Micromechanical Analysis of the Effective Elastic Properties of Carbon Nanotube Reinforced Composites

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Abstract

We seek to obtain continuum level elastic properties for carbon nanotubes and carbon nanotube reinforced composites through a variety of analytical micromechanics techniques. Using the in-plane elastic properties of graphene sheets, the effective properties of carbon nanotubes are calculated using a modified composite cylinders micromechanics technique in order to represent the hollow nanotube as a transversely isotropic solid cylinder. Having a solid fiber then allows for the calculation of an Eshelby tensor and hence, the use of either the generalized self-consistent or Mori-Tanaka techniques to calculate effective elastic properties of composites consisting of aligned single-walled effective carbon nanotubes embedded in a polymer matrix of EPON 862 at various effective carbon nanotube volume fractions. The results of these so called two-step approaches are compared to a single step composite cylinders approach wherein an additional phase consisting of the polymer matrix is placed around the carbon nanotube prior to obtaining the effective carbon nanotube properties, thereby obtaining the effective composite properties in a single calculation.

The effects of an interphase layer between the nanotubes and the polymer matrix as result of the interaction of the two species as discussed in the literature is also investigated using the single-step approach and found to have significant influence on the effective properties. Finally, the quantification and modeling of nanotube clustering in aligned nanotube composites is accomplished herein using Dirichlet tessellation in conjunction with an n-phase generalized self-consistent technique. Results indicate that, while the clustering effect does contribute to some reduction in composite properties, other factors such as cluster misalignment and poor fiber-matrix bonding may play a significantly larger role.
Obtaining Effective Elastic Properties of CNT Composites via Micromechanics

- Generalized self-consistent and Mori-Tanaka approaches
- Multiphase composite cylinders model
- Capturing the effects of
  - Interphase between CNTs and matrix
  - Clustering in CNT composites

- Specimens Provided by Dr. Barrera
- TEM Imaging by Piyush Thakre
Generalized Self-Consistent and Mori-Tanaka Approaches for Effective Elastic Properties

Step 1: Effective Carbon Nanotubes

- Single Wall Carbon Nanotube
- Transversely Isotropic Effective Carbon Nanotube

Step 2: The Generalized Self-Consistent Technique or The Mori-Tanaka Method

- Generalized Self-Consistent
- Mori-Tanaka

Effective Composite (Transversely Isotropic)

Capturing Random Orientation Effects

Average over all possible orientations

- Effective Composite (Transversely Isotropic about θ₁)
- Effective Composite (Transversely Isotropic about θ₂)
- Effective Composite (Transversely Isotropic about θₙ)

Effective Composite (Isotropic)
Comparing Randomly Oriented Results to Well-Aligned Results

- Rule of Mixtures returned for Axial Modulus
- Significant increase in composite axial stiffness for aligned CNTs over random
- Increase in composite transverse stiffness for random over aligned CNTs at lower volume fractions
- Matrix dominance out to 60% volume fraction in composite transverse modulus for aligned CNTs due to large difference between CNT and matrix moduli
Comparing Randomly Oriented Results to Well-Aligned Results

- Matrix Stiffness used in simulations: 3.07 GPa
- Graphene Tube Stiffness used in simulations: 1100 GPa
- Experimental results from Dr. Barrera’s Group:
  - Neat Polymer = 2.026 GPa
  - Functionalized 1 = F-SWNT-COOH
  - Functionalized 2 = SWNT-R-NH2
- Additional Experimental results from Schadler et al\(^1\)

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Identifying Clustering and Alignment in Composite Samples

Focus will be on:

(1) Clustering in well aligned composites
(2) Random Orientation

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- TEM Imaging by Piyush Thakre

Clustering of Unfunctionalized Single-Wall Carbon Nanotube Ropes in Polypropylene (TEM)

Alignment of Carbon Nanotubes within Clusters in a Polypropylene Matrix (TEM)
Incorporating Effects of Clustering: Multiphase CC/N-Phase Self-Consistent

Methodology:
1. Tessellation routine used to define associated matrix which gives the local volume fraction
2. Effective properties of associated matrix/CNT system obtained using multiphase composite cylinders method
3. Effective properties of clustered composites obtained using N-phase self-consistent
General Procedure: Defining Local Volume Fraction

- Non fiber area converted from polygon to circle concentric with and surrounding the fiber, maintaining the same area and thus the same local volume fraction.
Effects of Clustering at Different Global Volume Factions (1%, 3%, 5%, 10%, 20%, 25%)

Deviation from random distribution increases with increasing global volume fraction.
Single-Step Approach
Effective Elastic Properties: Multiphase Composite Cylinders

- Mori-Tanaka and Multiphase Composite Cylinders provide very similar results
- Matrix dominance of transverse properties out to 60% volume fraction due to the large difference in CNT and matrix moduli
Parametric Studies on Nanotube:Matrix Stiffness Ratio

Normalized Transverse Modulus Comparison of 1-Step and 2-Step CC/SC Trends
For Various CNT:Matrix Stiffness Ratios

- 1 Step - Ratio: 1100:3
- 2 Step - Ratio: 1100:3
Parametric Studies on Nanotube:Matrix Stiffness Ratio

Normalized Transverse Modulus Comparison of 1-Step and 2-Step CC/SC Trends
For Various CNT:Matrix Stiffness Ratios

Normalized $E_{22}$

Volume Fraction of CNTs

1 Step - Ratio: 1100:3
1 Step - Ratio: 697:3
2 Step - Ratio: 697:3
2 Step - Ratio: 1100:3
Parametric Studies on Nanotube:Matrix Stiffness Ratio

Normalized Transverse Modulus Comparison of 1-Step and 2-Step CC/SC Trends For Various CNT:Matrix Stiffness Ratios

Normalized E22

Volume Fraction of CNTs

- 1 Step - Ratio: 1100:3
- 1 Step - Ratio: 294:3
- 2 Step - Ratio: 294:3
- 2 Step - Ratio: 1100:3
Parametric Studies on Nanotube:Matrix Stiffness Ratio

Normalized Transverse Modulus Comparison of 1-Step and 2-Step CC/SC Trends For Various CNT:Matrix Stiffness Ratios

- 1 Step - Ratio: 1100:3
- 1 Step - Ratio: 70:3
- 2 Step - Ratio: 70:3
- 2 Step - Ratio: 1100:3
Parametric Studies on Nanotube:Matrix Stiffness Ratio

Normalized Transverse Modulus Comparison of 1-Step and 2-Step CC/SC Trends For Various CNT:Matrix Stiffness Ratios

Normalized E_{22} vs Volume Fraction of CNTs

- 1 Step - Ratio: 1100:3
- 1 Step - Ratio: 20:3
- 2 Step - Ratio: 20:3
- 2 Step - Ratio: 1100:3
Parametric Studies on Nanotube:Matrix Stiffness Ratio

Normalized Transverse Modulus Comparison of 1-Step and 2-Step CC/SC Trends For Various CNT:Matrix Stiffness Ratios

- 1 Step - Ratio: 1100:3
- 1 Step - Ratio: 11:3
- 2 Step - Ratio: 11:3
- 2 Step - Ratio: 1100:3

Volume Fraction of CNTs

Normalized E22
Interphase Modeling through Multiphase Composite Cylinders

- Stiff interphase can greatly increase composite stiffness at below 60% volume fraction
- Compliant interphase further delays effect of CNTs out to 92% volume fraction
Interphase Modeling through Multiphase Composite Cylinders

Effects of Interphase Stiffness
Thickness of Interphase = 4 CNT Radii
CNT/Matrix Stiffness Ratio = 1100/3

Small interphase thickness is equivalent to a large shift volume fraction and vice versa
Interphase Modeling through Multiphase Composite Cylinders

Effects of Interphase Stiffness
Thickness of Interphase = 2 CNT Radii
CNT/Matrix Stiffness Ratio = 1100/3

- Small interphase thickness is equivalent to a large shift volume fraction and vice versa
Interphase Modeling through Multiphase Composite Cylinders

Effects of Interphase Stiffness
Thickness of Interphase = 0.5 CNT Radii
CNT/Matrix Stiffness Ratio = 1100/3

- Interphase Stiffness = 30 GPa
- Interphase Stiffness = 20 GPa
- Interphase Stiffness = 15 GPa
- Interphase Stiffness = 1.5 GPa
- Interphase Stiffness = 0.3 GPa

Small interphase thickness is equivalent to a large shift volume fraction and vice versa
Comparison of Single and Two Step Results with Finite Element Simulations

- Periodic Unit Cell of Nanotubes Arranged in Regular Hexagonal Array
- Periodic Boundary Conditions

![Graph showing Transverse Modulus vs. Vol Fraction for Composite w/SWCNTs](image)

**Note:** CC = Composite Cylinders, SC = Self-Consistent, MT = Mori-Tanaka, FEM = Finite Element Results done by D. Hammerand (SNL)
Future Work

- Random Orientation of CNTs with the inclusion of interphase
- Clustering of CNTs with the inclusion of interphase
- Clustering of effective SWCNT bundles
- Interface modeling via cohesive zones
- Incorporation of viscoelasticity of matrix