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Nanomechanics and the Viscoelastic Behavior of Carbon Nanotube-Reinforced Polymers

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ABSTRACT

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Recent experimental results demonstrate that substantial improvements in the mechanical behavior of polymers can be attained using small amounts of carbon nanotubes as a reinforcing phase. While this suggests the potential use of carbon nanotube-reinforced polymers (NRPs) for structural applications, the development of predictive models describing NRP effective behavior will be critical in the development and ultimate employment of such materials. To date many researchers have simply studied the nanoscale behavior of NRPs using techniques developed for traditional composite materials. While such studies can be useful, this dissertation seeks to extend these traditional theories to more accurately model the nanoscale interaction of the NRP constituent phases.

Motivated by micrographs showing that embedded nanotubes often exhibit significant curvature within the polymer, in the first section of this dissertation a hybrid finite element-micromechanical model is developed to incorporate nanotube

waviness into micromechanical predictions of NRP effective modulus. While also suitable for other types of wavy inclusions, results from this model indicate that moderate nanotube waviness can dramatically decrease the effective modulus of these materials.

The second portion of this dissertation investigates the impact of the nanotubes on the overall NRP viscoelastic behavior. Because the nanotubes are on the size scale of the individual polymer chains, nanotubes may alter the viscoelastic response of the NRP in comparison to that of the pure polymer; this behavior is distinctly different from that seen in traditional polymer matrix composites. Dynamic mechanical analysis (DMA) results for each of three modes of viscoelastic behavior (glass transition temperature, relaxation spectrum, and physical aging) are consistent with the hypothesis of a reduced mobility, non-bulk polymer phase in the vicinity of the embedded nanotubes.

These models represent initial efforts to incorporate nanoscale phenomena into predictive models of NRP mechanical behavior. As these results may identify areas where more detailed atomic-scale computational models (such as *ab initio* or molecular dynamics) are warranted, they will be beneficial in the modeling and development of these materials. These models will also aid the interpretation of NRP experimental data.

For my parents, Frank and Betsy

Their constant support and encouragement made this possible.

In loving memory of my grandmother, Jane Fisher (1924-2002)

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CHAPTER 1: INTRODUCTION

Since their discovery in the early 1990s (IIjima 1991), carbon nanotubes have excited scientists and engineers with their wide range of unusual physical properties. These outstanding physical properties are a direct result of the near-perfect microstructure of the nanotubes (NTs), which at the atomic scale can be thought of as a hexagonal sheet of carbon atoms rolled into a seamless, quasi-one-dimensional cylindrical shape. Besides their extremely small size, it has been suggested that carbon nanotubes are half as dense as aluminum, have tensile strengths twenty times that of high strength steel alloys, have current carrying capacities 1000 times that of copper, and transmit heat twice as well as pure diamond (Collins and Avouris 2000). To take advantage of this unique combination of size and properties, a wide variety of applications have been proposed for carbon nanotubes, including: chemical and genetic probes, field emission tips, mechanical memory, supersensitive sensors, hydrogen and ion storage, scanning probe microscope tips, and structural materials (Collins and Avouris 2000). It has been suggested that nanotechnology, largely fueled by the remarkable properties of carbon nanotubes, may ultimately transform technology to a greater extent than the advances of the silicon revolution (Jamieson 2000).

While the outstanding properties of carbon nanotubes have led to a wide range of hypothesized applications, in this thesis we limit our analysis to the use of carbon nanotubes as a filler phase for structural reinforcement in a host polymer, a material we will refer to as a *nanotube reinforced polymer (NRP)*. A great deal of interest in NRPs for structural applications exists due to a number of potential benefits that are predicted with such materials. A number of these benefits are highlighted below (and discussed in more detail in Chapter 2):

- *High stiffness of carbon nanotubes.* Numerical simulations predict tensile moduli on the order of 1 TPa, making nanotubes perhaps the ultimate high-stiffness filler material. Recent experimental work typically confirms these predictions.

- *High elastic strains of the nanotube.* Numerical simulations predict elastic (recoverable) strains in the nanotube as large as 5%, suggesting an order of magnitude increase in NRP tensile strength compared to traditional composites.

- *Extremely high strength- and stiffness-to-weight ratios.* Given the exceptional strength and stiffness of the NT filler material, it may be possible match traditional composite properties with much smaller amounts of nanotubes. Alternatively, it may be possible to fabricate high volume fractions NRPs, resulting in strength and stiffness weight ratios unachievable with traditional composite materials. Both scenarios suggest the possibility of substantial weight savings for weight-critical applications.[1]

- *Multifunctionality.* In addition to their outstanding mechanical properties, NTs have also been shown to have exceptional electrical and heat-related properties, suggesting materials that may be designed to meet mechanical as well as secondary material property specifications.

- *Increase in the working/use temperature range.* In some cases large increases in the glass transition temperature of NRPs, in comparison with the blank polymer material, have been reported. Such increases could extend the range of temperatures over which the material will exhibit glassy behavior, increasing the working temperature range of the polymer in structural applications.

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[1] NASA predicts that SWNT composites will reduce spacecraft weight by 50% or more. (http://mmptdpublic.jsc.nasa.gov/jscnano/)

Despite these potential benefits, a number of critical issues must be overcome before the full benefit of such materials can be realized. Such issues include:

- *The high-cost and availability of the raw nanotube material.* As of October 2002, two grams of high quality, low defect, purified SWNTs were available from Carbon Nanotechnologies Incorporated (http://www.cnanotech.com/) for $750/gram. At the same time another supplier, CarboLex (http://carbolex.com/), offers as-prepared, unprocessed SWNTs for $100/gram, and touts that their production output is up to 250 grams per week. These prices are several orders of magnitude higher than the cost of high strength carbon fibers used in composites applications. Methods to develop a continuous, cost-efficient method of producing low-defect carbon nanotubes are under development.

- *Bonding between the nanotube and the polymer.* Proper bonding between the nanotubes and the polymer is critical for sufficient load transfer between the phases. Several examples of excellent load transfer between nanotubes and a polymer have been demonstrated, but more research in this area is needed. Functionalization of the nanotubes is also being investigated by several groups as a way to increase the chemical reactivity of the nanotubes and thus improve the bonding between the NTs and the polymer.

- *Dispersion of the nanotubes within the polymer.* Due to van der Waals attractive forces nanotubes are notoriously difficult to disperse in a polymer. Proper dispersion will be necessary for optimal, and more importantly uniform, material properties.

- *Orientation and geometry of the nanotubes within the polymer.* To tailor the properties of NRPs it is desirable to be able to control the orientation of the nanotubes within the polymer. While methods have been developed to orient free-standing and as-grown NTs, methods to orient nanotubes in bulk polymers have yet to be developed. In addition, electron microscopy images of nanotube-reinforced polymers also show that the NTs typically remain curved (wavy) when embedded within a polymer. The impact of this waviness on the effective modulus of the NRP is modeled in Chapter 3 of this work.

- *Differences between nanotubes forms.* The properties of nanotubes are known to be dependent on the method of production and the form of the nanotube (single-walled nanotube, multi-walled nanotube, or nanotube bundle). The relationship between these variables and mechanical properties needs to be further elucidated.

- *Accurate models of NRP behavior.* Accurate models of NRP behavior are necessary to aid in the interpretation of experimental results and, in the long term, to allow aggressive design strategies that fully leverage the benefits of such materials. In particular, the viscoelastic behavior of nanotube-reinforced polymers is often substantially different than that of the pure (blank) polymer; this behavior is modeled in terms of a reduced mobility non-bulk interphase region (in the vicinity of the nanotubes) in Chapter 4 of this dissertation.

Over the last several decades research in the area of composite materials, and in particular polymer matrix composites, has become quite mature. However, in many cases it will be necessary to extend these theories, which have been developed for macroscale composites, to account for phenomena that are particular to the use of nanoscale reinforcement. The work presented in this thesis represents two examples of such model extensions:

- The incorporation of nanotube waviness, which is typically observed in high magnification electron microscopy images of nanotube-reinforced polymers, into micromechanical predictions of the elastic stiffness of these materials.

- The impact of the nanotubes on the mobility of the polymer chains and the resulting effective viscoelastic behavior of the NRP.

This dissertation has been organized in the following format. To firmly ground the reader in the current state of the art, an in-depth discussion of the theoretical and experimental properties of nanotubes and nanotube-reinforced polymers is provided in Chapter 2. In Chapter 3 a hybrid finite element – micromechanical model developed to incorporate the waviness of the embedded nanotubes into micromechanics prediction of effective elastic moduli of NRPs is presented. In Chapter 4 the impact of the nanotubes on the overall viscoelastic behavior of the NRP is discussed. While Chapters 3 and 4 are both related to the effective mechanical properties of nanotube-reinforced polymers, each chapter has been written as a self-contained unit and may be read independent of the other. Chapter 5 summarizes this work and highlights future directions of research that will facilitate the development of accurate models of nanotube-reinforced polymer behavior.