MODELLING CARBON NANOTUBE "BRIDGES" IN UNIDIRECTIONAL FIBER COMPOSITES AND UNDERSTANDING THEIR EFFECT ON MICRO-SCALE STRESS CONCENTRATIONS

Valentin Romanov [a*], Stepan V. Lomov, Ignaas Verpoest, Larissa Gorbatikh

[a]*Department of Materials Engineering (MTM), University of Leuven (KU Leuven), Kasteelpark Arenberg 44 - bus 2450 B-3001 Leuven, Belgium*
** Valentin.Romanov@mtm.kuleuven.be*

Keywords: multi-level modeling, finite elements, carbon nanotubes, fiber-reinforced composite

Abstract

In this study we show that CNTs have a potential to re-distribute stresses in the composite and to suppress stress concentrations. For this, not only the position and concentration of CNTs are important but also the morphology of the nanostructure (namely CNT orientation and waviness) play a critical role. This was illustrated on the case of CNT "bridges" with two morphologies: (1) aligned and quasi-straight CNTs and (2) randomly oriented and highly curved CNTs.

1. Introduction

It has been experimentally shown that the formation and propagation of transverse cracks in fiber-reinforced composites can be hindered by adding small amounts of carbon nanotubes (CNTs) in the matrix [1, 2]. This is usually attributed to the increased toughness of the matrix and/or the strength of the fiber/matrix interface. The energy dissipating mechanism leading to these improvements is the pull-out of CNTs bridging crack surfaces. On the other hand, the presence of CNTs in a composite is expected to affect stress distribution and possibly to influence stress concentrations that are responsible for the onset of damage.

We recently developed a model of a composite reinforced with microscopic fibers and CNTs [3]. In this model fibers and nanotubes are modeled together without intermediate homogenization steps. The model is based on the Finite Element (FE) approach, three-dimensional (3D), fully parametric and uses the Embedded Elements (EE) technique to deal with reinforcements of different dimensions. Our previous numerical studies [4, 5] showed that the presence of CNTs in the matrix may drastically change stresses in the composite. CNTs were shown to introduce inhomogeneity in the stress field, which depended on such parameters as CNT waviness, orientation, concentration and localization. For instance, uniformly dispersed CNTs in the matrix tended to reduce the overall average stress in the matrix, whereas CNTs grown on the fiber surface were likely to reduce stresses on the fiber/matrix interface. Agglomerated CNTs, on the other hand, were shown to generate higher stress concentrations than in their absence. These studies concluded that CNTs can have both magnifying and suppressing effects on stress concentrations. It all depends on the structure that CNTs form.

In this work we hypothesize that CNTs have a potential to re-distribute stresses in the matrix between fibers for the purpose of releasing stress concentrations in some local areas without magnifying stresses in the rest of the material. We further advance the developed model towards modeling of CNT "bridges" between fibers and assessing their effect on the stress reduction. Two types of the CNT bridges are considered: (1) aligned and quasi-straight CNTs and (2) randomly oriented and highly curved CNTs.

2. FE model

In the present study, a 3D unit cell of a unidirectional (UD) carbon fiber composite with the fiber volume fraction of 60% is subjected to transversal tension (Fig.1). A square packing of fibers with the diameter of 7 μm is assumed. Symmetric boundary conditions are applied at every outer surface of the unit cell except at the right side where a displacement in the *x* direction is applied corresponding to the average transverse strain of 0.3%.

In the literature CNTs are often assumed straight [6-9]. However, in reality they are curved in the 3D space. The waviness of CNTs has a strong effect on composite properties [10-14], significantly decreasing the effective mechanical properties. Thus, adequate modeling of wavy nanotubes is of high importance [15]. In the present work CNTs are introduced in the unit cell one by one, and their complex geometry is taken into account. The CNT generation algorithm is implemented in Matlab. It is numerically efficient and able to generate geometry for different types of CNT nano-structures. The configurations that were modelled in the present study are: (1) bridges with aligned and quasi-straight CNTs (Fig.1b) and (2) randomly oriented and highly curved CNTs (Fig.1a). The localization of the CNT bridges is constrained to the narrow region between the two fibers.

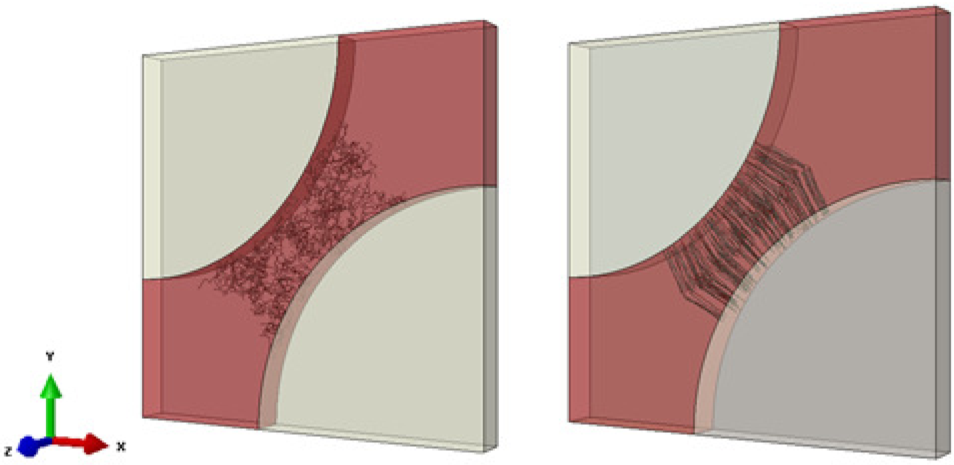

Figure 1. A 3D model of a unidirectional composite with CNT bridges between fibers: (a) a bridge of randomly oriented and highly curved CNTs; (b) a bridge of aligned and quasi-straight CNTs.

Each CNT has a length of 0.7 μm and a diameter of 9 nm. It is constructed via ten vertices that are sequentially generated randomly with equal segment distance L_{segm} between neighboring vertices and joined together with a 3D spline. A wavy cylinder (=CNT) is later obtained in Abaqus by sweeping of a circle along such a spline.

In the case of the bridge with aligned CNTs, CNTs are generated as follows (Fig.2a). The first vertice of a CNT is positioned randomly on the one twelfth of the fiber surface that is closest to the other fiber. Then, the rest nine vertices are sequentially generated so that each vertice-to-vertice line is deviating by not more than 10° from the direction normal to the fiber surface. By such a procedure a locally grown quasi-straight CNT forest is formed which will be referred as "aligned CNT bridge" further in the text.

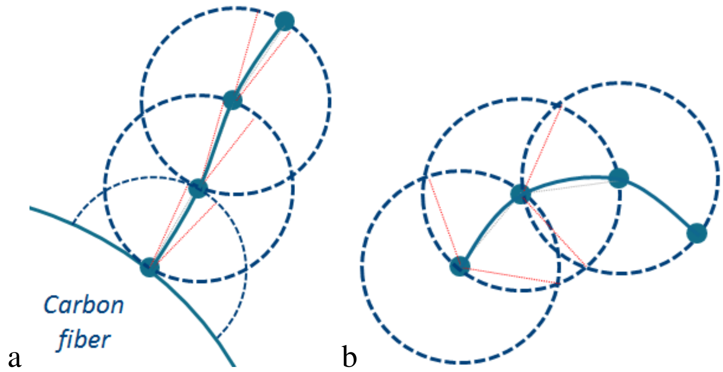

Figure 2. Schematics of CNT generation for CNTs: (a) aligned and quasi-straight CNT bridge; (b) randomly oriented and highly curved CNT bridge.

The generation procedure for the bridge with randomly oriented and highly curved CNTs is as follows (Fig.1b). For each CNT the first vertice is positioned randomly in the narrow matrix zone between the two fibers. The rest of the points are generated in such a way that the distance between them and all of the rest of the vertices of a given CNT is greater than $1.25*L_{segm}$. It is done in order to prevent too sharp angles in the geometry of the CNTs and to avoid self-intersection. By such a procedure a bridge with randomly oriented and highly curved CNTs is formed which will be referred as "random CNT bridge" further in the text.

Both models contain 245 nanotubes which corresponds to the CNT weight fraction of 0.25% in the matrix. CNTs are modelled with Young's modulus of E=475 GPa and Poisson's ratio ν=0.4, the epoxy matrix with E_m=3 GPa and ν_m=0.4 and carbon fibers are treated as transversely isotropic with E_1=276 GPa, E_2=E_3=10.3 GPa, G_{23}=3.8 GPa, G_{13}=27.9 GPa, υ_{13}=0.26, where "1" is the fiber direction (z-direction in Fig.1). The unit cell thickness is 0.5 μm, which is considered to be adequate since CNTs are uniformly and homogeneously distributed through the thickness of the unit cell. Perfect contact between all entities and elastic behavior of all materials are assumed. The CNTs, the matrix and the carbon fibers are modeled as solid bodies and meshed with 8-node solid elements. The numerical analysis is performed in Abaqus FE package.

3. Results and discussion

Fig.3 presents contour plots of the maximum principal stress in the matrix obtained for the reference composite without CNTs and for the two models with CNT bridges. The contour plots are shown for the central slice through the unit cell thickness. The color scales are set the same for all three configurations in order to allow comparison. The gray and black colors represent higher and lower stresses, respectively, outside the color scheme.

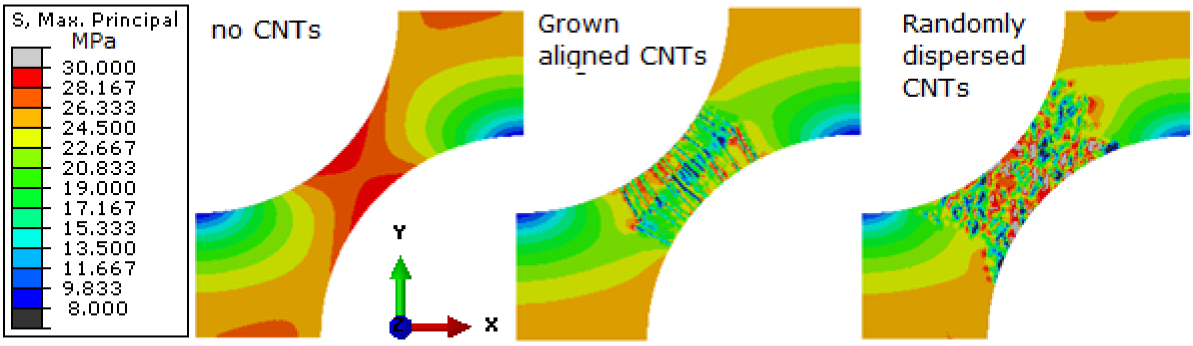

Figure 3. Contour plots of the maximum principal stress in the matrix for composites (a) without CNTs, (b) with aligned and quasi-straight CNT bridge; (b) randomly oriented and highly curved CNT bridge.

It is apparent that the presence of CNT bridges changes the stress distribution between the two fibers. CNTs introduce strong stress heterogeneity, which depends on the structure of the CNT bridge. The high microscopic stress concentrations between the two fibers become re-distributed, but this re-distribution is very different in these two CNT configurations. The bridge with the randomly oriented and highly curved CNTs produces stress distribution in the matrix that is also quite random. Locally, stresses can be even higher than in the reference case without CNTs. The high stress concentrations are marked with the grey color. The bridge with the aligned and quasi straight CNTs, on the other hand, produces stress distribution that is somewhat similar to the topology of the bridge. Interestingly, the micro-scale stress concentrations become suppressed (the red zone between the two fibers is no longer there). Thus, the nano structure of the CNT bridge plays an important role in the reduction of stress concentrations.

To compare both CNT configurations in quantitative terms, the radial stress component on the fiber/matrix interface S_r is calculated. This stress component is generally reported to be the one that governs the first damage in the composite - debonding of the polymer matrix from the fiber. In the present study, $S_r(\theta)$ is defined by polar angle θ and averaged through the thickness of the model (the insert in Fig.4a). Fig.4 represents $S_r(\theta)$ curves for the two CNT configurations. The curve corresponding to the reference case is also added.

In the case of the CNT bridge with aligned and quasi- straight CNTs there is a local drop in the angle range of 120°-150° which corresponds to the location of the bridge. The small scatter is explained by the random position of CNTs through the thickness of the model. Oriented radially to the fiber surface and located on the fiber/matrix interface area CNTs suppress the matrix deformation normal to the fiber surface and, hence, decrease S_r at fiber/matrix interface. This effect becomes more significant for denser CNT forests [16].

In the case of the CNT bridge with random and highly curved CNTs the curve shows quite irregular behavior. First, once it enters the zone of the CNT bridge at the angle of 120° it follows the reference curve. The sudden rise of S_r is then followed by the slope drop until the end of the CNT region at the angle of 150°. Such behavior can be explained by the randomness of the CNT orientation within the bridge.

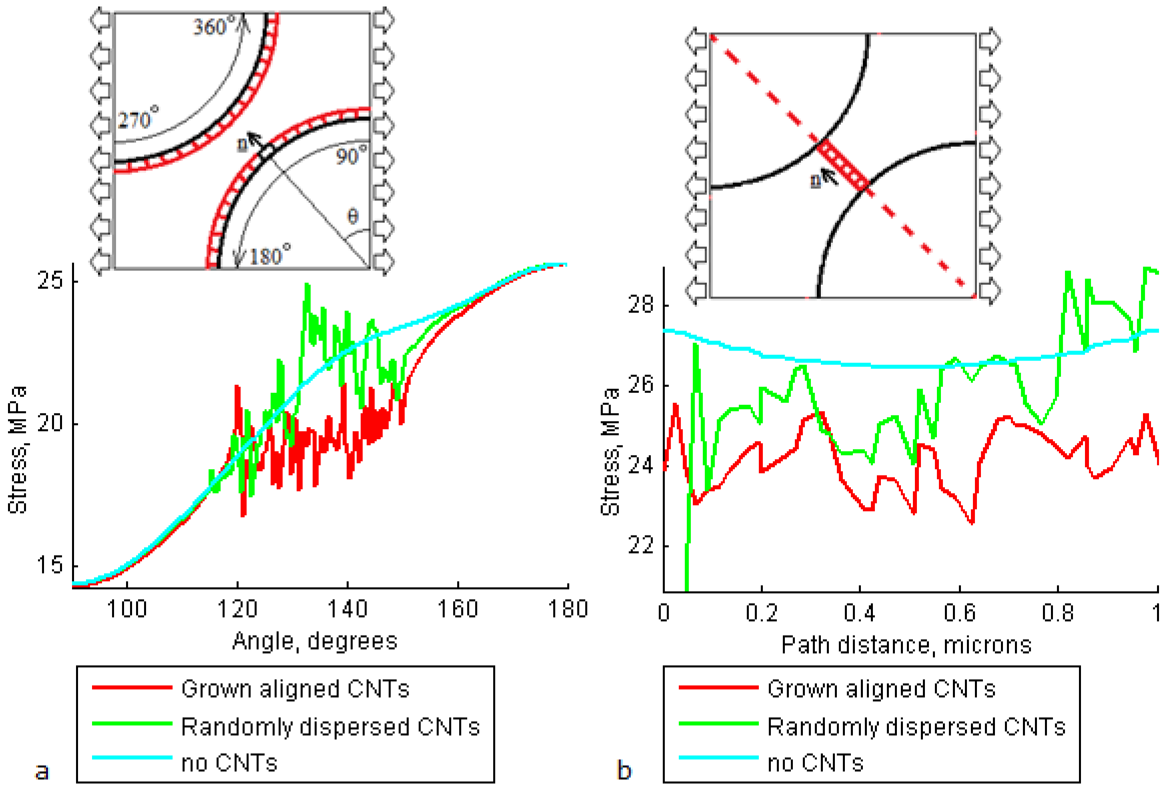

Figure 4. Radial stress component S_r averaged through thickness of the model (a) at the fiber/matrix interface and (b) along the shortest line between the two fibers.

S_r is also analyzed along the shortest line between the fiber surfaces (Fig.4b). It is calculated in matrix elements closest to that line and averaged through the thickness of the model. It is apparent that the bridge with aligned CNTs decreases stresses along the whole path and keeps them quasi-uniform apart from the natural deviations that come from the randomness of the CNT placement through-the-thickness of the model. The bridge with randomly oriented CNTs, on the other hand, does not show any strong improvement in comparison with the reference case.

From the analysis we can say that the two CNT configurations show completely different effect on the stress distribution. The equal amount of CNTs and the same zone of nano-reinforcement are not the only factors that have to be taken into account. The topology of individual CNTs including their orientation and waviness are factors that cannot be neglected.

4. Conclusions

Two configurations of the CNT reinforced bridges were analyzed. It was shown that the CNTs had a significant effect on the heterogeneity of the stress field in the narrow matrix region where the CNT bridges were located. Randomly oriented and highly curved CNTs did not lead to any consistent stress reduction. Aligned and quasi-straight CNTs, on the other hand, were very efficient in decreasing stresses in the matrix of the CNT bridge. They also provided a drastic decrease in the radial interface stress. It was also noted that in order to control micro-scale stresses in nano-engineered composites, not only the location of the CNT bridge and the CNT concentration are important but also the morphology of the nanostructure inside the bridge (namely CNT orientation and waviness) play a defining role.

Overall, we were able to show that CNTs have a potential to re-distribute stresses in the composite and to suppress stress concentrations.

References

[1] De Greef, N., et al., *The effect of carbon nanotubes on the damage development in carbon fiber/epoxy composites.* Carbon, 2011. **49**(14): p. 4650-4664.
[2] Yokozeki, T., Y. Iwahori, and S. Ishiwata, *Matrix cracking behaviors in carbon fiber/epoxy laminates filled with cup-stacked carbon nanotubes (CSCNTs).* Composites Part a-Applied Science and Manufacturing, 2007. **38**(3): p. 917-924.
[3] Romanov, V., et al., *A novel approach to modelling of fiber-reinforced composites with carbon nanotubes* in *19th Iternational Conference on Composite Materials (ICCM19)*. 2013: Montreal, Canada.
[4] Romanov, V., et al., *Modeling stress distribution in unidirectional carbon fiber composites with grown carbon nanotubes*, in *6th International Conference on Carbon NanoParticle based Composites (6th CNPComp)*. 2013: Dresden, Germany.
[5] Romanov, V., et al., *The effect of grown carbon nanotubes on stress distribution in unidirectional carbon fiber composites*, in *Composite Week at Leuven*. 2013: Leuven, Belgium.
[6] Kirtania, S. and D. Chakraborty, *Multi-scale modeling of carbon nanotube reinforced composites with a fiber break.* Materials & Design, 2012. **35**: p. 498-504.
[7] Li, X.T., et al., *Computational modeling and evaluation of the thermal behavior of randomly distributed single-walled carbon nanotube/polymer composites.* Computational Materials Science, 2012. **63**: p. 207-213.
[8] Bhuiyan, M.A., et al., *Defining the lower and upper limit of the effective modulus of CNT/polypropylene composites through integration of modeling and experiments.* Composite Structures, 2013. **95**: p. 80-87.
[9] Chao, F., A. Kumar, and S. Mukherjee, *Finite element analysis of single-walled carbon nanotubes based on a rod model including in-plane cross-sectional deformation.* International Journal of Solids and Structures, 2013. **50**(1): p. 49-5656.
[10] Li, C.Y. and T.W. Chou, *Failure of carbon nanotube/polymer composites and the effect of nanotube waviness.* Composites Part a-Applied Science and Manufacturing, 2009. **40**(10): p. 1580-1586.
[11] Bhuiyan, M.A., et al., *Understanding the effect of CNT characteristics on the tensile modulus of CNT reinforced polypropylene using finite element analysis.* Computational Materials Science, 2013. **79**(0): p. 368-376.
[12] Yanase, K., S. Moriyama, and J.W. Ju, *Effects of CNT waviness on the effective elastic responses of CNT-reinforced polymer composites.* Acta Mechanica, 2013. **224**(7): p. 1351-1364.
[13] Dastgerdi, J.N., G. Marquis, and M. Salimi, *The effect of nanotubes waviness on mechanical properties of CNT/SMP composites.* Composites Science and Technology, 2013. **86**: p. 164-169.
[14] Kundalwal, S.I. and M.C. Ray, *Effect of Carbon Nanotube Waviness on the Elastic Properties of the Fuzzy Fiber Reinforced Composites.* Journal of Applied Mechanics-Transactions of the Asme, 2013. **80**(2).
[15] Matveeva, A., et al. *Investigation of the mechanical properties of injection moulded cnt reinforced thermoplastic polymer parts*. in *SAMPE-USA conference*. 2013. LongBeach.
[16] Romanov, V., et al., *Can carbon nanotubes grown on fibers fundamentally change stress distribution in a composite?* Accepted in Composites Part A: Applied Science and Manufacturing, 2014.