

# MACROSCALE EXPERIMENTAL EVIDENCE OF A REDUCED-MOBILITY NON-BULK POLYMER PHASE IN NANOTUBE-REINFORCED POLYMERS

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## ABSTRACT

Because of their outstanding physical properties, the use of carbon nanotubes within a polymer matrix has been proposed as a means to fabricate multifunctional composite materials with outstanding mechanical, electrical, and thermal properties. To date, experimental work studying the mechanical response of a nanotube reinforced polymer (NRP) has typically focused on the effective elastic modulus of the material, where recent experimental work has demonstrated significant modulus enhancement using small loadings of nanotubes. 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 has been suggested that the polymer segments in the vicinity of the nanotubes will be characterized by a molecular mobility that is different from that of the bulk polymer. This results in the significant differences between the viscoelastic behavior of the NRP, in comparison to the response of the pure polymer, seen experimentally.

To further characterize these differences, we have studied the temperature- and frequency-dependent behavior of polycarbonate-nanotube systems with different weight fractions of multiwalled carbon nanotubes (MWNTs). Our experimental results show that the effective viscoelastic behavior of the nanotube-reinforced samples are consistent with the presence of a non-bulk polymer phase with restricted molecular mobility within the NRP. These results suggest that analysis of the effective viscoelastic behavior of

nanotube-reinforced polymers provided by macroscale mechanical experiments can provide important information concerning the nanoscale interaction between the nanotubes and the polymer.

## 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.<sup>1</sup> These properties have led to interest in nanotube-reinforced polymers (NRPs) as ultra-light structural polymers with excellent mechanical properties. Additional interest has been motivated by efforts to exploit the unique combination of NT mechanical and electrical properties to enable multifunctional polymeric materials.

Several experimental studies have found moderate 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.<sup>2</sup> Another study found increases of about 20% in the tensile and compressive moduli of an epoxy reinforced with 5 wt% MWNTs.<sup>3</sup>

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

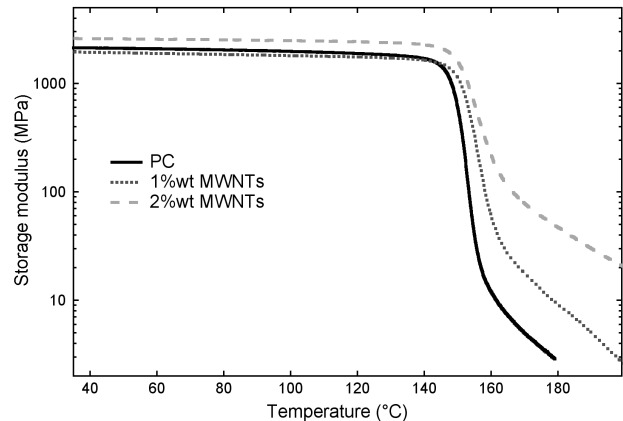
response of these materials. Working with an epoxy reinforced with 1 wt% MWNTs, Gong and co-workers found a 30% increase in the elastic modulus and a 25°C increase in the glass transition temperature ( $T_g$ ) when a nonionic surfactant was used as a processing agent.<sup>4</sup> While another group 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.<sup>5</sup> They attributed this behavior to decreased chain mobility of polymer segments near the nanotube surface.

Because the nanotubes are on the same length scale as the polymer chains, it has been suggested that the polymer segments in the vicinity of the nanotubes will be characterized by a molecular mobility that is different from that of the bulk polymer. This results in the significant differences between the viscoelastic behavior of the NRP, in comparison to the response of the pure polymer, seen experimentally.<sup>4,5</sup> To further characterize these differences we have studied the temperature- and frequency-dependent behavior of polycarbonate-nanotube systems with different weight fractions of multiwalled carbon nanotubes (MWNTs). Our experimental results show that the effective viscoelastic behavior of the nanotube-reinforced samples are consistent with the presence of a non-bulk polymer phase within the NRP with restricted molecular mobility. These results suggest that analysis of the effective viscoelastic behavior of nanotube-reinforced polymers found from macroscale mechanical experiments can provide important information concerning the nanoscale interaction between the nanotubes and the polymer.

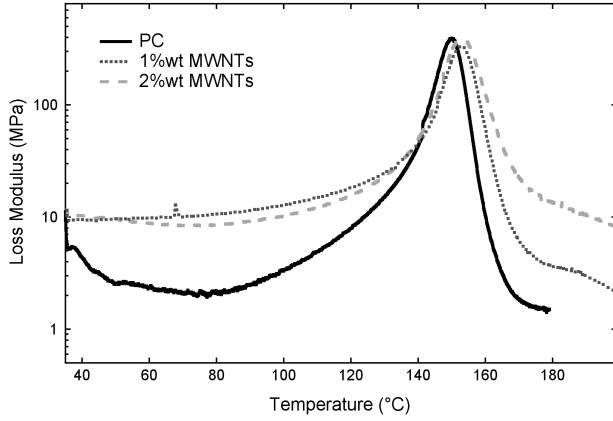
### ANALYSIS

We have studied the tensile response of both pure and nanotube-reinforced (1 and 2 wt%) polycarbonate samples using dynamic mechanical analysis (DMA 2980, TA Instruments). The NT-polycarbonate samples were created using a solution-evaporation procedure and hot-pressed for form samples in a procedure described elsewhere.<sup>6</sup> Samples of pure polycarbonate were fabricated using an identical procedure. Typical sample dimensions were (thickness x width x length) 0.5 x 6 x 10 mm. The temperature dependence of the samples was measured in the linear viscoelastic regime at a constant frequency ( $\omega = 1$  Hz) using a standard temperature sweep (2°C/min).

The storage and loss moduli for the blank and reinforced samples as a function of temperature are shown in Figures 1 and 2, respectively. In Figure 1 we see an increase in the storage moduli for the 2 wt% MWNT sample at both low and high temperatures when compared to the response of the pure polycarbonate. While a similar improvement is not seen with the 1 wt% MWNT sample at low temperatures, we see that the high temperature (above  $T_g$ ) storage moduli of the sample is also greatly enhanced. Figure 2 shows a slight shifting of the peak of the loss modulus curves with the addition of nanotubes. Also evident is a slight broadening of the peaks of the loss modulus response, which is indicative of an increase in the range of molecular mobility within the system. Because this broadening seems to predominantly occur on the high temperature side of the peaks, this suggests that the incorporation of NTs into the system effectively reduces the molecular mobility of certain regions of the polymer within the NRP. This behavior is consistent with the results of other experimental studies of the impact of the nanotubes on the temperature-dependence of NRPs.<sup>4,5,7</sup> Both the increase in the glass transition temperature and the broadening of the loss modulus peak with the addition of the carbon nanotubes can be qualitatively explained by the presence of a reduced mobility polymer phase surrounding the nanotubes.

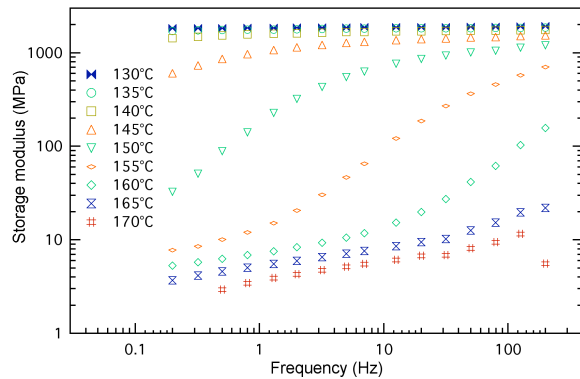


**Figure 1. Storage moduli of polycarbonate-NT system as a function of temperature.**



**Figure 2. Loss moduli of the polycarbonate-NT system as a function of temperature.**

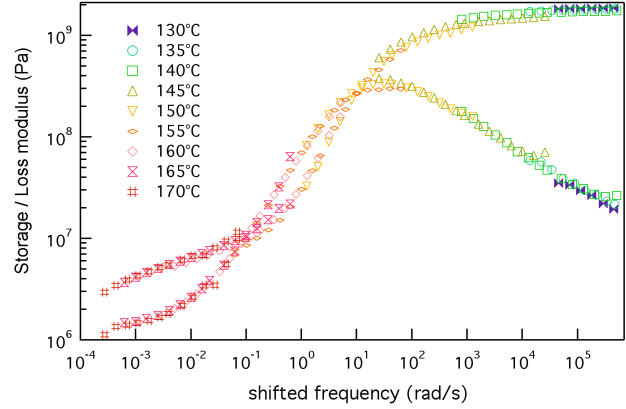
To supplement these temperature-dependence results, we studied the frequency response of the samples by testing a short frequency range (0.2 to 200 Hz, governed by the equipment limitations) over a series of temperatures (130 to 170°C). An example of how the frequency-dependence of the response changes as a function of temperature is shown in Figure 3 for the pure polycarbonate sample. Complimentary to the temperature-scan experiments presented in Figures 1 and 2, within this range of temperatures we again see evidence of the transition region of the material response.



**Figure 3. Storage modulus as a function of frequency for the pure polycarbonate sample tested at different temperatures.**

Following the general principles of linear viscoelasticity, we can use a form of time-temperature superposition to acquire representative data over eight decades of frequency at a particular temperature by horizontally shifting the data at different temperatures

to form a master reference curve at a given reference temperature. This procedure is demonstrated in Figure 4 for the pure polycarbonate data for a reference temperature of 150°C.



**Figure 4. Time-temperature superposition of the experimental data collected for the pure polycarbonate sample. The reference temperature is 150°C.**

Given a master reference curve (as shown in Figure 4 for the pure polycarbonate sample), the time-dependent response of a viscoelastic material can be described using a number of expressions. For example, the time-dependent modulus of a viscoelastic material can be described using a Prony series representation of the form

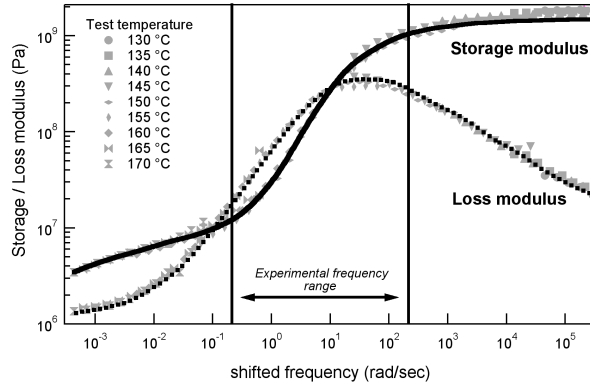
$$E(t) = E_{\infty} + \sum_j E_j e^{-t/\tau_j} \quad (1)$$

where  $E_{\infty}$  is the rubbery asymptotic modulus,  $E_j$  are the Prony series coefficients, and  $\tau_j$  are the relaxation times. Likewise, the frequency response (storage modulus  $E'$  and loss modulus  $E''$ ) can likewise be written in terms of the Prony series parameters such that

$$E'(\omega) = E_{\infty} + \sum_{j=1}^N \frac{E_j \tau_j^2 \omega^2}{1 + \tau_j^2 \omega^2} \quad (2)$$

$$E''(\omega) = \sum_{j=1}^N \frac{E_j \tau_j \omega}{1 + \tau_j^2 \omega^2}$$

The Prony series coefficients in (2) for each sample were found by fitting the storage and loss moduli experimental reference curves, obtained over the extended frequency range using time-temperature superposition (see Figure 4), to a 30-term Prony series using the linear least squares solver DYNAMFIT.<sup>8</sup> An additional constraint, which can be imposed within DYNAMFIT, enforces the physically sensible condition that all Prony coefficients  $E_j$  be greater than zero. The curve-fitting procedure evenly weighed the contributions from the storage and loss moduli functions and was chosen to minimize the root mean square error between the experimental data and the Prony series fit. An example of such a fit is shown in Figure 5 (similar results were obtained for the NT-reinforced samples and are not shown here).



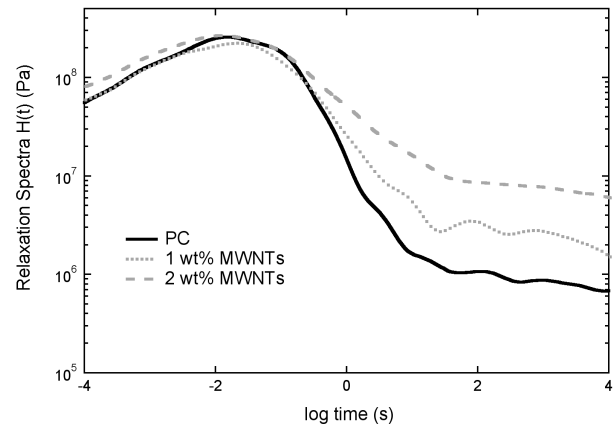
**Figure 5. Prony series fit to the pure polycarbonate frequency response. The reference temperature is 150°C.**

Once the Prony series coefficients have been found, one can show that the relaxation spectrum  $H(t)$  can be approximated using Alfrey's rule,<sup>9</sup> such that

$$H(t) \approx \sum_{j=1}^N \frac{t}{\tau_j} E_j e^{-\frac{t}{\tau_j}} \quad (3)$$

Using this procedure the relaxation spectra for the blank and reinforced polycarbonate samples were obtained and are shown in Figure 6. Here we see an increase in the relaxation spectrum with increasing volume fraction of nanotubes at longer times, as well as a slight broadening of the peak towards longer times. These are indicative of the introduction of longer time scale relaxation processes and an increased number of

relaxation modes within the NRP, respectively. These changes in viscoelastic behavior are again consistent with the hypothesis of a reduction in molecular mobility. Meanwhile, the location of the peak does not appreciably change with the addition of the nanotubes, suggesting that the primary relaxation mechanism within the NRP is the same as that within the bulk polymer sample. This suggests that while the nanotubes reduce the molecular mobility of the polymer chains in their vicinity, the mobility of the polymer chains far removed from the nanotubes is unaffected by the presence of the NTs and maintains its bulk characteristics.



**Figure 6. Relaxation spectra of the NT-polycarbonate samples.**

## 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 a 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. These variations in molecular mobilities will lead to differences in viscoelastic behavior between the bulk polymer and the

polymer comprising the interphase region surrounding the NTs. However, it will be very difficult to obtain direct experimental measurements of the interphase properties in NRPs because of the extremely small thicknesses of such regions. This suggests that the ability to infer the nanoscale interaction between the embedded nanotubes and the polymer from macroscale experimental analysis will be useful.

Both the temperature-dependent response and the relaxation spectra of the nanotube-reinforced polycarbonate samples are consistent with the existence of a reduced mobility, non-bulk polymer phase in the NRP. While the temperature-dependent response indicates differences in effective viscoelastic behavior as a function of NT loading, frequency domain data can be analyzed using suitable micromechanics techniques, which allow the change of molecular mobility to be quantified via comparison of the blank and reinforced-polymer behavior.<sup>10,11</sup> Further, differences in effective viscoelastic behavior, in comparison to the pure polymer response, have been shown to be more sensitive when studied via a frequency-domain analysis. An understanding of the impact of the nanotubes on the effective viscoelastic response of the NRP will be critical as efforts to develop accurate models of the time- and temperature-dependent properties of the material progress.

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