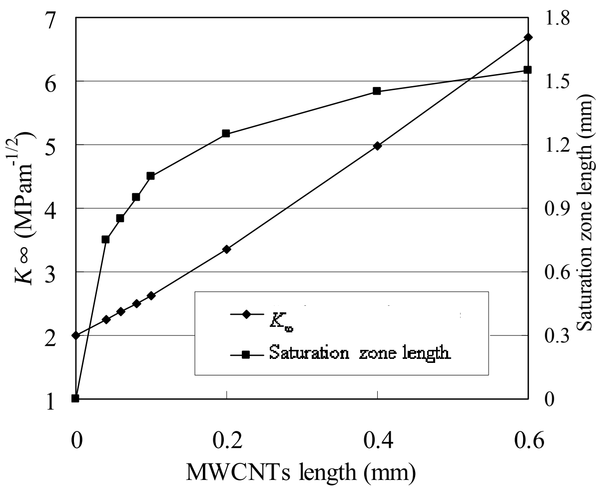


(b) K_∞ -MWCNTs density curve

Figure 5 Effect of the long WMCNTs density on K_R-Δa curve



(a) K_R -Δa curves for the DCB specimen with different MWCNTs length



(b) K_∞ and saturation zone length -MWCNTs length curve

Figure 6 Effect of the length of WMCNTs on K_R-Δa curve

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