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 [1-3]. 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 molecular mobility that is different from that of the bulk polymer, resulting in the significant differences between the viscoelastic behavior of the NRP, in comparison to the response of the pure polymer, seen experimentally [4, 5]. 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.

A polymer can be defined as a substance composed of molecules which have long sequences of one or more species of atoms or groups of atoms linked to each other by primary, usually covalent, bonds [6]. On the nanoscale, polymer deformation requires highly cooperative motion amongst adjacent polymer chains (and perhaps between different segments of the same polymer chain). The molecular mobility of these polymer chains is the critical parameter governing the time- and temperature-dependent behavior of these materials. Molecular simulations of nanotube-polymer systems suggest that the nanotubes alter the local polymer morphology in the vicinity of the nanotubes, resulting in a local polymer structure (and corresponding molecular mobility) different from that of the bulk polymer [7-9]. Because this region of non-bulk polymer
behavior in the NRP is much larger than that for traditional micron-sized fibers, its contribution to the effective viscoelastic response of the material is expected to be significant [10].

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). Typical sample dimensions were (thickness x width x length) 0.5 x 6 x 10 mm. The temperature dependence of the samples was measured by applying a constant frequency (\(\omega = 1\) Hz), small amplitude (3 \(\mu\)m) strain and a standard temperature sweep (2°C/min). The frequency response of the samples was studied by testing a short frequency range (0.1 to 100 Hz, governed by the equipment limitations) over a series of temperatures and using a form of time-temperature superposition to acquire representative data over eight decades of frequency at a particular temperature.

The storage and loss moduli for the blank and reinforced samples as a function of temperature are shown in Figure 1 and Figure 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.\(^1\) Figure 2 shows a slight shifting of the peak of the loss modulus curves with the addition of nanotubes. (It is unclear at this time why the shift for 1 wt% MWNT is slightly larger than that for the 2 wt% sample; this anomaly will be investigated in future experiments.) Also evident is a slight broadening of the peaks of 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. 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.

\(^1\) Because of the large modulus increases at higher temperatures, we believe that the apparent decrease in storage modulus at low temperatures is due to experimental error; this is the subject of ongoing analysis.
Figure 1. Storage moduli as a function of temperature.

Figure 2. Loss moduli as a function of temperature.
The time-dependent modulus of a viscoelastic material can be described using a Prony series representation of the form

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

(1)

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

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

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

(2)

The Prony series coefficients in (2) for each sample were found by fitting the storage and loss moduli data, obtained over the extended frequency range using time-temperature superposition, to a 30-term Prony series using the linear least squares solver DYNAMFIT [11]. An additional constraint, which can be imposed within DYNAMFIT, enforces the condition that all Prony coefficients $E_j$ be greater than zero. Once the Prony series coefficients have been found, one can show that the relaxation spectrum $H(t)$ can be approximated using the Alfrey’s rule [12], such that

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

(3)
Using this procedure the relaxation spectra for the blank and reinforced polycarbonate samples were obtained and are shown in Figure 3. 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 and maintains its bulk characteristics.

![Figure 3. Relaxation spectrum for polycarbonate-based samples.](image)

Thus 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 readily indicates the difference in viscoelastic behavior, 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 [10, 13]. An understanding of the
impact of the nanotubes of the effective viscoelastic response of the NRP will be critical to develop accurate models of the long-term properties of the material.

REFERENCES


