

CHAPTER 5: CONCLUSIONS AND FUTURE WORK

Summary

Theoretical predictions of the mechanical properties of carbon nanotubes, and in particular their predicted high strengths (on the order of 60 GPa) and moduli (~1 TPa), make them attractive candidates as a reinforcement filler material in polymer-based structural composites. Recent experimental testing of individual nanotubes and nanotube bundles has verified these predictions. In addition, their outstanding electrical and thermal properties suggest that carbon nanotubes incorporated into polymers can significantly enhance these properties as well. The possibility of multifunctional composite materials with controllable electrical and thermal properties, in addition to order-of-magnitude enhancements in the mechanical behavior, has resulted in a tremendous amount of work dedicated to these material systems within the last few years.

Initial experimental work on carbon nanotube-reinforced polymers has demonstrated that large increases in effective moduli and strength can be attained with the addition of small amounts of carbon nanotubes. However, modeling the effective properties of a nanotube-reinforced polymer is made difficult because of complexities

related to: the structure and properties of the nanotubes, the orientation and dispersion of the nanotubes within the polymer, the characteristics of the interface and load transfer between the NTs and the polymer, and an understanding of the impact of the nanotubes on the molecular mobility of the polymer chains. Accurate models of how these issues influence the effective properties of the nanotube-reinforced polymer will be necessary in order to optimize the fabrication and effective properties of nanotube-polymer systems.

Modeling of NRP effective behavior is complicated by the range of length scales characteristic of these materials. It will be necessary for models developed at these different length scales, from atomistic simulations to continuum theories, to work in concert to accurately model the NRP mechanical response. Such an approach is demonstrated in this work, where we have sought to extend traditional micromechanics and viscoelastic models of composite and polymer behavior to account for nanoscale characteristics of these materials.

Two models have been developed in this dissertation as a means to incorporate nanoscale information into predictions of macroscale effective behavior. In Chapter 3, we discussed a hybrid finite element-micromechanics method that allows one to incorporate the waviness of the embedded nanotubes into micromechanics predictions of the effective elastic moduli using a multiphase composite approach. While this procedure was demonstrated using the Mori-Tanaka method, in general this type of

analysis can be used with any micromechanical approach. The results of this work show that nanotube waviness significantly reduces the NRP effective modulus compared to predictions obtained assuming straight nanotubes.

The effective viscoelastic response of nanotube-reinforced polycarbonate was discussed in Chapter 4. Our experimental data suggests that the viscoelastic response of the NRP is significantly different from that of the bulk polymer; for all tests this difference is consistent with the presence of regions of non-bulk polymer with restricted mobility within the material. We believe that this interphase region is a direct consequence of the size scale of the nanotubes and their nanoscale interactions with the polymer chains. A second micromechanical-based model was developed to describe the impact of a reduced mobility interphase on the effective viscoelastic response of the NRP. Our results suggest that accounting for this interphase region will be critical in developing accurate models of the viscoelastic response of the NRP. Additional experimental work in this area is ongoing.

Each of the models presented in this dissertation are viewed as preliminary descriptions of the NRP effective behavior, and can be extended with the addition of nanoscale information to complement the continuum approaches used here. For example, atomistic simulations of the interface between the nanotube and the polymer and/or the mobility of polymer chains in the direct vicinity of the nanotubes will provide additional details of the nanoscale response that will influence the NRP

mechanical behavior. Experimental work at both the nano- and micro-scale will provide additional insight into the effective behavior of these systems.

One of the inherent difficulties with modeling carbon nanotube-reinforced polymers is the large number of parameters that are expected to impact the effective response of the NRP, but are currently not well understood. As discussed in Chapter 2, these issues include the dispersion and orientation of the nanotubes within the polymer, as well as an understanding of the interfacial characteristics and load transfer capabilities of a particular NT-polymer system. The work in this dissertation highlights embedded nanotube waviness and the existence/properties/extent of an interphase region surrounding the NT as two additional parameters that must also be considered. Given the complexity of modeling these systems, it would be desirable to develop experimental techniques capable of isolating a subset of these parameters for in-depth study. Such a model NRP has been proposed (Ruoff 2001) and is based on an ordered array of carbon nanotubes, which when infiltrated with a suitable polymer will yield a nanotube-reinforced polymer with highly uniform and controllable NT diameter, spacing, and alignment. This system will greatly facilitate the interpretation of experimental results, and we believe will lead to breakthroughs in our understanding of NRP behavior. This proposed avenue of future research is discussed below.

Aligned Carbon Nanotube Array Composites

The development of aligned carbon nanotube array (polymer) composites will greatly facilitate experimental and theoretical work in this area. The fabrication of such systems will involve four steps:

- 1) the fabrication of porous anodic alumina (PAA) to create a well-ordered, uniform template with precise control over the pore geometries,
- 2) synthesis of carbon nanotubes via pyrolysis of hydrocarbon gases within the pores of the PAA template,
- 3) etching of the alumina substrate to partially expose one end of the nanotubes, and
- 4) infiltration of polymer as a matrix material.

This work will be a collaboration with the Ruoff group at Northwestern, and significant progress has already been demonstrated for Steps 1 and 2 above (Xu 2002b). For completeness, the steps of the fabrication process will be outlined below; further details of the procedure are described elsewhere (Xu 2002b).

As shown in Figure 72, the formation of PAA is achieved through a two-step anodization process, which has been shown to leave a well-ordered pore geometry

with controllable dimensions (Masuda, Yamada et al. 1997). The geometry of the porous structure is controlled by various parameters in the fabrication process, including the electrolyte used (pore diameter D as shown in Figure 73), the anodization voltage (interpore spacing d), the anodization time (film thickness t), and the reaction temperature. Pore diameters between 30-230 nm, interpore spacing between 200-460 nm, and film thickness on the order of hundreds of μm have been reported (Kyotani, Tsai et al. 1996; Li, Muller et al. 2000). It is anticipated that the lateral film dimensions (represented by w in Figure 73) could be 1 cm or larger (Xu 2002a).

Once a suitable template has been developed, carbon nanotubes can be grown within the pores via pyrolysis of hydrocarbon gases. Similar methods have previously been used to grow carbon nanotubes and are discussed in the literature (Kyotani, Tsai et al. 1996; Che, Lakshmi et al. 1998; Li, Papadopoulos et al. 1999). This deposition procedure has been shown to produce carbon nanotubes that closely match the geometry of the underlying template, such that well-ordered arrays of nanotubes with excellent alignment and spacing can be produced. An example of such an array is shown in Figure 74.

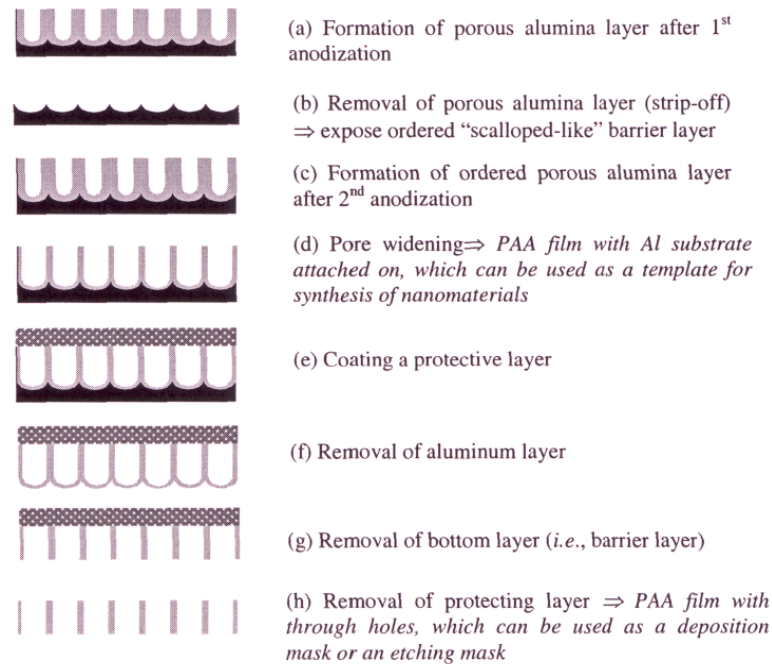


Figure 72. Schematic of the porous anodic alumina (PAA) fabrication method (Xu 2002b).

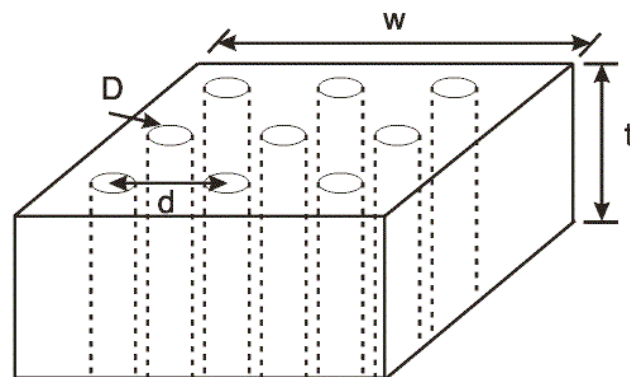


Figure 73. Schematic illustration of the geometry of the PAA films.

Once carbon nanotubes have been deposited in the pores of the PAA template, etching procedures can be developed to dissolve the alumina and leave free standing nanotubes (Kyotani, Tsai et al. 1996). Here, however, we wish to partially etch only one side of the alumina template, leaving a “paint-brush” geometry where the NTs are embedded within the alumina template at one and exposed at the other end. We believe that given such a structure, we can fill the empty space surrounding the exposed ends of the nanotubes with a polymer, in effecting creating a nanotube-reinforced polymer with uniform, well-ordered, and aligned nanotubes.

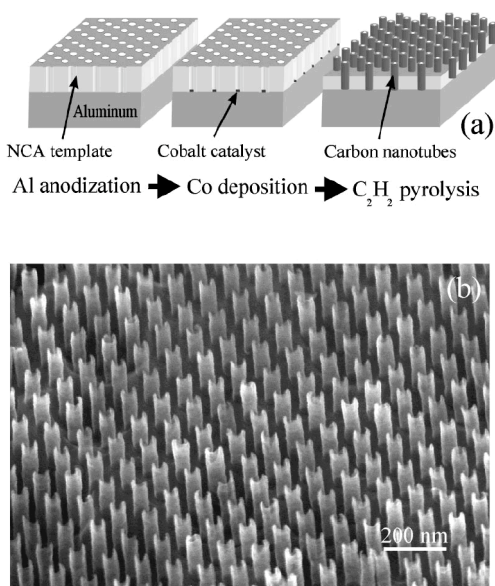


Figure 74. Fabrication of ordered carbon nanotube arrays. (Li, Papadopoulos et al. 1999).

The advantage of the proposed nanotube-polymer system is that it eliminates, or allows one to control, several composite parameters that are expected to influence the effective behavior of these systems. This will allow experiments to be devised to specifically isolate particular parameters for study. For example, experimental testing and modeling of the proposed ordered carbon nanotube array composites would have the following advantages:

1. The regular, aligned structure will simplify the modeling of the effective properties.
2. Control over the carbon deposition procedure will provide consistent NT properties and uniform NT geometry.
3. The geometry of the NTs will eliminate several NRP fabrication parameters, including:
 - a. orientation of the nanotubes,
 - b. dispersion of the nanotubes, and
 - c. heterogeneity of the sample.
4. The sample configuration will facilitate experiments that isolate NT- and matrix-dominated properties (see Figure 75). In particular, transverse (to the long axis of the nanotubes) tension and shear tests will be more sensitive to changes in the mechanical behavior of the interphase.

5. The geometry of the NTs will facilitate nanoscale experimentation, particularly NT pullout tests which can be done to evaluate the interfacial behavior of the material (see Figure 75).
6. Control of the interpore spacing and NT diameters will allow one to vary both the nanotube and interphase volume fractions.

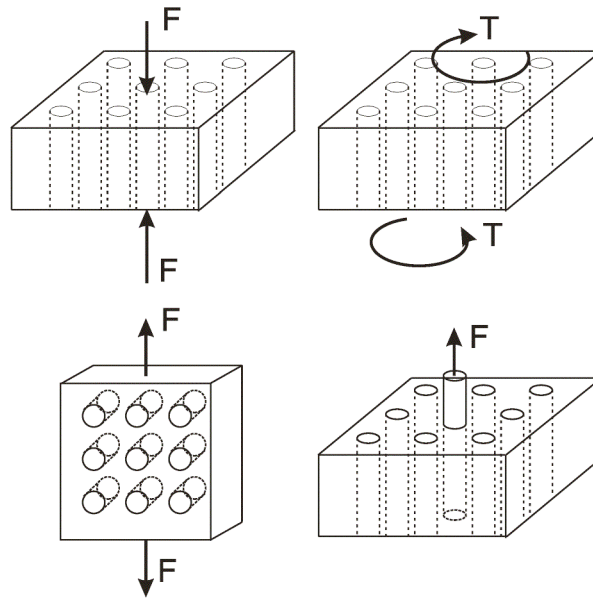


Figure 75. Proposed experiments on the aligned carbon nanotube array composites.

The simplifications brought about by the proposed model geometry, in conjunction with appropriately designed experiments, will lead to additional insight into the mechanical behavior of nanotube-reinforced polymers. The properties

achievable with such a composite may also be competitive from the prospective of practical applications.

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APPENDIX

Summary of the nanotube-reinforced polymer literature

**Key: AD = arc discharge, LV = laser vaporization,
CVD = chemical vapor deposition, NA = not applicable**

Paper	Polymer	NT	Notes
(Ajayan, Stephan et al. 1994)	Epoxy	AD MWNTs	Shear-induced alignment of NTs
(Ajayan, Schadler et al. 2000)	Epoxy	SWNT bundles	Curving and stretching of the NTs on loading; at fracture see pulling apart of the bundles, not NT fracture
(Andrews, Jacques et al. 2002)	Polystyrene	MWNTs (0-25% wt)	Significant increases in effective elastic modulus
(Bower, Rosen et al. 1999)	Thermoplastic (polyhydroxy-aminoether)	MWNTs	Alignment via mechanical stretching above T_g
(Bradshaw, Fisher et al. 2002)	NA	NA	Numerical computation of the dilute strain concentration tensor to account for NT waviness
(Chen, Shaffer et al. 2000)	Polypyrrole (PPy)	AD NTs	Mainly interested in electrical properties; some impedance spectroscopy data
(Cochet, Maser et al. 2001)	Conducting polymer polyaniline (PANI)	AD SWNTs (10, 20, 30, 40, 50% wt)	"In-situ" polymerization; Raman measurements suggest effective site-selective interactions between the PANI and the MWNTs facilitating charge-transfer processes

(Cooper, Young et al. 2001)	Epoxy (Araldite LY5052)	LV SWNTs; AD SWNTs, MWNTs (1% wt)	Looked at differences in the Raman responses of the NTs; interested in the use of NTs as strain sensors
(Curran, Ajayan et al. 1998)	PmPV	AD MWNTs	Polymer chains "wrap" helically about the NTs; TEM evidence of good adhesion
(Fan, Wan et al. 1999)	Polypyrrole (PPY)	CVD NTs	The CNTs function as a template for PPY polymerization.
(Fisher, Bradshaw et al. 2002a)	NA	NA	Model to incorporate nanotube waviness into micromechanical predictions of NRP effective modulus.
(Fisher, Bradshaw et al. 2002b)	NA	NA	Micromechanics predictions of NRP effective stiffness are much greater than experimental results
(Gong, Liu et al. 2000)	Epoxy	AD MWNTs	Shift in T_g attributed to the role of the surfactant.
(Grimes, Mungle et al. 2000)	PEMA	AD SWNT bundles (0-23% wt)	Effective electrical properties
(Hadjiev, Iliev et al. 2001)	Epoxy (Epon 862/EPI-CURE W)	LV SWNTs (1% wt)	Raman data suggests direct coupling of NT to epoxy; load is transferred predominantly along the nanorope axis
(Haggenmueller, Gommans et al. 2000)	PMMA	SWNTs	Alignment via combination of solvent casting and melt processing of the NRP.
(Jia, Wang et al. 1999)	PMMA	NTs	CNTs participate in PMMA polymerization; effective properties decrease for greater than 7 wt% NTs due to residual stresses in the matrix
(Jin, Bower et al. 1998)	PHAE (thermoplastic)	AD MWNTs	NT alignment via mechanical stretching above T_g ; loading to 500% strain without fracture

(Jin, Sun et al. 2000)	PEG, P2VP, P4VP, PVPh; PEO	AD MWNTs	Interested in nonlinear optical effects; create "polymer-coated" and "polymer-grafted" MWNTs
(Jin, Pramoda et al. 2001)	PMMA using a melt-blending process	AD MWNTs	Large increases in storage modulus at high temperature; suggest increases are due to the amorphous nature of the polymer matrix
(Liao and Li 2001)	Polystyrene	NTs	Molecular mechanics model of the interface; estimated the interfacial shear stress to be 160 MPa
(Lordi and Yao 2000)	PmPV, PMMA, PPA	(10,10) SWNTs	MD work suggesting that the helical nature of PmPV allows it to closely interact with the NTs.
(Lourie, Cox et al. 1998)	Epoxy (Araldite LY564, Ciba-Geigy)	AD MWNTs	Interested in the buckling and collapse of NTs in microtomed TEM samples
(Lourie and Wagner 1998a)	Epoxy	SWNT; AD MWNTs; carbon fiber	Raman analysis of the compressive stresses caused by polymer shrinkage upon cure
(Lourie and Wagner 1998b)	Epoxy	SWNT bundles	Aligned SWNT bundles bridging cracks/holes in the polymer
(Lourie and Wagner 1999)	Epoxy (Araldite LY564, Ciba-Geigy)	AD MWNTs	Formation of damage doublets in adjacent CNTs, comparable to those in fiber reinforced composites; due to redistribution of stress from a failed fiber to its unfailed neighbors
(Lozano and Barrera 2001)	Polypropylene	Pyrograf nanofibers, 100 nm ave. diameter	Nanofibers raised working temperature 100 °C and dynamic modulus increased 350%, but no change in strength
(McCarthy, Coleman et al. 2000)	ImPV, a PPV derivative	AD and CVD NTs	Crystalline polymer nucleates from NT defects; show that the polymer coats the NT as a periodic, ordered structure.
(Odegard, Gates et al. 2001a)	LaRC-SI polyimide with PmPV interface	SWNTs	Equivalent continuum model of NT and interphase as an effective fiber for micromechanics predictions

(Qian, Dickey et al. 2000)	Polystyrene (PS)	MWNTs (1% wt)	~ 35% increase in modulus and ~ 25% in ultimate stress
(Sandler, Shaffer et al. 1999)	Epoxy	CVD MWNTs	Antistatic applications; large increases in electrical conductivity for low volume fractions of NTs
(Schadler, Giannaris et al. 1998)	Epoxy (Shell Epon 828)	MWNTs (5% wt)	Results suggest that only the outer layer of the MWNT is loaded in tension, whereas all tubes loaded in compression
(Shaffer and Windle 1999)	Poly(vinyl alcohol) (PVOH)	CVD MWNTs (0-60 wt%)	Minimal enhancement below T_g , significant increase in mechanical properties above T_g
(Stéphan, Nguyen et al. 2000)	PMMA (spin-coating)	AD SWNTs	Polymer intercalation between NTs within a bundle
(Tang and Xu 1999)	poly(phenylacetylene) (PPA)	MWNTs	NTs helically wrapped by the PPA chains; NTs protect PPA from photodegradation under harsh laser irradiation.
(Wagner, Lourie et al. 1998)	Urethane/diacrylate oligomer (EBERCRYL 4858)	AD MWNTs	MWNT-polymer stress transfer efficiency estimated to be an order of magnitude larger than in conventional fiber-based composites
(Wood, Zhao et al. 2000)	Urethane/diacrylate oligomer (EBERCRYL 4858)	SWNTs (0.1% wt)	Use of NTs as sensitive nanoscale strain gauges, where 0.1 wt% NT causes the polymer to become Raman active
(Wood, Zhao et al. 2001)	Urethane/diacrylate oligomer (EBERCRYL 4858)	SWNTs (flow orientated)	Difference between mechanical and spectroscopic data at high strain caused by the interface yielding in shear, halting stress transfer to the NTs
(Zhao, Wood et al. 2001)	Urethane/diacrylate oligomer (EBERCRYL 4858)	SWNTs (0.1% wt)	Interested in the use of NTs as strain sensors

Tensor representation using contracted notation

For a linear elastic material, the state of stress at a point can be represented by stress components σ_{ij} , which are related to strain components ϵ_{ij} via

$$\sigma_{ij} = C_{ijkl} \epsilon_{kl}, \quad (74)$$

$$\epsilon_{ij} = S_{ijkl} \sigma_{kl} \quad (75)$$

where $(i, j, k, l = 1, 2, 3)$ and C_{ijkl} and S_{ijkl} are referred to as the stiffness and compliance tensors, respectively. Repeated indices imply summation over those indices.

It is standard practice in the micromechanics and composites community to utilize contracted (alternatively called Voigt or two-index) notation in order to simplify notation. In general such notation involves the following replacement scheme to simplify tensor indices

$$\begin{aligned} 11 &\rightarrow 1, & 22 &\rightarrow 2, & 33 &\rightarrow 3 \\ 23 &\rightarrow 4, & 31 &\rightarrow 5, & 12 &\rightarrow 6 \end{aligned} \quad (76)$$

Using this replacement scheme, the components of the stress, strain, and stiffness tensors can be written as

$$\begin{aligned}
\sigma_{11} &= \sigma_1, & \sigma_{22} &= \sigma_2, & \sigma_{33} &= \sigma_3, \\
\sigma_{23} &= \sigma_{32} = \sigma_4 = \sigma_4, & & & & \\
\sigma_{13} &= \sigma_{31} = \sigma_5 = \sigma_5, & & & & \\
\sigma_{12} &= \sigma_{21} = \sigma_6 = \sigma_6. & & & &
\end{aligned} \tag{77}$$

$$\begin{aligned}
\sigma_{11} &= \sigma_1, & \sigma_{22} &= \sigma_2, & \sigma_{33} &= \sigma_3, \\
2\sigma_{23} &= \sigma_{23} = \sigma_4 = \sigma_4, & & & & \\
2\sigma_{13} &= \sigma_{13} = \sigma_5 = \sigma_5, & & & & \\
2\sigma_{12} &= \sigma_{12} = \sigma_6 = \sigma_6. & & & &
\end{aligned} \tag{78}$$

$$\begin{aligned}
C_{1111} &= C_{11}, & C_{1122} &= C_{12}, & C_{1133} &= C_{13}, & C_{1123} &= 2C_{14}, & C_{1131} &= 2C_{15}, & C_{1112} &= 2C_{16}, \\
C_{2211} &= C_{21}, & C_{2222} &= C_{22}, & C_{2233} &= C_{23}, & C_{2223} &= 2C_{24}, & C_{2231} &= 2C_{25}, & C_{2212} &= 2C_{26}, \\
C_{3311} &= C_{31}, & C_{3322} &= C_{32}, & C_{3333} &= C_{33}, & C_{3323} &= 2C_{34}, & C_{3331} &= 2C_{35}, & C_{3312} &= 2C_{36}, \\
C_{2311} &= C_{41}, & C_{2322} &= C_{42}, & C_{2333} &= C_{43}, & C_{2323} &= 2C_{44}, & C_{2331} &= 2C_{45}, & C_{2312} &= 2C_{46}, \\
C_{3111} &= C_{51}, & C_{3122} &= C_{52}, & C_{3133} &= C_{53}, & C_{3123} &= 2C_{54}, & C_{3131} &= 2C_{55}, & C_{3112} &= 2C_{56}, \\
C_{1211} &= C_{61}, & C_{1222} &= C_{62}, & C_{1233} &= C_{63}, & C_{1223} &= 2C_{64}, & C_{1231} &= 2C_{65}, & C_{1212} &= 2C_{66}.
\end{aligned} \tag{79}$$

Such substitution permits the constitutive equations describing the stress-strain response of the material to be written in contracted notation as

$$\sigma_i = C_{ij} \epsilon_j, \quad \epsilon_i = S_{ij} \sigma_j, \tag{80}$$

where $(i,j = 1,2,..6)$ and due to energy considerations, $C_{ij} = C_{ji}$ and $S_{ij} = S_{ji}$.

In general there are 36 independent constants C_{ij} (and likewise S_{ij}) necessary to describe the stress-strain response of an elastic material. However, for special classes of materials the number of elastic constants is reduced due to special symmetry

conditions. Two common cases of material symmetry that are used throughout this work are transversely isotropic and isotropic symmetry. For a material that is transversely isotropic with a 2-3 plane of isotropy, the contracted stiffness tensor is of the following form

$$\begin{matrix}
 \begin{matrix} \square \\ \square \\ \square \\ \square \\ \square \\ \square \end{matrix} & \begin{matrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{matrix} & \begin{matrix} \square \\ \square \\ \square \\ \square \\ \square \\ \square \end{matrix} & \begin{matrix} C_{11} \\ C_{12} \\ C_{12} \\ 0 \\ 0 \\ 0 \end{matrix} & \begin{matrix} C_{12} \\ C_{22} \\ C_{23} \\ 0 \\ 0 \\ 0 \end{matrix} & \begin{matrix} C_{12} \\ C_{23} \\ C_{22} \\ 0 \\ 0 \\ 0 \end{matrix} & \begin{matrix} 0 \\ 0 \\ 0 \\ \frac{C_{22} - C_{23}}{2} \\ 0 \\ 0 \end{matrix} & \begin{matrix} 0 \\ 0 \\ 0 \\ 0 \\ C_{55} \\ 0 \end{matrix} & \begin{matrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ C_{55} \end{matrix} & \begin{matrix} \square \\ \square \\ \square \\ \square \\ \square \\ \square \end{matrix} & \begin{matrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{matrix} & \begin{matrix} \square \\ \square \\ \square \\ \square \\ \square \\ \square \end{matrix}
 \end{matrix} \tag{81}$$

For an isotropic material the constitutive equation is further simplified such that

$$\begin{matrix}
 \begin{matrix} \square \\ \square \\ \square \\ \square \\ \square \\ \square \end{matrix} & \begin{matrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{matrix} & \begin{matrix} \square \\ \square \\ \square \\ \square \\ \square \\ \square \end{matrix} & \begin{matrix} C_{11} \\ C_{12} \\ C_{12} \\ 0 \\ 0 \\ 0 \end{matrix} & \begin{matrix} C_{12} \\ C_{11} \\ C_{12} \\ 0 \\ 0 \\ 0 \end{matrix} & \begin{matrix} C_{12} \\ C_{12} \\ C_{11} \\ 0 \\ 0 \\ 0 \end{matrix} & \begin{matrix} 0 \\ 0 \\ 0 \\ \frac{C_{11} - C_{12}}{2} \\ 0 \\ 0 \end{matrix} & \begin{matrix} 0 \\ 0 \\ 0 \\ 0 \\ \frac{C_{11} - C_{12}}{2} \\ 0 \end{matrix} & \begin{matrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ \frac{C_{11} - C_{12}}{2} \end{matrix} & \begin{matrix} \square \\ \square \\ \square \\ \square \\ \square \\ \square \end{matrix} & \begin{matrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{matrix} & \begin{matrix} \square \\ \square \\ \square \\ \square \\ \square \\ \square \end{matrix}
 \end{matrix} \tag{82}$$

While contracted notation can be a useful tool in that it significantly simplifies the bookkeeping required for the tensor manipulation, care must be taken to ensure that the tensor contraction is maintained in a consistent manner throughout the

analysis. For example, for the contraction of the Eshelby tensor it is necessary to include a factor of two for the shear strain components to maintain the appropriate tensorial relationship (as demonstrated later in this Appendix). Consistent use of tensorial shear strain ϵ_{ij} and engineering shear strain γ_{ij} (where $\gamma_{ij} = \frac{1}{2}\epsilon_{ij}$) throughout the analysis is critical.

Components of the Eshelby S_{ijkl} tensor along the x_3 axis

For an ellipsoidal inclusion aligned along the 3-axis with aspect ratio $\alpha = \frac{L}{d}$, the components of the Eshelby tensor are given as (Tandon and Weng 1986)

$$\begin{aligned}
S_{1111} = S_{2222} &= \frac{3}{8(1-\nu_0)} \frac{\nu^2}{\nu^2-1} + \frac{1}{4(1-\nu_0)} \frac{\nu}{\nu^2-1} \frac{9}{4(\nu^2-1)} g \\
S_{3333} &= \frac{1}{2(1-\nu_0)} \frac{\nu}{\nu^2-1} + \frac{3\nu^2-1}{\nu^2-1} \frac{\nu}{\nu^2-1} + \frac{3\nu^2}{\nu^2-1} \frac{g}{\nu^2-1} \\
S_{1122} = S_{2211} &= \frac{1}{4(1-\nu_0)} \frac{\nu^2}{2(\nu^2-1)} + \frac{\nu}{\nu^2-1} \frac{\nu}{\nu^2-1} + \frac{3}{4(\nu^2-1)} \frac{g}{\nu^2-1} \\
S_{1133} = S_{2233} &= \frac{1}{2(1-\nu_0)} \frac{\nu^2}{\nu^2-1} + \frac{1}{4(1-\nu_0)} \frac{3\nu^2}{\nu^2-1} \frac{g}{\nu^2-1} \quad (83) \\
S_{3311} = S_{3322} &= \frac{1}{2(1-\nu_0)} \frac{\nu}{\nu^2-1} + \frac{1}{\nu^2-1} + \frac{1}{2(1-\nu_0)} \frac{\nu}{\nu^2-1} + \frac{3}{2(\nu^2-1)} \frac{g}{\nu^2-1} \\
S_{1212} = S_{2121} &= \frac{1}{4(1-\nu_0)} \frac{\nu^2}{2(\nu^2-1)} \frac{\nu}{\nu^2-1} + \frac{3}{4(\nu^2-1)} \frac{g}{\nu^2-1} \\
S_{3131} = S_{3232} &= \frac{1}{4(1-\nu_0)} \frac{\nu}{\nu^2-1} \frac{\nu^2+1}{\nu^2-1} + \frac{1}{2} \frac{\nu}{\nu^2-1} \frac{3(\nu^2+1)}{\nu^2-1} \frac{g}{\nu^2-1}
\end{aligned}$$

where ν_0 is the Poisson ratio of the matrix, and

$$\begin{aligned}
g &= \frac{\nu}{(\nu^2-1)^{3/2}} \frac{\nu}{\nu^2-1} (\nu^2-1)^{1/2} \cosh^{-1} \frac{\nu}{\nu^2-1} \\
&= \frac{\nu}{(1-\nu^2)^{3/2}} \frac{\nu}{\nu^2-1} \cos^{-1} \frac{\nu}{\nu^2-1} (1-\nu^2)^{1/2}
\end{aligned} \quad (84)$$

for prolate and oblate shapes inclusion cross-sections, respectively. All other components of the Eshelby tensor are zero.

For an ellipsoidal inclusion with an infinite aspect ratio ($l/d \rightarrow \infty$) parallel to the 3-axis, the components of the Eshelby tensor simplify to:

$$\begin{aligned}
 S_{3333} &= S_{3311} = S_{3322} = 0 \\
 S_{1111} &= S_{2222} = \frac{5\nu_0^4\nu_0}{8(1-\nu_0)} \\
 S_{1122} &= S_{2211} = \frac{4\nu_0\nu_0}{8(1-\nu_0)} \\
 S_{1133} &= S_{2233} = \frac{\nu_0}{2(1-\nu_0)}
 \end{aligned} \tag{85}$$

$$S_{1212} = \frac{3\nu_0^4\nu_0}{8(1-\nu_0)}$$

$$S_{3131} = S_{3232} = \frac{1}{4}.$$

For spheroidal inclusions the Eshelby components further simplify to:

$$\begin{aligned}
 S_{1111} &= S_{2222} = S_{3333} = \frac{7\nu_0^5\nu_0}{15(1-\nu_0)} \\
 S_{1122} &= S_{2233} = S_{3311} = \frac{5\nu_0\nu_0}{15(1-\nu_0)} \\
 S_{1212} &= S_{2323} = S_{3131} = \frac{4\nu_0^5\nu_0}{15(1-\nu_0)}.
 \end{aligned} \tag{86}$$

The different Eshelby components presented above are those of a fourth-order tensor that by definition relate the (stress-free) transformation strain to the perturbed strain in an inclusion via

$$\epsilon_{ij}^{pt} = S_{ijkl} \epsilon_{kl}^*, \quad (87)$$

where the perturbed strain ϵ_{ij}^{pt} represents the difference between the far-field applied strain ϵ_{ij}^0 and the average strain in the inclusion ϵ_{ij}^r via $\epsilon_{ij}^{pt} = \epsilon_{ij}^r - \epsilon_{ij}^0$.

It is customary in micromechanics, and the composites field in general, to take advantage of contracted (or two-index) notation to simplify the bookkeeping of the tensor indices. However, specific care must be taken when contracting the Eshelby tensor for such analyzes. The difficulty arises in contracting those terms of the Eshelby tensor relating the shear components of the perturbed and transformation strains, and is best described via an example. Writing out (87) for the case of ϵ_{23}^{pt} ,

$$\begin{aligned} \epsilon_{23}^{pt} = & S_{2311} \epsilon_{11}^* + S_{2312} \epsilon_{12}^* + S_{2313} \epsilon_{13}^* \\ & + S_{2321} \epsilon_{21}^* + S_{2322} \epsilon_{22}^* + S_{2323} \epsilon_{23}^*, \\ & + S_{2331} \epsilon_{31}^* + S_{2332} \epsilon_{32}^* + S_{2333} \epsilon_{33}^* \end{aligned} \quad (88)$$

which for a general ellipsoidal inclusion simplifies to the following non-zero components of the Eshelby tensor

$$\square_{23}^{\text{pt}} = S_{2323}\square_{23}^* + S_{2332}\square_{32}^* = 2S_{2323}\square_{23}^*, \quad (89)$$

where $\square_{23}^* = \square_{32}^*$ and $S_{2323} = S_{2332}$. This can be represented using contracted notation as

$$\square_4^{\text{pt}} = S_{44}\square_4^*. \quad (90)$$

where $S_{44}=2S_{2323}$. Thus the complete representation of the Eshelby tensor in contracted notation is:

$$\begin{aligned} S_{11} &= S_{1111}, & S_{22} &= S_{2222}, & S_{33} &= S_{3333}, \\ S_{12} &= S_{1122}, & S_{13} &= S_{1133}, & S_{23} &= S_{2233}, \\ S_{21} &= S_{2211}, & S_{31} &= S_{3311}, & S_{32} &= S_{3322}, \\ S_{44} &= 2S_{2323}, & S_{55} &= 2S_{1313}, & S_{66} &= 2S_{1212}. \end{aligned} \quad (91)$$

Inter-relations between elastic constants

Input Constants	Output Constants				
	E =	ν =	G =	K =	λ =
E, ν	-	-	$\frac{E}{2(1+\nu)}$	$\frac{E}{3(1-2\nu)}$	$\frac{E\nu}{(1+\nu)(1-2\nu)}$
E, G	-	$\frac{E-2G}{2G}$	-	$\frac{EG}{3(3G-E)}$	$\frac{G(E-2G)}{3G-E}$
E, K	-	$\frac{3K-E}{6K}$	$\frac{3KE}{9K-E}$	-	$\frac{3K(3K-E)}{9K-E}$
E, λ	-	$\frac{2\nu}{E+\nu+R}$	$\frac{E-3\nu+R}{4}$	$\frac{E+3\nu+R}{6}$	-
ν , K	$3K(1-2\nu)$	-	$\frac{3K(1-2\nu)}{2(1+\nu)}$	-	$\frac{3K\nu}{1+\nu}$
ν , λ	$\frac{\nu(1+\nu)(1-2\nu)}{\nu}$	-	$\frac{\nu(1-2\nu)}{2\nu}$	$\frac{\nu(1+\nu)}{3\nu}$	-
ν , G	$2G(1+\nu)$	-	-	$\frac{2G(1+\nu)}{3(1-2\nu)}$	$\frac{2G\nu}{1-2\nu}$
G, K	$\frac{9KG}{3K+G}$	$\frac{3K-2G}{6K+2G}$	-	-	$\frac{3K-2G}{3K}$
G, λ	$\frac{G(3\nu+2G)}{\nu+G}$	$\frac{\nu}{2(\nu+G)}$	-	$\frac{3\nu+2G}{3}$	-
K, λ	$\frac{9K(K-\nu)}{3K-\nu}$	$\frac{\nu}{3K-\nu}$	$\frac{3}{2}(K-\nu)$	-	-

Table 11. Inter-relations among the elastic constants. $R = \sqrt{E^2 + 9\nu^2 + 2E\nu}$

VITA

Frank Thomas Fisher was born in Abington, PA on February 8, 1972, to Frank and Betsy Fisher, and grew up with younger brothers Mike and Sean in the nearby Philadelphia suburb of Warminster, PA. After graduating from Archbishop Wood High School for Boys (Warminster, PA) in 1990, he attended the University of Pittsburgh (Pittsburgh, PA) where he graduated with undergraduate degrees in Mechanical Engineering (Magna Cum Laude) and Applied Mathematics (Summa Cum Laude) in 1995.

After graduation Frank enrolled in the doctoral program in Mechanical Engineering at Northwestern University in Evanston, IL. He soon joined the research group of Professor Cate Brinson and began studying the viscoelastic behavior of polymer matrix composites, with a focus on viscoelasticity and related phenomena. In 1998 he received an MS degree in Mechanical Engineering for his work studying the influence of a viscoelastic interphase on the physical aging of a three-phase composite (“Viscoelastic Behavior of Polymer Matrix Composites with Interphase Effects: Theoretical Models and Finite Element Analysis”).

Long interested in education and with the full support of Professor Brinson, Frank temporarily suspended his PhD studies in September 1999 and enrolled in the Learning Sciences program in the School of Education and Social Policy at

Northwestern. Here he worked with Dr. Penelope Peterson as part of the NSF-funded VaNTH Engineering Research Center for Bioengineering Educational Technologies through the Biomedical Engineering Department at Northwestern. His research focused on the theory of adaptive expertise, the concept that in addition to concept knowledge successful experts display additional cognitive dispositions that facilitate the use of their expertise. Frank adapted this idea for the learning and practice of engineering, developing measures to evaluate and study adaptiveness in undergraduate engineering students. He received an MA degree in Learning Sciences in December 2000.

Frank returned to complete his PhD in Mechanical Engineering in September 2000, beginning work on a new NASA-funded project modeling the mechanical properties of carbon nanotube-reinforced composites. After graduation Frank will continue his research at Northwestern as a post-doctoral fellow in the Department of Mechanical Engineering, before starting a career in academia, where he can continue to pursue his interests in Mechanical Engineering and Engineering Education.

Frank Fisher is co-author of the following publications:

F. T. Fisher, L. C. Brinson, A. Eitan, and L. S. Schadler (2002). Reduced polymer chain mobility in low volume fraction carbon nanotube-reinforced polycarbonate: Spectral response and effective viscoelastic properties. Manuscript in preparation.

R. D. Bradshaw, F. T. Fisher, L. C. Brinson (2002). Fiber waviness in nanotube-reinforced polymer composites: II. Modeling via numerical approximation of the dilute strain concentration tensor, to appear in *Composites Science and Technology*.

Fisher, F. T., R. D. Bradshaw, L. C. Brinson (2002). Fiber waviness in nanotube-reinforced polymer composites: I. Modulus predictions using effective nanotube properties, to appear in *Composites Science and Technology*.

Fisher, F. T., R. D. Bradshaw, L. C. Brinson (2002). Effects of nanotube waviness on the modulus of nanotube-reinforced polymers. *Applied Physics Letters*, 80(24): 4647-4649.

F.T. Fisher and L.C. Brinson (2002). Viscoelasticity and physical aging of carbon nanotube-reinforced polymers. Proceedings for the 2002 Society for Experimental Mechanics Annual Conference, June 10-12, Milwaukee, WI.

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