Multiscale Modeling of Graphite Plain-Weave Composites with a SWNT-Reinforced Epoxy Matrix

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Abstract

The objective of this study is to develop a multiscale modeling approach to predict the influence of molecular structure and microstructure on the bulk-level properties of a graphite/epoxy plain-woven fabric composite in which the resin-rich regions are reinforced with carbon nanotubes. The modeling approach incorporates molecular modeling and micromechanics techniques. A parametric study shows that nanotube length has a strong influence on the predicted bulk properties for nanotubes below 100 nm long. Above 100 nm, further increases in length have a negligible impact on bulk properties. It is also shown that nanotube volume fraction has a strong impact on the axial and bending laminate properties. Furthermore, nanotube functionalization to the surrounding epoxy in the resin-rich regions of the woven composite has little impact on the overall performance of the composite.

Introduction

Woven-fabric composites have received considerable attention in recent years on account of their increased damage tolerance with respect to unidirectional and angle-ply composite laminates and because of the relative ease and low cost of fabrication of composite structures made from woven fabric pre-pregs. Woven-fabric composites are formed by the process of interlacing two individual fiber bundles or tows perpendicular to one another and impregnating with a matrix to form a single layer. As a result of the architecture of these composites, matrix-rich regions are formed in the gaps between the interlaced fiber bundles. These regions, where cracks can easily initiate and propagate, are difficult to reinforce with traditional microscale reinforcement. It has been suggested that carbon nanotubes are ideal candidates for reinforcing these resin-rich interlaminar regions because of their size and outstanding mechanical properties [1, 2]. In order to test this hypothesis in an efficient manner, multiscale computational modeling can be used to perform parametric studies on the expected mechanical response of these materials as a function of material geometry.

The objective of this study was to develop a multiscale modeling approach to predict the influence of molecular structure and microstructure on the bulk-level properties of a graphite/epoxy plain-woven fabric composite in which the epoxy is reinforced with single-walled carbon nanotubes (SWNTs). A recently developed molecular modeling approach [3, 4] was used to establish the effective properties of the SWNT-reinforced epoxy matrix material that was used as an input into the fiber-undulation micromechanical modeling approach [5]. The strain gradient approach [6] was also used to describe the overall bulk-level properties of the woven fabric composite materials. A series of parametric studies were performed to establish structure-property relationships that can ultimately be used to tailor the composite material for specific applications. The mechanical response of plain-weave composite was predicted as a function of SWNT length, volume fraction, and interfacial bonding with the surrounding epoxy polymer. In this paper, a description of the modeling techniques will be followed by the presentation of the results and subsequent discussion.

SWNT/Epoxy nanocomposite

The first step of the multiscale modeling process was to establish the properties of a SWNT/Epoxy nanocomposite that was used as the resin-rich portion of the plain-woven fabric composite in the subsequent micromechanics modeling. The approach used in this study utilized a method previously developed to predict the expected bulk elastic properties of a SWNT/polymer nanocomposite as a function of SWNT geometry, orientation, volume fraction, and interfacial bonding conditions [3, 4].

According to the previous studies [3, 4], a SWNT and the immediate surrounding polymer molecules can be modeled at an equivalent-continuum effective fiber (Figure 1). There two primary advantages to modeling the SWNTs in this manner. First, an effective fiber with either a circular cylindrical geometry (for very long SWNTs) or an elongated spheroidal geometry (for SWNTs of finite length) can be easily used as an input into standard micromechanical modeling techniques [7]. Second, the effective fiber models the overall mechanical response of the SWNT and the SWNT/polymer interface. The interface can be modeled separately as a third phase in a micromechanical modeling approach [8], however, including the interfacial response in the effective fiber is much more efficient. For this study, the elastic properties of the effective fibers determined by Odegard et al. [3] for both functionalized and non-functionalized SWNTs are used. The elastic stiffness constants of the two types of effective fibers are given in Table 1.

Table 1 – Elastic stiffness tensor components of the non-functionalized and functionalized effective fiber

Elastic constant	Non-functionalized effective fiber (GPa)	Functionalized effective fiber (GPa)	Epoxy (GPa)
C_{11}	548.7	487.7	7.2
C_{22}	16.8	24.5	7.2
C_{33}	16.5	20.6	7.2
C_{23}	12.9	16.4	3.7
C_{13}	16.0	20.0	3.7
C_{12}	15.8	21.2	3.7
C_{44}	7.1	12.7	1.8
C_{55}	144.0	155.4	1.8
C_{66}	144.9	137.0	1.8

With the elastic constants in hand, they were used as an input into a micromechanics model [9] to predict the bulk properties of the SWNT/epoxy nanocomposite. The properties of the epoxy are given in Table 1, and correspond to a Young's modulus and Poisson's ratio of 4.7 GPa and 0.34, respectively. It was assumed that the SWNTs were dispersed in the epoxy with a random orientation. The Young's modulus and shear modulus of the composite was determined as a function of SWNT length and volume fraction, and are plotted in Figures 2 and 3, respectively.

From Figure 2, it is clear that below SWNT lengths of 100 nm, increasing lengths result in increasing elastic properties. Above the 100 nm threshold, further increases in nanotube length do not result in increases in nanocomposite stiffness. From Figure 2 it is also evident that functionalization of the SWNTs resulted in a very small decrease in elastic properties of the overall composite. In a previous study [3], it was speculated that this decrease is the result of the degradation of the SWNT/polymer interfacial structure in the presence of functionalization, despite the presence of the relatively stiff covalent bonds that do not exist in the non-functionalized composite. From Figure 3 similar trends are observed. As the SWNT volume fraction increases, there is a dramatic increase in the elastic properties. Also, the non-functionalized SWNTs result in a composite with slightly higher elastic properties relative to the composite with functionalized SWNTs.

Micromechanical modeling

The results from the previous section (Figures 1 & 2) were used as an input into the resin-rich portion of the fiber undulation model [5]. The fiber undulation model was developed in order to consider the continuity and undulation of the fibers in a woven fabric composite. The geometry of the microstructure is defined by the parameters h, h_t, a, and a_u, as shown in Figure 4. For this study, the assumed values of these parameters are listed in Table 2. It was assumed that the fill and warp tows were a graphite/epoxy composite with the longitudinal modulus E_L, transverse modulus E_T, longitudinal shear modulus G_{LT}, and Poisson's ratio ν_{LT} shown in Table 2 [5].

Table 2 – Parameters for the fiber undulation model.

Parameter	Value
h	1 mm
h_t	0.8 mm
a	2 mm
a_u	0.5, 1.0, 1.5 mm
E_L	132 GPa
E_T	9.31 GPa
G_{LT}	4.61 GPa
ν_{LT}	0.28

The fiber undulation model provided the predicted structural stiffness components give by the standard lamina equation [10]

$$\left[\frac{N}{M}\right]=\left[\begin{array}{c|c}A & B\\ \hline B & D\end{array}\right]\left[\frac{\varepsilon^0}{\kappa}\right] \tag{1}$$

where N, M, ε^0, and κ are the sub-matrices of lamina in-plain forces, moments, neutral-axis strains, and curvatures, respectively. The sub-matrices A, B, and D represent the axial stiffnesses, coupling stiffnesses, and bending stiffnesses, respectively. By determining these stiffness parameters as a function of the properties displayed in Figures 2 and 3, they can be directly determined as a function of SWNT length, volume fraction, and interfacial bonding.

Results

Figures 5 and 6 show the predicted extensional stiffness component A_{xx}, which relates the force applied in the x-direction with the resulting strain in the x-direction, and the bending stiffness component D_{xx}, respectively, as a function of the length of SWNTs that are dispersed in the polymer matrix with random orientations with a volume fraction of 1%. The data is shown in the case of three different yarn undulation lengths a_u: $a_u = 1/4\,a$, $1/2\,a$, and $3/4\,a$. Also, for each yarn undulation length, the predicted results from functionalized and non-functionalized SWNTs are shown.

The results shown in Figures 5 and 6 indicate that SWNT length has a significant influence on the extensional and bending stiffness of the plain woven composite. As the SWNT length increases, the stiffness in the direction of the undulation increases for SWNT lengths below 100 nm. Above this critical SWNT length, further increases in length yield negligible increases in lamina stiffness. It is also clear that as the yarn undulation length increases, the stiffness of the lamina decreases. Although the matrix/SWNT bonding characteristics have a small impact on overall composite behavior, it is clear that for this particular material, SWNT functionalization slightly degrades the mechanical properties with respect to the non-functionalized composite. This could be due to a change in the molecular bonding characteristics of the SWNT (changing stiffer cp_2 bonds to cp_3 bonds) or in the re-arrangement of the atoms in the presence of functionalization.

Figures 7 and 8 show the extensional and bending stiffness components, respectively, for a range of SWNT volume fractions, yarn undulation lengths, and SWNT/epoxy bonding conditions. The figures demonstrate that small increases in SWNT volume fraction result in significant increases in the lamina stiffness, both in extension and bending. Furthermore, the results indicate that the length of the undulation, for a fixed SWNT length, has the same influence as shown in Figures 5 and 6 for a fixed SWNT volume fraction. Finally, it is clear from Figures 7 and 8 that the SWNT functionalization has a small influence on the overall mechanical behavior of the plain-woven fabric composite.

Summary and Conclusions

A modeling approach was developed to predict the bulk-level mechanical response of plain-weave composite materials in which the resin-rich regions were filled with randomly-oriented carbon nanotubes. This model was developed to facilitate the design of these materials to optimize the elastic response as a function of nanotube length, volume fraction, and functionalization to the surrounding polymer matrix. It was shown that below 100 nm, the nanotube length had a significant impact on the axial and bending properties of the plain-weave composite. Above 100 nm, further increases of nanotube length had a negligible impact on mechanical performance. It was also shown that nanotube volume fraction had a strong impact on the axial and bending laminate properties. Furthermore, nanotube functionalization to the surrounding polymer in the resin-rich regions of the woven composite had little impact on the overall performance of the composite.

These results indicate that the elastic properties of plain-weave composite materials can be significantly improved by adding carbon nanotubes to the resin-rich regions of the composite, particularly if large volume fractions are added. Because the functionalization of the nanotubes with surrounding polymer is usually a difficult (and thus expensive) step in the polymer fabrication process, and because there is little influence of chemical functionalization on the overall elastic properties, it is suggested that carbon nanotubes be added to the resin-rich regions of the composite without functionalization. It is also suggested that nanotubes with at least a length of 100 nm be used.

Acknowledgements

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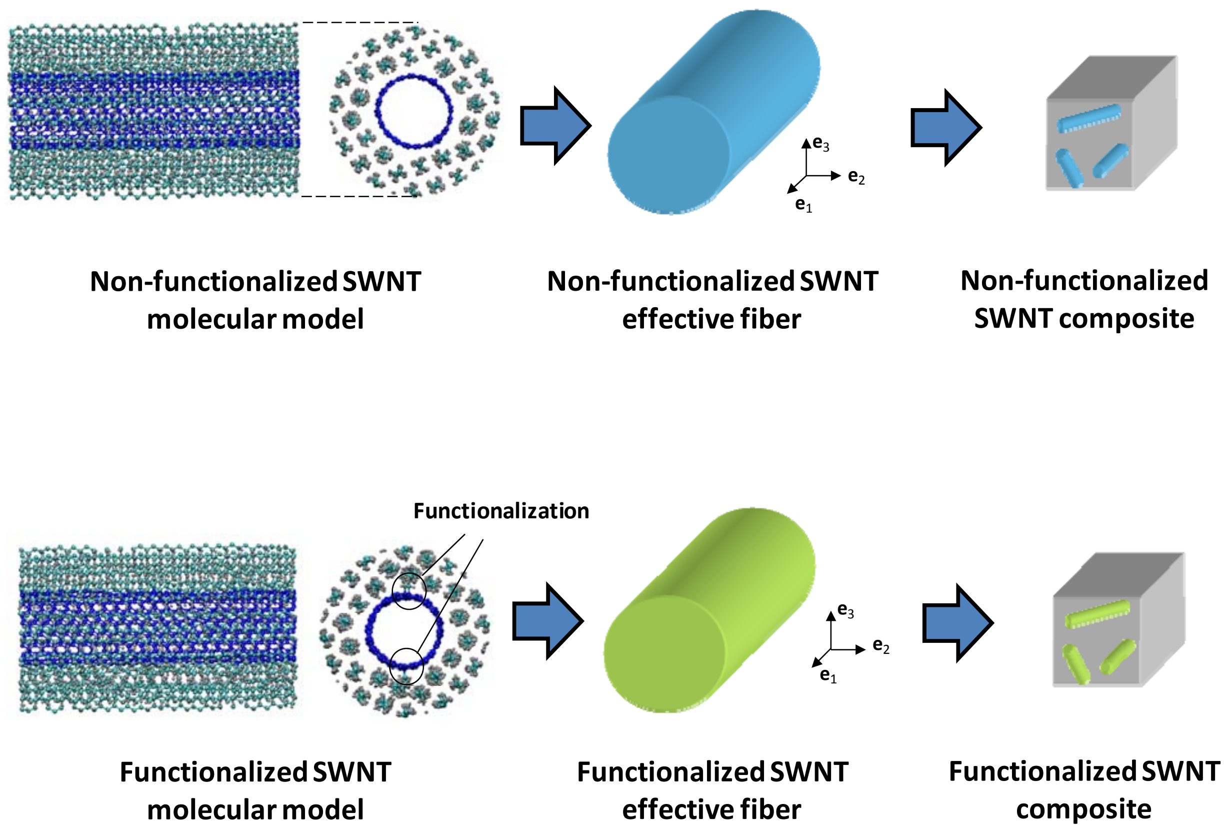

Figure 1 – Equivalent-continuum modeling of a SWNT/polymer composite

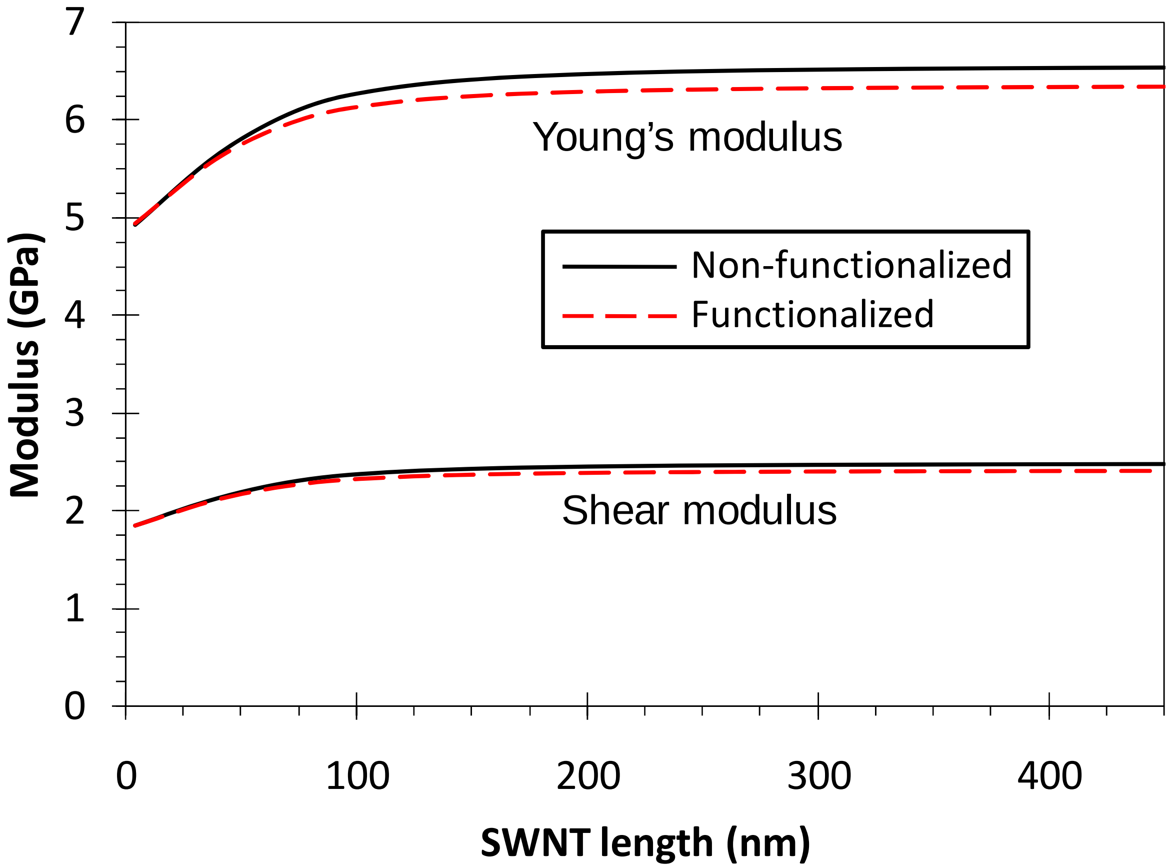

Figure 2 – Elastic moduli of a SWNT/ epoxy nanocomposite as a function of nanotube length and SWNT/epoxy bonding for a 1% SWNT volume fraction

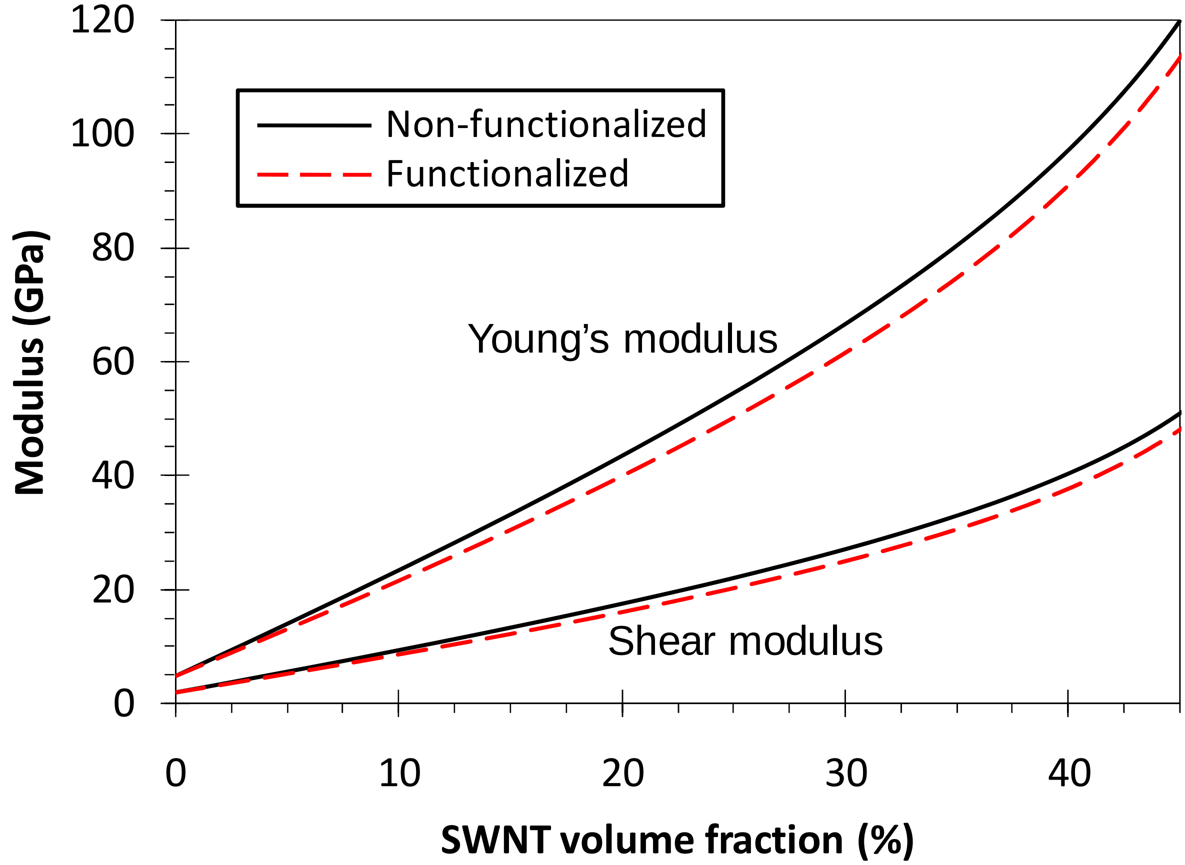

Figure 3 – Elastic moduli of a SWNT/ epoxy nanocomposite as a function of nanotube volume fraction and SWNT/epoxy bonding for SWNTs of length 400 nm

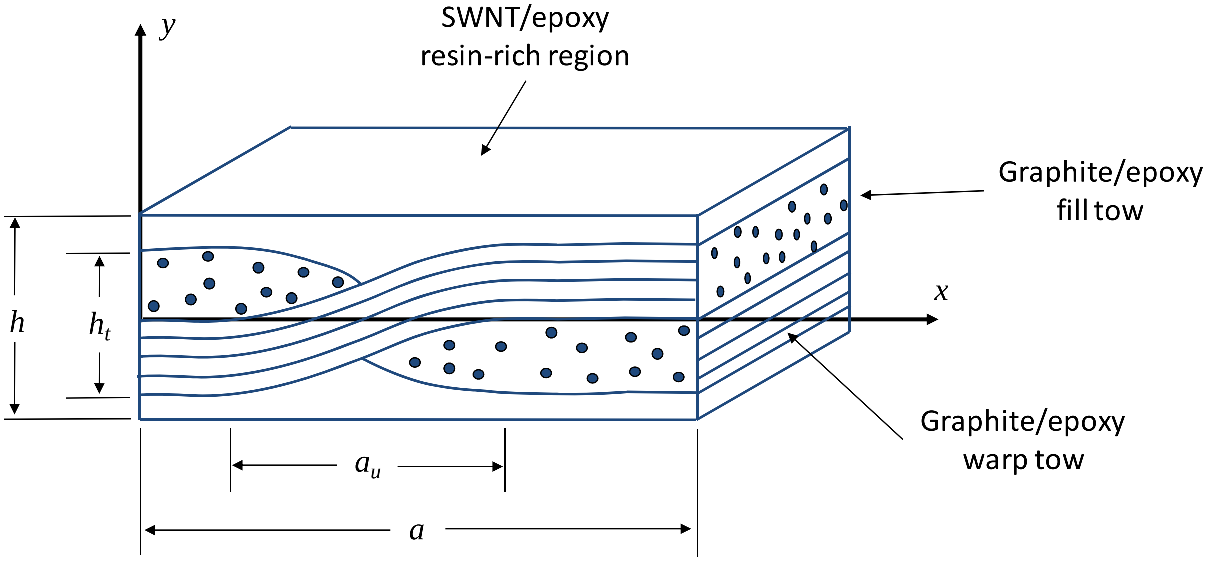

Figure 4 – Fiber undulation model

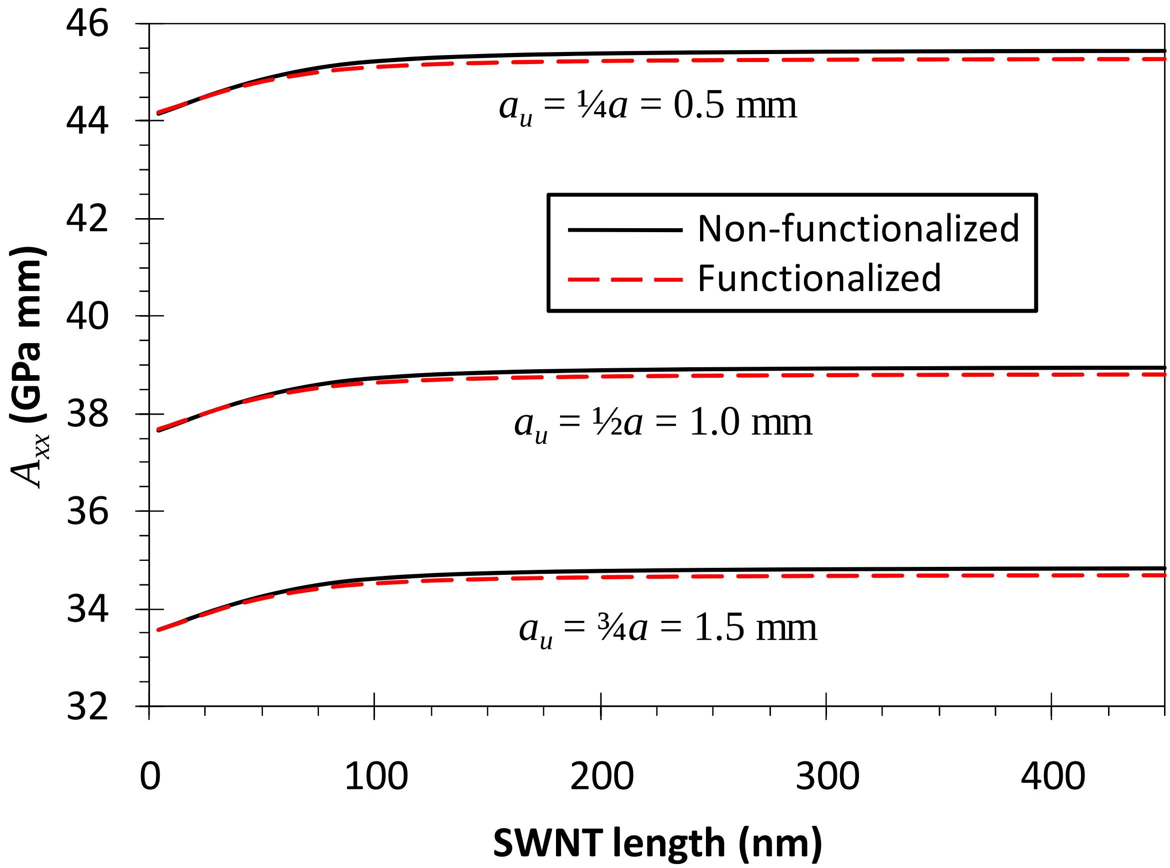

Figure 5 – Extensional stiffness of a SWNT/graphite/epoxy plain weave composite as a function of nanotube length, yarn undulation length, and SWNT/epoxy bonding.

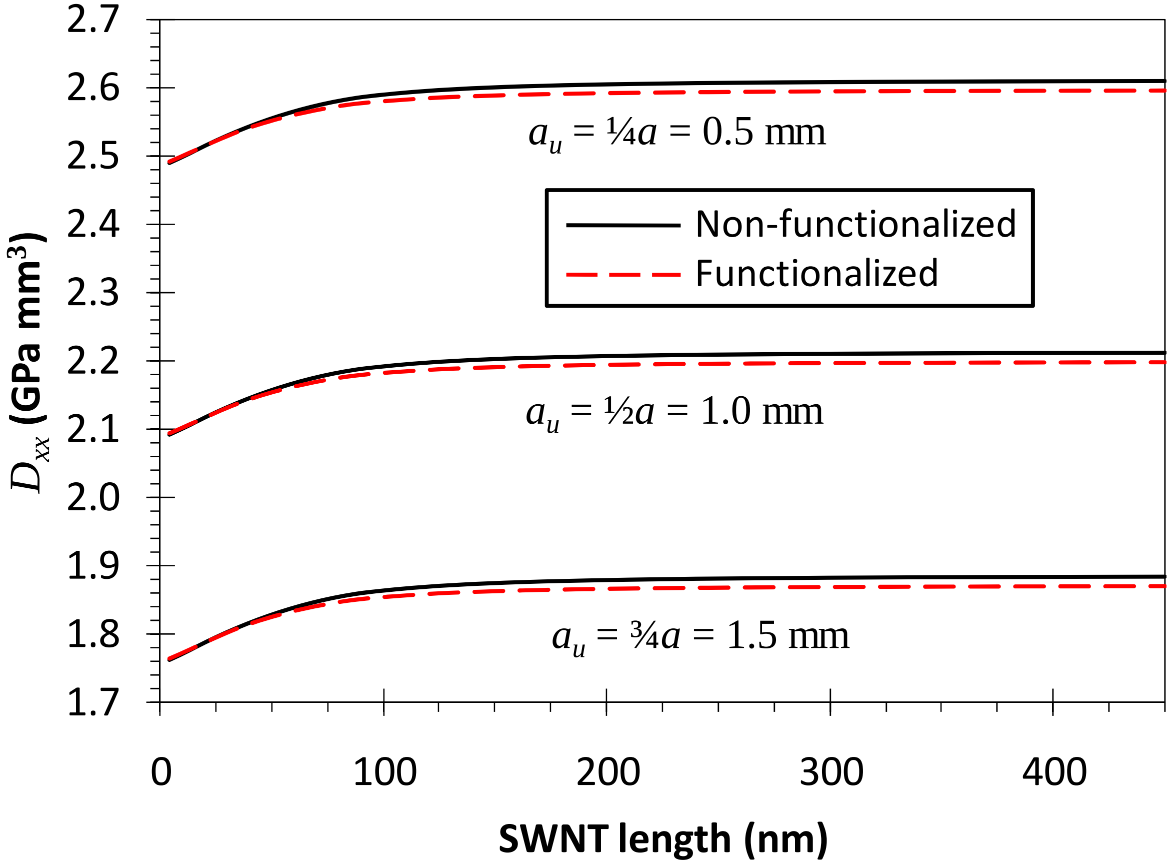

Figure 6 – Bending stiffness of a SWNT/graphite/epoxy plain weave composite as a function of nanotube length, yarn undulation length, and SWNT/epoxy bonding.

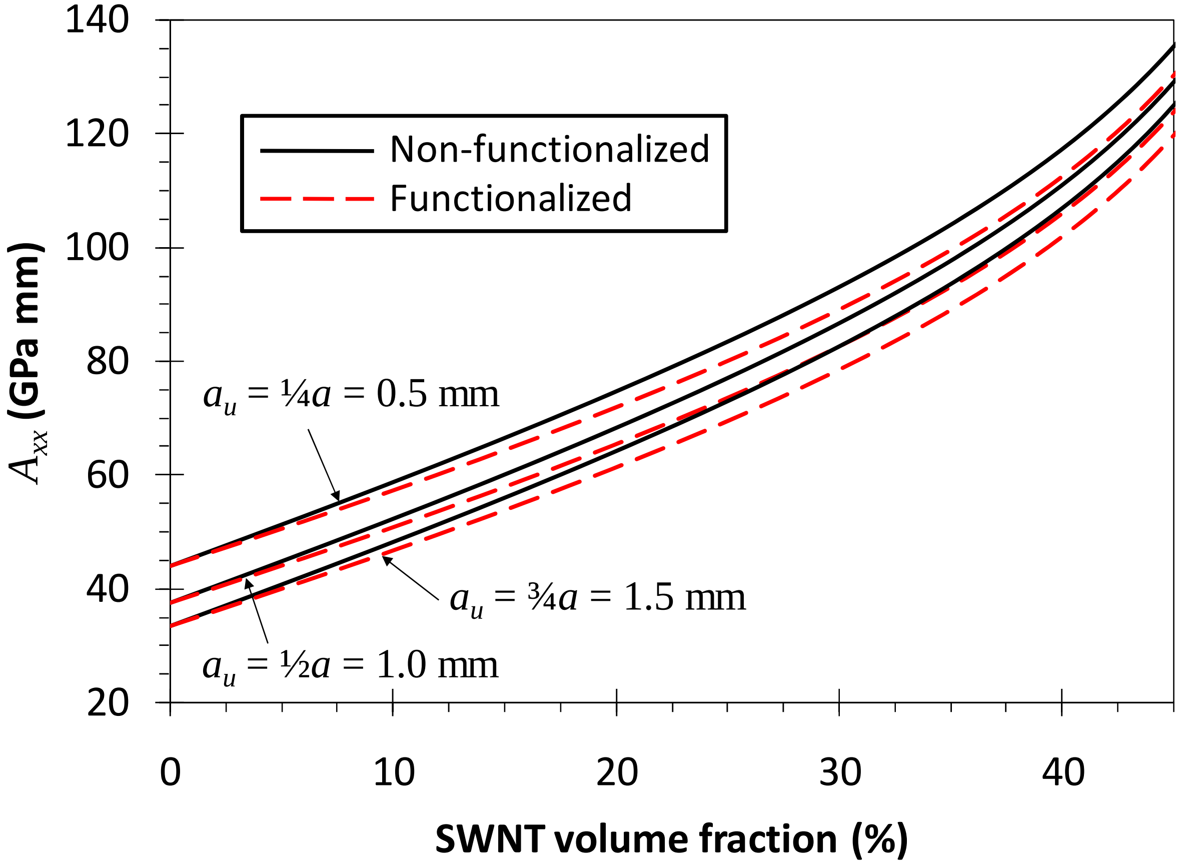

Figure 7 – Extensional stiffness of a SWNT/graphite/epoxy plain weave composite as a function of nanotube volume fraction, yarn undulation length, and SWNT/epoxy bonding.

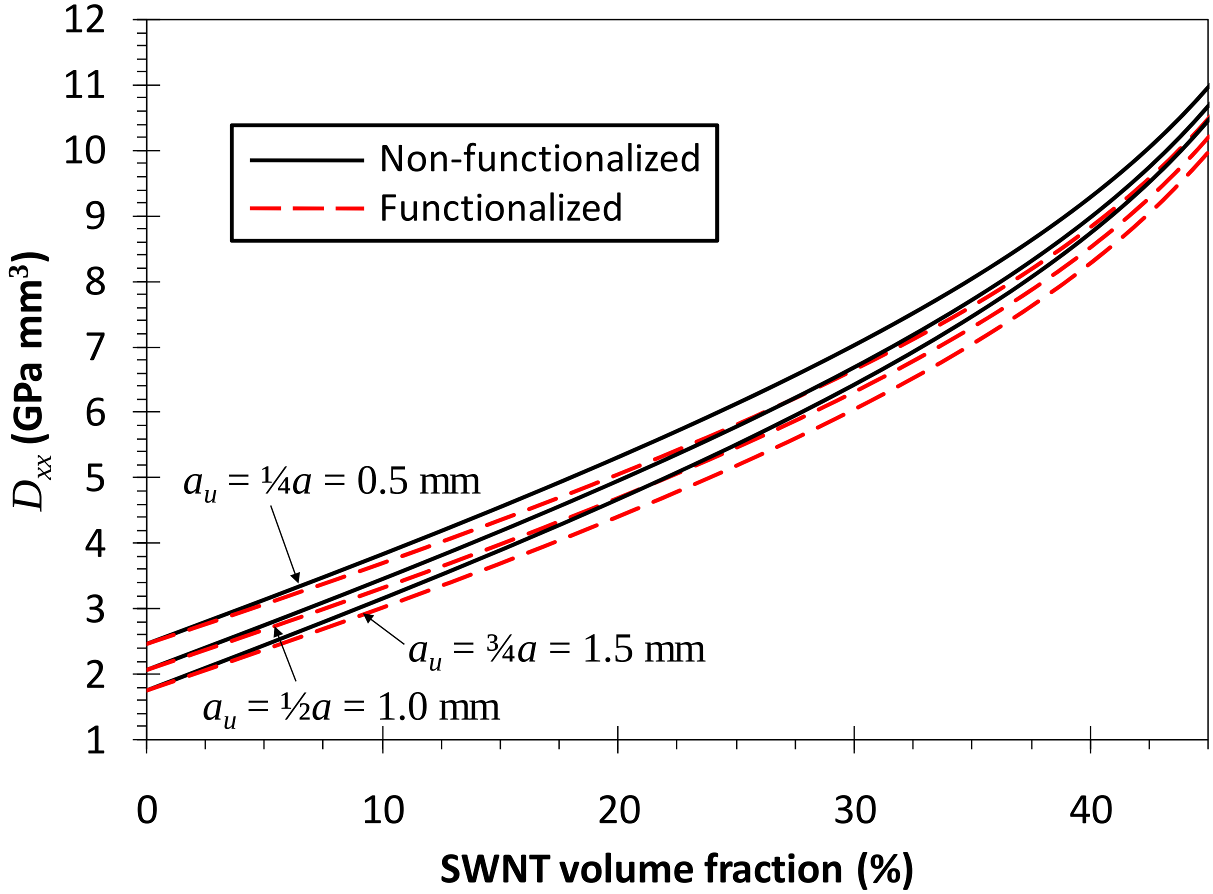

Figure 8 – Bending stiffness of a SWNT/graphite/epoxy plain weave composite as a function of nanotube volume fraction, yarn undulation length, and SWNT/epoxy bonding.