SPECTRAL RESPONSE AND EFFECTIVE VISCOELASTIC PROPERTIES OF MWNT-REINFORCED POLYCARBONATE

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ABSTRACT
The impact of embedded carbon nanotubes on the effective viscoelastic response of a nanotube-reinforced polycarbonate system is characterized by studying the temperature- and frequency-dependent behaviour of the material. Macroscale experimental results demonstrate that the effective relaxation spectra of the samples is consistent with non-bulk polymer regions of restricted molecular mobility. Such low mobility regions are attributed to localized nanoscale interactions between the nanotubes and individual polymer chains.
Keywords: carbon nanotubes, reinforced polymers, viscoelasticity, relaxation spectra

1. INTRODUCTION

Due to their size and outstanding mechanical, electrical, and thermal properties, carbon nanotubes (NTs) have been proposed for a number of applications. One potential application, that has been the subject of numerous investigations, is the use of NTs as a small volume fraction filler phase in nanotube-reinforced polymers (NRPs). Of particular interest is the use of NRPs for structural applications, where recent experimental results demonstrate moderate improvements in the effective elastic behaviour of these materials [1-8]. Various issues have been identified in the literature as being critical to obtaining the optimal performance of these materials, including: dispersion of the NTs within the polymer, nanotube orientation, alignment, and waviness [9-11], and the NT-polymer interface and load transfer mechanisms [4, 12]. The different nanotube forms (single-walled, multi-walled, and bundles) and the various methods of NT fabrication will also influence the efficiency of the nanotubes as a reinforcing phase within a polymer matrix.

However, to date a limited amount of experimental research has looked at the effective viscoelastic (time- and temperature-dependent) behaviour of nanotube-reinforced polymers [1, 2, 13, 14]. These experimental results indicate that the temperature-dependence of the viscoelastic response of these systems is different than that of the pure polymer. Other forms of nanoscale inclusions, such as vapor-grown carbon nanofibres [15], nano-sized cellulose whiskers [16], nanoclays [17-22], graphite [23], and silica nanoparticles [24] have also been found to significantly alter the viscoelastic response of the polymer matrix composite in comparison to that of the bulk polymer. This is in direct contrast to results obtained for polymers containing micron-sized elastic inclusions. For these materials, the time-independent elastic behaviour of the inclusion does not affect the viscoelastic response of the polymer matrix, leading to composites where the time-dependent (analogously, frequency- or temperature-dependent) response of the composite mirrors that of the matrix [25, 26]. In the current work, the effective viscoelastic response is studied via examination of the spectral response of the NRP using time-temperature superposition, which provides a better understanding of the changes in viscoelastic response of the material due to the embedded nanotubes.

It is suggested that the change in viscoelastic behaviour, in the case of nanoscale-reinforced materials, is due to altered molecular mobility of the polymer chain segments in the vicinity of the nanoinclusions. Both the similarity in length scales between the inclusions and the individual polymer chains and their high surface-to-volume ratios lead to significant regions of altered polymer mobility, which has been discussed extensively for small amounts of both nanoclay [17-22] and more recently for carbon nanotube [1, 2, 13, 14] inclusions. Here discussion will be limited to changes in local polymer mobility due to mechanical interaction/entanglements of the polymer chains with the embedded nanotubes. However, ongoing efforts to strengthen the nanotube-polymer interface via chemical functionalisation may be expected to enhance these effects [27-29].

To study the effective viscoelastic response of NRPs, samples of polycarbonate (PC) reinforced with multiwalled carbon nanotubes were synthesized for experimental characterization. The polymer was General Electric Lexan 121, a bisphenol-A based polycarbonate with a melt-flow index of 17.5. The MWNTs (outer diameter ~30 nm) used here were catalytically grown via chemical vapor deposition using Xylene-ferrocene as the carbon source. The lengths of the MWNTs are on the order of tens of microns. Briefly, the fabrication of the NRP samples was as follows: first, the NTs and PC were separately dispersed/dissolved in N-Methyl Pyrrolidone (NMP), respectively. The NT dispersion and PC solution were then mixed together and sonicated for 60 min to ensure a uniform dispersion of the NTs within the polymer. The solvent was then removed from the mixture using methanol as an anti-solvent, such that the nanotube-polycarbonate composite immediately precipitated while the NMP was removed into the methanol phase. After drying the samples at 80 °C under vacuum, the samples were hot-molded at 260 °C into a rectangular shape for mechanical testing. Thicknesses for the as-molded samples were approximately 0.5-1 mm. For comparison, samples of pure polycarbonate were fabricated using the same solvent-processing method. As shown in Fig. 1, transmission electron microscopy images of the nanotubes in NMP show excellent dispersion.

Fig. 1: TEM image of MWNTs dispersed in NMP prior to composite fabrication.

All experimental data were collected using a TA Instruments DMA 2980 dynamic mechanical analyzer and a film tension clamp. The results for two distinct types of mechanical tests are presented in this paper. In each case the samples were subjected to a sinusoidal displacement of 3 μm (resulting in strains less than 0.1%). For temperature sweeps to measure the glass transition temperature (T_g), the samples were tested at a constant frequency of 1 Hz while the temperature was increased from room temperature to at least 180 °C at a rate of 2 °C/min. For the frequency domain analysis, the samples were tested under isothermal conditions from 0.2 to 200 Hz at five frequencies per decade, evenly spaced in log frequency space. After the testing at a particular temperature was completed, the temperature was then jumped 5 °C (taking less than 1 min), held isothermally for 5 min, and then the frequency scanning at the new test temperature conducted. This procedure was repeated until the final test temperature was reached.

For completeness, the storage and loss moduli of the samples as a function of temperature are shown in Fig. 2. Consistent with other experimental data [1, 2, 13], the impact of the NTs on the temperature-dependent behaviour of the NT-polycarbonate system can be summarized as follows:

1. modest increases in the low temperature (below the polymer T_g) storage modulus,
2. significant increases in the high temperature (above T_g) response of the material,
3. slight shifting of the effective glass transition temperature with the addition of the nanotubes (as defined by the peak of the loss modulus), usually to temperatures greater than the T_g of the polymer,
4. broadening of the loss moduli and loss tangent (not shown) peaks on the high-temperature side.

Note that the changes in viscoelastic behaviour presented here are caused by the addition of a very small amount (1 or 2 wt%) of carbon nanotubes in the current samples. It is expected that these changes in viscoelastic behaviour will be magnified for larger weight fractions of nanotubes, which is the subject of ongoing work.

However, a detailed analysis of the temperature-dependent properties of NRPs is necessarily limited due to the lack of quantitative models developed for such a response. Thus to further elucidate and quantify the impact of the nanotubes on the effective viscoelastic behaviour of the NRPs, the principle of time-temperature superposition is used to study changes in the relaxation spectra of an NRP system. The relaxation spectra, which is directly related to changes in molecular mobility, can be obtained via analysis of frequency domain data as described in detail elsewhere [14]. Briefly, the time-dependent modulus of a viscoelastic material can be described using a Prony series representation of the form:

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

where E_∞ is the rubbery asymptotic modulus, E_j are the Prony series coefficients, and τ_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:

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

The Prony series coefficients (2) in were found in the following manner. First, frequency domain data in the range of 0.2 to 200 Hz (limited by the range of the DMA instrument) were collected under isothermal conditions at temperatures between 130 and 170 °C. Then using standard time-temperature superposition [25], the data at different temperatures were shifted horizontally to obtain master reference curves at a given temperature, as shown in Fig. 3 and Fig. 4. Finally, these experimental reference curves were then fit with a 30-term Prony series
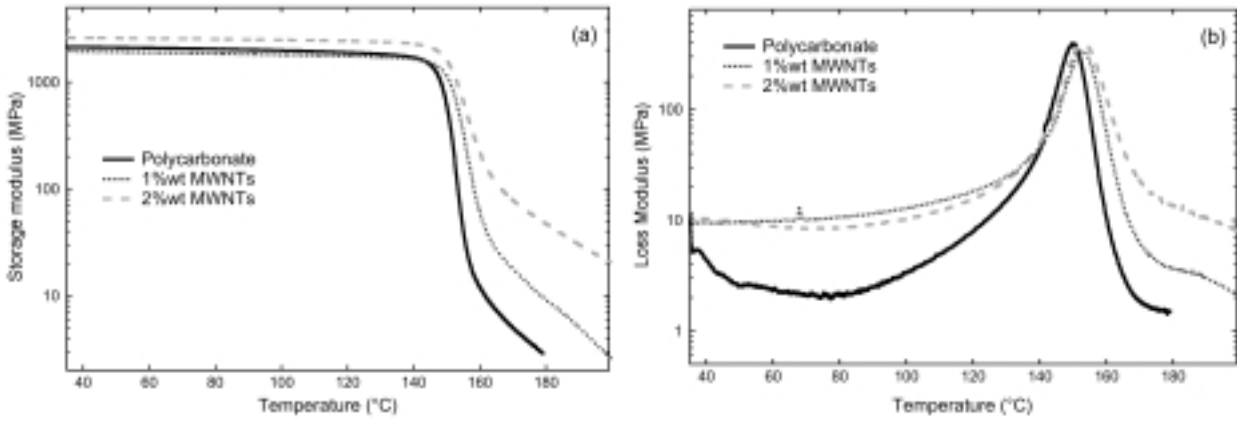
Fig. 2: Storage (a) and loss (b) moduli of the polycarbonate-MWNT samples as a function of temperature.
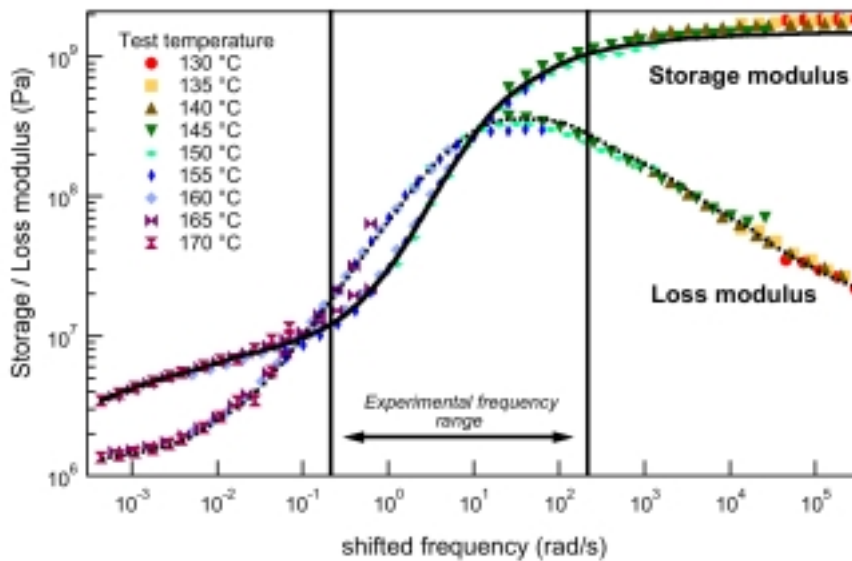

Fig. 3: Storage and loss moduli of the pure polycarbonate sample as a function of frequency. Experimental data collected within a frequency range of 0.2 to 200 Hz at different isothermal temperatures were shifted via time-temperature superposition to form a master reference curve at 150 °C.

using the linear least squares solver DYNAMFIT [30]; here the relaxation times t_j are assumed to be evenly spaced in log time, and the corresponding Prony coefficients E_j determined. From here the relaxation spectrum $H(\tau)$ can be approximated using Alfrey's rule [25] such that:

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

Using this procedure, the relaxation spectra for the blank and reinforced polycarbonate samples were obtained from the experimental data and are shown in Fig. 5. Here one sees a significant increase in the relaxation spectrum at longer times, and a corresponding broadening of the primary relaxation peak,

with increasing nanotube loading. This change in relaxation spectrum is attributed to an increased number of relaxation modes introduced at longer time scales that contribute to the effective viscoelastic response of the NRP. These changes in viscoelastic behaviour are consistent with the presence of regions of reduced polymer chain mobility due to the presence of the embedded nanotubes.

However, the location of the peak of the relaxation spectra does not appreciably change with the addition of the nanotubes, which suggests that the primary relaxation mechanism within the NRP is the same as that within the bulk polymer sample. Thus while the polymer chains in the immediate neighbor-
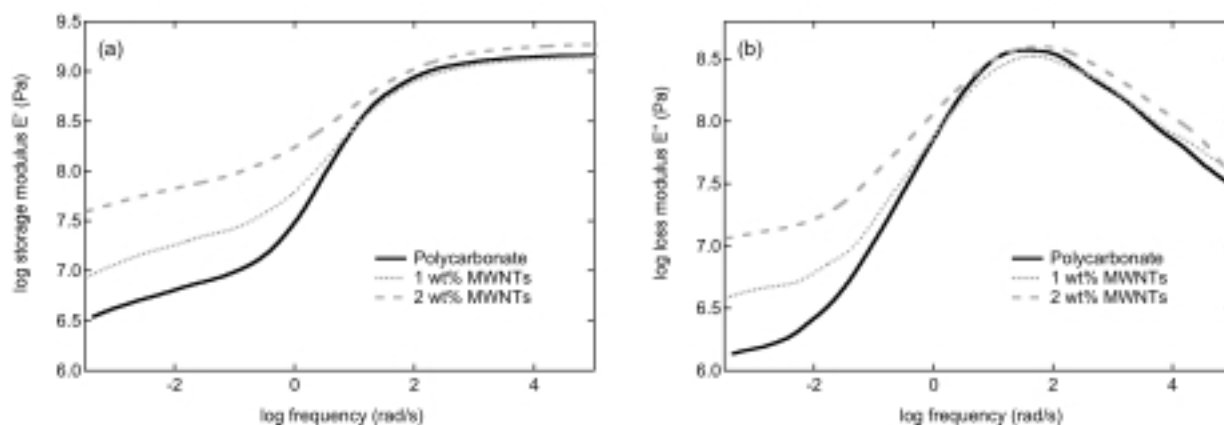
Fig. 4: Storage (a) and loss (b) moduli master reference curves for polycarbonate-MWNT samples at a reference temperature of 150 °C.

hood of nanotubes are constrained, exhibiting reduced mobility and longer relaxation times than the bulk polymer response, the mobility of the polymer chains far removed from the nanotubes is unaffected and maintains the viscoelastic characteristics of the bulk polymer. In this manner the analysis of the relaxation spectra provides a full description of effective viscoelastic behaviour of these materials, which support a three phase nanotube / non-bulk polymer interphase / bulk polymer matrix model for these systems [14]. The results of the relaxation spectra analysis are consistent with the frequency-domain behaviour exhibited in Fig. 4.

In summary, for the first time the principle of the relaxation spectra was used to study the influence of nanotube loading on the effective viscoelastic behaviour of a nanotube-reinforced polymer system. Examination of the relaxation spectra is more insightful then the standard temperature domain analysis of these materials and provides a clear picture of the origin of differences in viscoelastic behaviour between the NRP and the pure polymer systems. Specifically, analysis of the relaxation spectra strongly supports the hypothesis of a reduced-mobility interphase region in the NRP with local, non-bulk polymer chain mobility, as evidenced by the increased contribution of longer-time relaxation processes in the case of the reinforced samples. An additional advantage of the frequency-domain analysis is that it lends itself to micromechanical modeling of the effective viscoelastic behaviour of the system
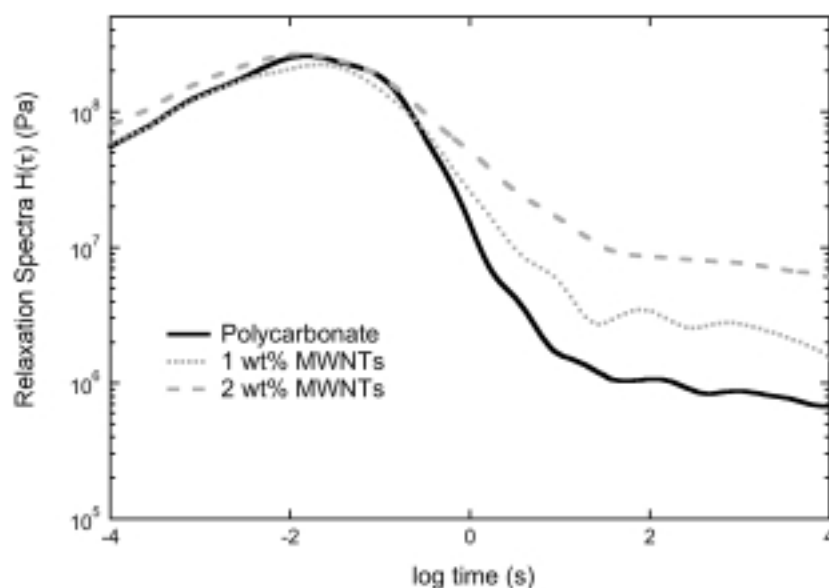

Fig. 5: Relaxation spectra for the polycarbonate-MWNT samples.

[14]. Finally, as the volume of this reduced-mobility polymer increases (at a much faster rate than the nanotube volume fraction [31]), a continuous network of this interphase is likely to form throughout the polymer. Similar in nature to the percolation effect observed with the electrical properties of nanotube-reinforced polymers [32, 33], such a network is likely to have a significant impact on the effective viscoelastic response of the NRP. Note that while demonstrated here for a nanotube-reinforced polymer, this analysis is in general applicable to any nanoparticle-reinforced polymer system. Further work utilizing this technique with higher loadings of nanotubes and different nanoparticle-polymer systems is ongoing.

ACKNOWLEDGEMENTS

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