

VISCOELASTICITY AND PHYSICAL AGING OF CARBON NANOTUBE-REINFORCED POLYMERS

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ABSTRACT

Recent experimental results demonstrate that substantial improvements in polymer stiffness can be attained by using small volume fractions of carbon nanotubes as a reinforcing phase. While these preliminary results are exciting, to date limited theoretical and experimental work has been done to investigate the impact of the nanotubes on the viscoelastic response of the polymer. Because the nanotubes are on the same length scale as the polymer chains, it is hypothesized that the polymer segments in the vicinity of the nanotubes will be characterized by a mobility that is different from the polymer chains in the bulk material. We present a model that accounts for this mobility change in the non-bulk polymer behavior via a change in the relaxation spectra describing the time-dependent response of the material. With this model and an appropriate micromechanical technique, it will be possible to infer the behavior of this non-bulk polymer phase from experimental data obtained via macroscale mechanical testing of the nanotube-reinforced sample. The model will be useful in interpreting experimental stiffness data obtained for nanotube-reinforced polymers, assessing changes in the mobility and mechanical behavior of polymer segments in the vicinity of the nanotubes, and will be necessary to obtain accurate long-term material performance predictions.

INTRODUCTION

The outstanding mechanical properties of carbon nanotubes (NTs) are due to the high bond strength of the constituent carbon-carbon bonds and their near perfect lattice structure. Modulus values and tensile strengths on the order of 1 TPa and 100 GPa, respectively, have been predicted based on atomistic simulations and recently verified experimentally [1]. These properties have led to interest in nanotube-reinforced polymers (NRPs) as ultra-light structural polymers with excellent mechanical properties. Additional interest has been spurred by efforts to exploit the unique combination of NT mechanical and electrical properties to enable multifunctional polymeric materials.

Several experimental studies have found large improvement in the mechanical behavior polymers reinforced with small amounts of carbon nanotubes. One group of researchers reported a 40% increase in elastic modulus and ~25%

increase in tensile strength of polystyrene reinforced with 1 wt% MWNTs [2]. Another study found increases of about 20% in the tensile and compressive moduli of an epoxy reinforced with 5 wt% MWNTs [3].

While a majority of the experimental work to date on nanotube-reinforced polymers has considered the elastic properties, a limited amount of work has considered the viscoelastic and temperature-dependent response of these materials. Working with an epoxy reinforced with 1 wt% MWNTs, Gong and co-workers found a 30% increase in the elastic modulus and a 25 °C increase in the glass transition temperature (T_g) when a nonionic surfactant was used as a processing agent, as shown in Figure 1 [4]. While another group found that the addition of catalytic nanotubes to poly(vinyl alcohol) did not cause a change in T_g , they did note a large relative increase in the polymer stiffness at temperatures above T_g and a broadening of the high-temperature side of the $\tan \delta$ peak [5]. They attributed this behavior to decreased chain mobility of polymer segments near the nanotube surface.

These results suggest that the NTs may affect the viscoelastic properties of the nanotube-reinforced polymers by changing the mobility of polymer segments in the vicinity of the nanotubes. Because the NTs are on the same size scale as the polymer chains¹ and have significant surface area to promote interaction with neighboring polymer segments, we suggest that it will be necessary to incorporate the local non-bulk behavior of the polymer in this region into viscoelastic models of NRP behavior. While it will be extremely difficult to experimentally measure the local properties of the non-bulk polymer region, in this paper we present a simplified model which will allow this region to be characterized based on the overall viscoelastic response of the composite obtained through macroscopic mechanical testing.

¹ Characteristic diameters of SWNTs, MWNTs, and NT bundles are roughly on the order of 1 nm, 30 nm, and 100 nm, respectively, and thus orders of magnitude smaller than the diameters of typical microscale fibers traditionally used in polymer composites (on the order of 10 μ m).

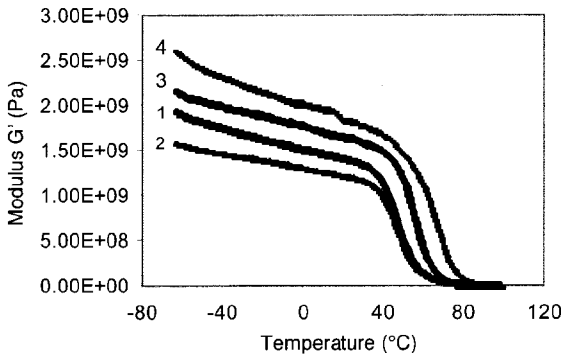


Figure 1. Storage modulus as a function of temperature for different epoxy samples. 1: epoxy; 2: epoxy + surfactant (C₁₂EO₈); 3: epoxy + 1 wt% MWNTs; 4: epoxy + surfactant + 1 wt% MWNTs. [4]

THE INTERPHASE AND POLYMER MOBILITY

Because the nanotube diameters are on the same length scale as the polymer chains, it is anticipated that the NTs will alter the local polymer morphology in the region directly surrounding the nanotube (see Figure 2). This change in local structure will result in a material with mechanical behavior different from that of the bulk polymer. We refer to the material displaying this non-bulk behavior as the interphase, borrowing a term used in the composites community that refers to the region separating the fiber and matrix phases. While in traditional composites research the interface region is generally attributed to a host of factors (such as the use of fiber sizings, mechanical imperfections, and unreacted polymer components), here we limit our discussion specifically to the change in molecular mobility of the polymer chains in this region due to the presence of, and interactions with, the nanotube inclusions.

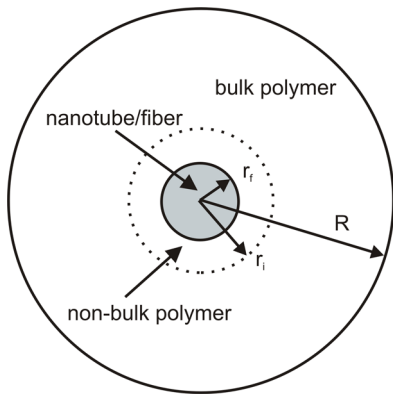


Figure 2. Schematic of bulk polymer and the non-bulk polymer (interphase) regions surrounding an inclusion. The thickness of the interphase is $t = r_i - r_f$.

Recent experimental work has estimated the interphase thickness for carbon fiber – epoxy composites to be on the order of 1 μm [6, 7]. Because the interphase region makes up a very small portion of the composite, its impact in terms of the viscoelastic response of the material is often neglected. However, recent molecular dynamic simulations

for a SWNT-polyethylene composite suggest that the local changes in the molecular polymer structure are on the same length as the diameter of the NT [8]. Because the nanotubes have significantly more surface area (per unit volume) than micron-sized inclusions, a significant fraction of the polymer in NRP systems will be in the near vicinity of an embedded nanotube and thus may be characterized by this non-bulk behavior. The non-bulk polymer behavior of this region is likely to significantly contribute to the overall viscoelastic response of the material, as this region comprises a much larger fraction of the total viscoelastic response of the material as shown in Figure 3, which shows that 10% (volume) SWNTs would result in over 50% of the polymer material belonging to the interphase region. Thus while the interphase region is often neglected for the case of traditional-sized fibers, interphase effects are anticipated to be important for even relatively low loadings of nanotube inclusions.

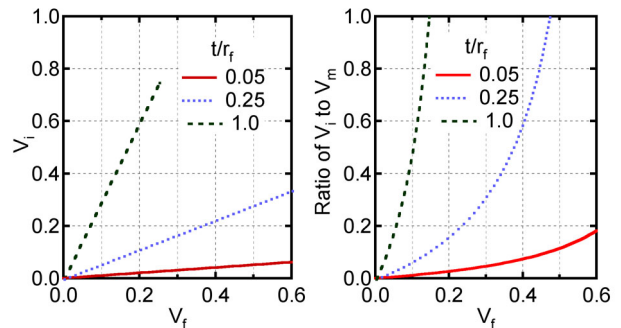


Figure 3. Interphase volume fraction (V_i) (left) and ratio of the interphase (non-bulk) to matrix (bulk) volume fraction (V_m) (right) as a function of fiber (nanotube) volume fraction for different ratios of interphase thickness (t) to fiber radius (r_f). Representative values of (t/r_f) are on the order of 0.05 for carbon fiber composites [6] and 1.0 for nanotube-reinforced polymers [8], respectively.

THE MODEL

We wish to model how an area of finite size directly surrounding the NTs, which has non-bulk properties because of an effective change in mobility, affects the overall response of the material. To accomplish this we will model the time-dependent modulus of the matrix and interphase regions using a Prony series representation of the form

$$E(t) = E_\infty + \sum_{j=1}^N E_j e^{-\frac{t}{\alpha\tau_j}}, \quad (1)$$

where E_∞ is the rubbery ($t \rightarrow \infty$) modulus, E_j and τ_j are the relaxation spectra and relaxation times describing the modulus response, and α is a scaling parameter that modifies the relaxation times and hence shifts the material response in the time domain as shown in Figure 4.

In this manner the scaling parameter α can be used to characterize polymer segment mobility in the interphase by modeling the impact of this mobility change on the time-dependent response of the non-bulk polymer. For $\alpha < 1$ the

polymer chains are more mobile, resulting in the time-dependent modulus having an earlier transition from glassy to rubbery behavior. The opposite is true for $\alpha > 1$, where the polymer segments are less mobile than the bulk phase and thus maintain glassy behavior over a longer period of time. By definition $\alpha = 1$ represents the behavior of the bulk polymer. Although here we only model the impact of the NTs as an effective shift in the relaxation times of the polymer, an extension of the model to account for a change in the magnitude of the local time-dependent modulus in the non-bulk polymer region, which is also consistent with the hypothesis of a change in segment mobility, could also be included. Likewise, consideration of a more complex form of α , such that different relaxation times are affected differently, could be considered.

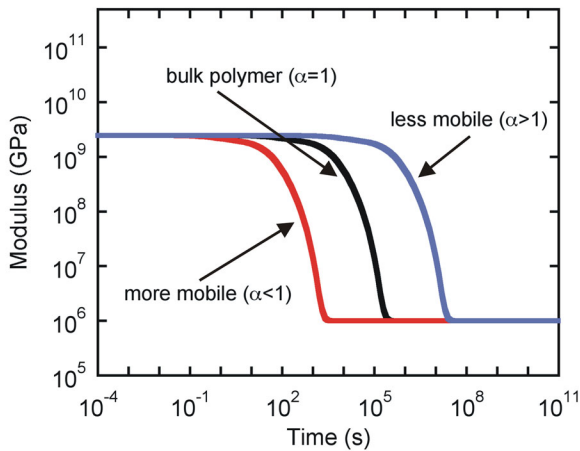


Figure 4. Schematic of the time-dependent modulus response of bulk and non-bulk polymers as characterized by the mobility scaling parameter α .

Thus using the interphase geometry of Figure 2 and the time-dependent moduli of the phase materials (including the scaling parameter α to account for different segment mobility in the non-bulk interphase region), we can implement an appropriate micromechanical method to predict the effective mechanical response of the system. Typically such analyses are carried out in the frequency domain through use of the Correspondence Principle, which simplifies the analysis and is directly applicable to frequency domain experimental data that may be obtained through dynamic mechanical analysis and other techniques. The Mori-Tanaka method is one micromechanical method that is suitable for the current analysis because 1) it can be used to model materials with random distributions of inclusions [9], and 2) it was shown previously to closely match the results of a finite element study of a three-phase composite with distinct viscoelastic interphase and matrix materials, even though it was necessary in the Mori-Tanaka model to treat the interphase as a region physically separated from the fiber [10].

PHYSICAL AGING

Physical aging is the reversible process that occurs when polymer materials cooled below their glass transition temperature slowly evolve towards their equilibrium state. This phenomenon occurs because at temperatures lower than T_g the polymer chains do not have sufficient thermal energy to instantaneously orientate themselves in a manner to achieve an equilibrium configuration. This slow evolution to the equilibrium configuration is accompanied by local structural relaxations in the polymer chains, similar to other time-dependent behavior of viscoelastic materials. Because it is reversible, the affects of physical aging can be erased (i.e. the material is rejuvenated) upon re-heating above the T_g of the material.

In a manner analogous to time-temperature superposition, the mechanical response at different aging times t_e (time since the material was last rejuvenated) can be superposed via horizontal shifting in the log time domain by an amount equal to the aging time shift factor $a_{t,e}$. These shift factors and aging times are related to the shift rate μ ,

$$\mu = - \frac{d \log a_{t,e}}{d \log t_e}, \quad (2)$$

such that μ characterizes the physical aging behavior of a polymer. While Struik has demonstrated that the shift rates describing all mechanical properties of a homogeneous polymer are identical [11], it is likely that the shift rate of the non-bulk polymer in the vicinity of the nanotube will be different than that of the bulk polymer due to differences in mobility. Finite element results suggest that an interphase with aging behavior different from that of the bulk polymer can significantly influence the overall shift rates of a composite [10].

Given sufficient time the polymer chains will eventually achieve an effective equilibrium condition, which is marked by an order of magnitude decrease in the shift rate [12]. However, for the case of nanotube-reinforced polymers it is possible that this effective equilibrium is complicated by nanotube-polymer interactions at the nanoscale. Because the polymer chains are of the same size scale as the much stiffer NTs, it is possible that the NTs “lock out” portions of the free volume, in effect making it inaccessible for segment reorientation. To our knowledge this topic has yet to be studied, although it could be an important feature to address for future viscoelastic models of NT-reinforced composites and will be addressed in future experimental work.

Besides the need to study physical aging in order to develop accurate long-term models of NRP behavior, such work may prove advantageous as a means to address the local changes in polymer mobility caused by the presence of the nanotubes. It has been shown that physical aging can be sensitive to the presence of an interphase material [10], and as such it may be possible to back out the local mobility of the interphase region based on the effective response of the composite as determined through macroscale testing. One manner in which the presence of a distinct interphase region can be distinguished is the appearance of thermorheologically complex material behavior, where simple curve shifting procedures such as time-temperature and time-aging time superposition are no longer valid.

Such a technique would be useful because the interphase region in nanotube-reinforced composites is not likely to be accessible to standard interphase experimental techniques due to its small size. In this regard it is worth noting that in a previous study we found that thermorheologically complex (TRC) behavior can be masked in the time-domain (appearing indistinguishable from experimental error), suggesting that frequency-domain experimental data may be preferred to identify TRC behavior and hence the presence of an interphase [10]. In our previous work we found that TRC behavior was particularly noticeable in the loss moduli data, as a broadening of the loss peak at longer aging times prevented a single shift factor from being able to simultaneously superpose low and high frequency data.

CONCLUSIONS

Due to their outstanding physical properties, a great interest exists in using carbon nanotubes as a filler material in polymeric systems. With the potential of strength- and modulus-to-weight ratios as much as an order of magnitude larger than traditional polymer matrix composites, NRPs are being heavily scrutinized for use as structural materials. While the single largest impediment to using nanotubes as a filler phase for polymers is currently cost, as nanotube production methods continue to develop nanotubes will gradually become commercially viable filler materials for multiphase materials.

Because the nanotubes are on the same length scale as the polymer chains, the polymer segments in the vicinity of the NT may have local mobility different from that the bulk polymer, and hence distinct mechanical properties. However, it will be very difficult to obtain direct experimental measurements of the interphase properties in NRPs because of the extremely small thickness (likely on the order of 1 nm) of such regions. Here we present a simple model that characterizes mobility changes as a scaling of the relaxation times for the non-bulk interphase material. Modeling the material as a three-phase (nanotube-interphase-matrix) composite in conjunction with an appropriate micromechanical method, it will be possible to infer the interphase properties through macroscale mechanical testing of the nanotube-reinforced polymer. While such a method has obvious limitations, this technique could be used for qualitative comparison between different nanotube-polymer systems.

We are currently developing an experimental program to study the impact of nanotube-polymer interactions on the viscoelastic behavior of nanotube-reinforced polymers. As outlined in this paper, the focus of our initial work will be identifying, through comparison of experimental data collected on blank (pure polymer) and nanotube-reinforced films, those aspects of current viscoelastic models that will need to be modified for use with NRPs. Planned experiments in this area will look at the tensile creep and

frequency-dependent response of these materials using dynamic mechanical analysis over a range of temperatures, with an emphasis on incorporating nanoscale information (such as interphase thicknesses estimated from molecular dynamics simulations) into our models. By performing these experiments over a range of nanotube volume fractions, we will be able to address issues, such as the mobility of the polymer interphase and the impact of the nanotubes on the effective physical aging characteristics of the NRP, related to the impact of the nanotubes on the viscoelastic response of the system.

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