CONSTITUTIVE MODELING OF NANOTUBE/POLYMER COMPOSITES WITH VARIOUS NANOTUBE ORIENTATIONS

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ABSTRACT

In this study, a technique has been proposed for developing constitutive models for polymer composite systems reinforced with single-walled carbon nanotubes (SWNT) with various orientations with respect to the bulk-material coordinates. A nanotube, the local polymer adjacent to the nanotube, and the nanotube/polymer interface have been modeled as an equivalent-continuum fiber by using an equivalent-continuum modeling method. The equivalent-continuum fiber accounts for the local molecular structure and bonding information and serves as a means for incorporating micromechanical analyses for the prediction of bulk mechanical properties of SWNT/polymer composite. As an example, the proposed approach is used for the constitutive modeling of a SWNT/LaRC-SI (with a PmPV interface) composite system, with aligned nanotubes, three-dimensionally randomly oriented nanotubes, and nanotubes oriented with varying degrees of axisymmetry. It is shown that the Young's modulus is highly dependent on the SWNT orientation distribution.

INTRODUCTION

In the last few years, nano-structured, non-metallic materials have generated considerable interest in the materials community partly because of their potential for large gains in mechanical and physical properties with respect to traditional structural materials. In particular, SWNT-reinforced polymer composites may provide significant increases in strength and stiffness when compared to typical carbon-fiber-reinforced polymeric composites. In order to facilitate the development of nanotube-reinforced polymer composites, constitutive relationships must be developed to predict the bulk mechanical properties of the composite as a function of molecular structure of the polymer, the nanotube, and the polymer/nanotube interface.

In this paper, a technique for developing constitutive models for a nanotube/polymer composite with various nanotube orientations is developed that takes into account the discrete nature of the atomic interactions at the nanometer length scale and the interfacial characteristics of the nanotube and surrounding polymer matrix by using the equivalent-continuum modeling technique developed by Odegard *et al.* [1]. The equivalent-continuum model of a nanotube/polymer composite representative volume element (RVE) developed by Odegard *et al*. [2] is used in micromechanical analyses to determine the bulk constitutive properties of the SWNT/polymer composite with aligned nanotubes, three-dimensionally randomly oriented nanotubes, and nanotubes oriented with varying degrees of axisymmetry. A brief summary of the equivalent-continuum modeling method is followed by a detailed description of the micromechanics analysis and presentation of results.

EQUIVALENT-CONTINUUM MODELING

Recently, Odegard *et al.* [2] developed an equivalent-continuum model of the RVE (referred to as an effective fiber for the remainder of this paper) for a nanotube/polymer composite. The polymer matrix was composed of the thermoplastic polyimide LaRC-SI, which has a Young's modulus and Poison's ratio of 3.8 GPa and 0.4, respectively. At the nanotube/polymer interface is a layer of PmPV [poly(m-phenylenevinylene) substituted with octyloxy chains] that allows for improved nanotube/polymer molecule interaction through non-covalent bonded interactions. This improved interaction corresponds to improved load transfer at the nanotube/polymer interface, relative to that associated with traditional structural polymers [3].

The mechanical properties of the effective fiber, which consists of the nanotube, the nanotube/PmPV interface, and a layer of PmPV molecules, were determined by using three steps. First, a model of the molecular structure of the nanotube and adjacent polymer chains was established by using molecular dynamics (MD) simulations. It was assumed that the basic interactions of the atoms consisted of the bond stretching, bond-angle variation, and non-bonded interactions described in Fig. 1. Second, an equivalent-truss model was developed in which the mechanical properties of the truss elements were determined based on the force constants that represent the bonded and non-bonded interactions of the atoms in the molecular model. Finally, an effective-fiber model was developed that represented the equivalent-truss model. The properties of the transversely-isotropic, homogeneous, effective fiber were determined by equating the strain energies of the truss and the effective-fiber models for five sets of loading conditions.

MICROMECHANICS ANALYSIS

Constitutive models of the effective fiber/polymer composite may be developed with a micromechanical analysis by using the mechanical properties of the effective fiber and the bulk polymer matrix material. For the composite considered in this study, the PmPV molecules near the polymer/nanotube interface were included in the effective fiber, and it was assumed that the matrix polymer surrounding the effective fiber had mechanical properties equal to those of the bulk LaRC-SI resin. Because the bulk LaRC-SI polymer molecules and the polymer molecules included in the effective fiber are physically entangled, perfect bonding between the effective fiber and the surrounding polymer matrix was assumed.

The micromechanics-based Mori-Tanaka method [4] was used to predict the elastic mechanical properties of the composite material. This method has been applied to transversely-isotropic inclusions by Qui and Weng [5]. For this method, the complete elastic stiffness tensor for the composite is given by Benveniste [6]

$$\mathbf{C} = \mathbf{C}^m + c_f \left\langle \left(\mathbf{C}^f - \mathbf{C}^m\right)\mathbf{A}^f \right\rangle \left(c_m \mathbf{I} + c_f \left\langle \mathbf{A}^f \right\rangle\right)^{-1} \tag{1}$$

where c_f and c_m are the fiber and matrix volume fractions, respectively, $\mathbf{I}$ is the identity tensor, $\mathbf{C}^m$ is the stiffness tensor of the matrix material, $\mathbf{C}^f$ is the stiffness tensor of the fiber, and $\mathbf{A}^f$ is the dilute mechanical strain concentration tensor for the fiber

$$\mathbf{A}^f = \left[\mathbf{I} + \mathbf{S}\mathbf{C}^{m^{-1}}\left(\mathbf{C}^f - \mathbf{C}^m\right)\right]^{-1} \tag{2}$$

The tensor $\mathbf{S}$ is Eshelby's tensor as given by Eshelby [7] and Mura [8]. The terms enclosed with angle-brackets in Eq. (1) represent the average value of the term over all orientations defined by transformation from the local fiber coordinates (x_1, x_2, x_3) to the global coordinates (x_1''', x_2''', x_3''') (Figure 2). For example, the transformed dilute mechanical strain concentration tensor for the fiber with respect to the global coordinates is

$$\bar{\mathrm{A}}^f_{ijkl} = a_{ip} a_{jq} a_{kr} a_{ls} \mathrm{A}^f_{pqrs} \tag{3}$$

where a_{ij} are the direction cosines for the transformation indicated in Fig. 2; that is,

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$$

$$\begin{aligned} a_{11} &= \cos\phi\cos\psi - \sin\phi\cos\gamma\sin\psi \\ a_{12} &= \sin\phi\cos\psi + \cos\phi\cos\gamma\sin\psi \\ a_{13} &= \sin\psi\sin\gamma \\ a_{21} &= -\cos\phi\sin\psi - \sin\phi\cos\gamma\cos\psi \\ a_{22} &= -\sin\phi\sin\psi + \cos\phi\cos\gamma\cos\psi \\ a_{23} &= \sin\gamma\cos\psi \\ a_{31} &= \sin\phi\sin\gamma \\ a_{32} &= -\cos\phi\sin\gamma \\ a_{33} &= \cos\gamma \end{aligned} \tag{4}$$

In general, the orientation average of the dilute mechanical strain concentration tensor is [9]

$$\left\langle \mathbf{A}^f \right\rangle = \frac{\int_{-\pi}^{\pi}\int_{0}^{\pi}\int_{0}^{\pi/2} \bar{\mathrm{A}}^f(\phi,\gamma,\psi)\,\rho(\phi,\psi)\sin(\gamma)\,\mathrm{d}\phi\mathrm{d}\gamma\mathrm{d}\psi}{\int_{-\pi}^{\pi}\int_{0}^{\pi}\int_{0}^{\pi/2} \rho(\phi,\psi)\sin(\gamma)\,\mathrm{d}\phi\mathrm{d}\gamma\mathrm{d}\psi} \tag{5}$$

where $\rho(\phi,\psi)$ is the orientation distribution function

$$\rho(\phi,\psi) = \exp\left[-s_1\phi^2\right]\exp\left[-s_2\psi^2\right] \tag{6}$$

and where s_1 and s_2 are factors that control the orientation. Three cases considered in this paper are:

$$\begin{aligned} &\text{case 1}: s_1 = 0, s_2 = 0 && \rho(\phi,\psi) = 1 \\ &\text{case 2}: s_1 = \infty, s_2 = \infty && \rho(\phi,\psi) = \delta(\phi - 0)\delta(\psi - 0) \\ &\text{case 3}: s_1 = k, s_2 = \infty && \rho(\phi,\psi) = \exp\left[-k\phi^2\right]\delta(\psi - 0) \end{aligned} \tag{7}$$

where $\delta(x - \bar{x})$ is Dirac's delta distribution, centered at $\bar{x}$. Case 1 is a completely three dimensionally randomly oriented composite. Case 2 corresponds to fibers completely aligned along the x_1''' axis. Case 3 is an axisymmetric distribution of fibers about the x_1''' axis. The constant k describes the relative amount of alignment of the fibers with respect to the x_1''' axis. For large values of k ($k \rightarrow \infty$), the axisymmetric distribution approaches the aligned case, and for small values of k ($k \rightarrow 0$), the fibers are axisymmetrically distributed over all values of the angle □ with respect to the x_1''' axis.

For the effective fiber/polymer composite considered in this study, the elastic stiffness components, volume fraction, length, and orientation of the effective fiber were used for the fiber properties in Eqs. (1) and (2). The effective fibers were assumed to have an ellipsoidal geometry for the Eshelby tensor in Eq. (2). It was also assumed that the nanotube volume is a hollow cylinder with a wall thickness of 0.34 nm for the conversion of effective fiber volume fraction to nanotube volume fraction.

RESULTS

The moduli of the effective fiber/polymer composite were determined for the three fiber orientation cases for a nanotube length of 200 nm, a nanotube radius of 0.41 nm, and a 1% nanotube volume fraction. A plot of the longitudinal and transverse Young's moduli (E_L and E_T, respectively) of the composite for case 3 is shown in Fig. 3 as a function of *k*. The Young's modulus of the random composite (case 1) and the longitudinal and transverse Young's moduli of the aligned composite (case 2), which are independent of *k*, are also plotted in Fig. 3. For small values of *k*, the longitudinal and transverse modulus values of case 3 approach the modulus of the random composite. For large values of *k*, the longitudinal and transverse moduli of case 3 approach the values of longitudinal and transverse moduli of the aligned orientation, respectively. Therefore, this example demonstrates that the model yields expected results for the prediction of constitutive properties for the SWNT/polymer composite.

SUMMARY AND CONCLUDING REMARKS

In this study, a method has been presented for linking atomistic simulations of SWNT/polymer composite systems to continuum models of the bulk material. The utility of this method was examined by modeling a SWNT/LaRC-SI composite with a PmPV interface while considering nanotube orientation. The Young's moduli of the composite were determined for the cases of aligned nanotubes, three-dimensionally randomly oriented nanotubes, and nanotubes with an axisymmetric orientation. It has been shown that there are limiting values for each case and that by increasing and decreasing values of the orientation parameter, *k*, the moduli of the axisymmetric composite approach the moduli of the aligned and random composites, respectively. It is expected that this analysis will be important for the development of SWNT composites where the SWNT orientation distribution cannot be described as perfectly aligned or three-dimensionally randomly oriented.

REFERENCES

1. Odegard, G.M.; Gates, T.S.; Nicholson, L.M., and Wise, K.E.: Equivalent Continuum Modeling of Nano-Structured Materials. NASA/TM-2001-210863.

2. Odegard, G.M.; Gates, T.S., and Wise, K.: Constitutive Modeling of Nanotube-Reinforced Polymer Composites, AIAA 2002-1427. *43rd AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference*. Denver, CO; 2002.

3. Star, A.; Stoddart, J.F.; Steuerman, D.; Diehl, M.; Boukai, A.; Wong, E.W.; Yang, X.; Chung, S.; Choi, H., and Heath, J.R.: Preparation and Properties of Polymer-Wrapped Single-Walled Carbon Nanotubes. *Angewandte Chemie International Edition in English*. Vol. 40, No. 9, 2001, pp. 1721-1725.

4. Mori, T. and Tanaka, K.: Average Stress in Matrix and Average Elastic Energy of Materials with Misfitting Inclusions. *Acta Metallurgica*. Vol. 21, 1973, pp. 571-574.

5. Qui, Y.P. and Weng, G.J.: On the Application of Mori-Tanaka's Theory Involving Transversely Isotropic Spheroidal Inclusions. *International Journal of Engineering Science*. Vol. 28, No. 11, 1990, pp. 1121-1137.

6. Benveniste, Y.: A New Approach to the Application of Mori-Tanaka's Theory in Composite Materials. *Mechanics of Materials*. Vol. 6, 1987, pp. 147-157.

7. Eshelby, J.D.: The Determination of the Elastic Field of an Ellipsoidal Inclusion, and Related Problems. *Proceedings of the Royal Society of London, Series A*. Vol. A241, 1957, pp. 376-396.

8. Mura, T.: *Micromechanics of Defects in Solids*. The Hague: Martinus Nijhoff, 1982.

9. Marzari, N. and Ferrari, M.: Textural and Micromorphological Effects on the Overall Elastic Response of Macrocopically Anisotripic Composites. *Journal of Applied Mechanics*. Vol. 59, 1992, pp. 269-275.

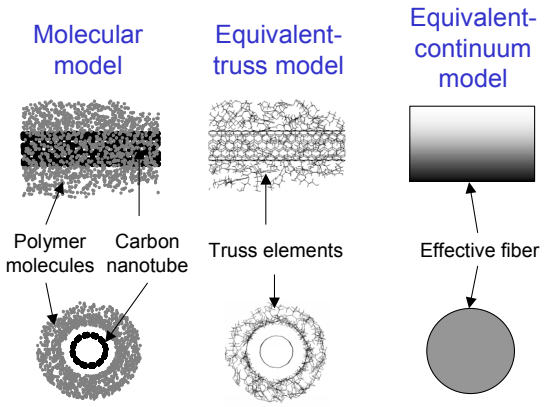

Fig. 1. Equivalent-continuum modeling

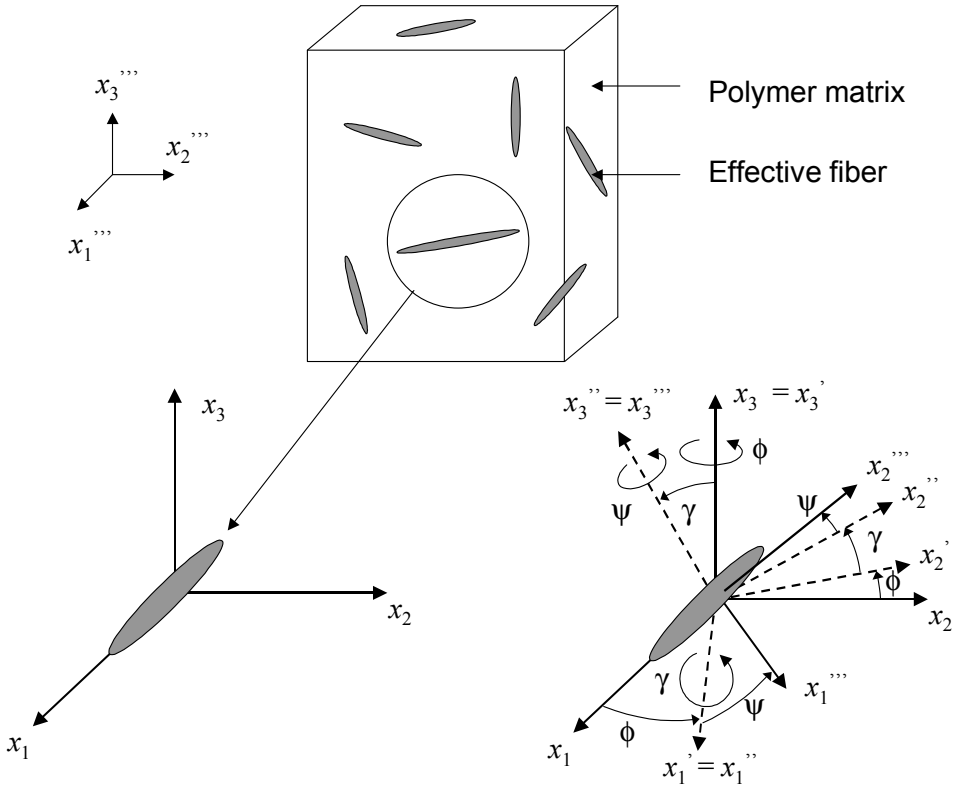

Fig. 2. Effective fiber orientation

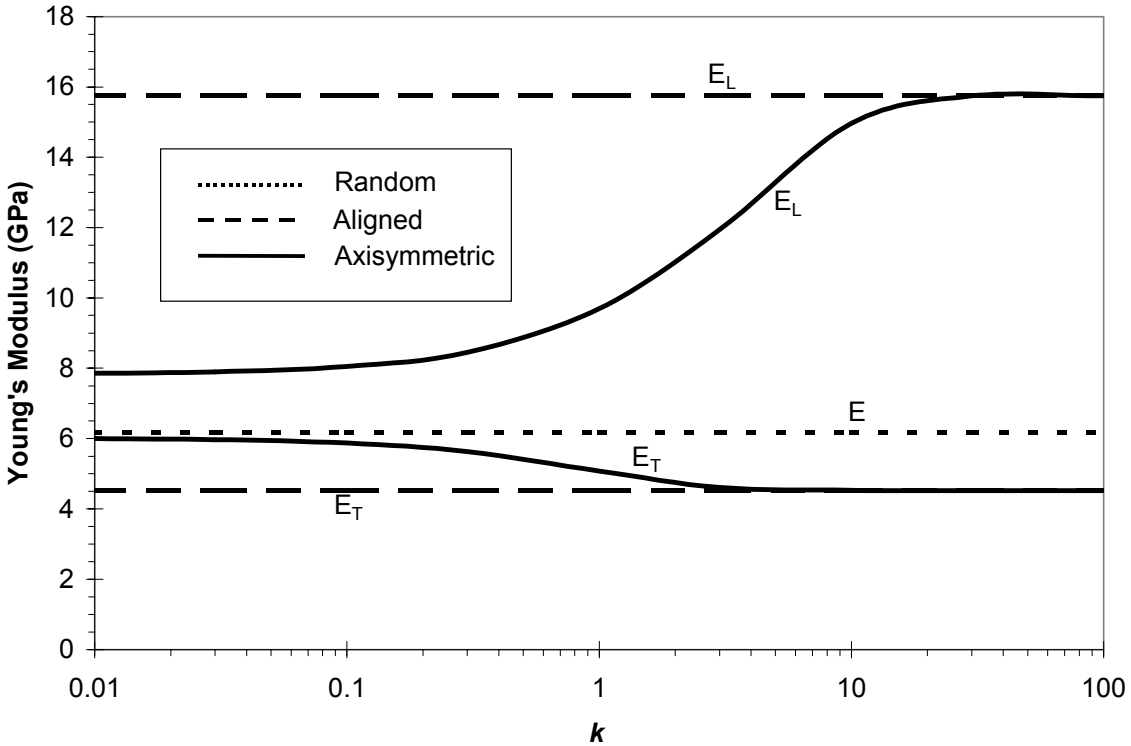

Fig. 3. Dependence of Young's modulus on the alignment constant *k*