

Hierarchical polymer dynamics in carbon nanocomposites with strong interfacial attraction

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ABSTRACT

Unlike the idealized “fairy dust” model of polymer nanocomposites, most industrial applications targeting enhanced mechanical performance require particle loadings above the percolation threshold. In such applications, strong interfacial binding between the nanoparticles and the polymer matrix is highly desirable. Despite extensive characterizational studies, the molecular-level coupling in such composites and their impact on the bulk polymer properties are still poorly understood. Here, we present direct neutron spectroscopy measurements of polymer dynamics in highly affine carbon PMMA composites with percolated carbon nanotube (CNT) networks. The data reveal slow domains of transiently pinned interfacial PMMA segments which, upon nanotube percolation, interconnect and form a kinetic cage that traps the faster non-interfacial polymer segments. Quantitatively, the composites experience an order of magnitude slowdown in bulk dynamics relative to PMMA, which persists from local atomic motions up to mesoscale relaxations.

Keywords: SWNT, nanocomposites, particle percolation, polymer mobility, mesoscale relaxations

1 INTRODUCTION

Owing to the unique mechanical properties of carbon nanotube CNTs [1], extensive efforts have been made to design CNT composites for advanced load-bearing applications. In such applications, the envisioned material design is usually based on the assumption that the inclusion of CNTs in a polymer matrix would impart the superior nanotube properties to the composite material [2]. But, in reality, the addition of nanoparticles to a polymer matrix usually disrupts the local structural and dynamical behavior of the polymer matrix [3, 4] and sometimes results in rather undesirable properties. Indeed, the performance of CNT composites still remains short of that of individual carbon nanotubes, which has been a major setback in their commercial use [5]. This unfulfilled promise is speculated to result primarily from weakness points at the CNT-polymer interfaces or the lack of stress-propagation pathways within the matrix. Lately, there has been a growing evidence that non-trivial enhancement in the mechanical performance of polymer nanocomposites can be

obtained through the percolation of the guest nanoparticles [6, 7] and their strong interfacial binding to the host polymer matrix [8]. The former ensures that the nanoparticle network forms easy pathways for stress propagation and results in an even distribution of the load while the latter promotes effective load transfer from the polymer to the nanoparticle network.

For CNT composites, the needle-like structure of CNTs causes the percolation to occur at remarkably low particle loading. The presence of a network of impenetrable rigid rods imposes strong topological constraints on the polymer chains, particularly when the radius of gyration of the polymer is comparable to the mesh size of the particle network. Generally, such composites do not follow conventional nanocomposite theory [9], which renders their properties extremely challenging to predict. The complication is exacerbated by the abundance of interface of CNTs (highest surface-area to volume ratio) which, in the the case of strong polymer/CNT attractions, can significantly perturb the adjacent polymer chains. Insights into the nature of such perturbations and their effect on the polymer properties have been possible through molecular dynamic simulations. Unfortunately, currently available simulations are limited to nanocomposites in the very dilute regime [10, 11] and extrapolation to the percolated regime is not straightforward. The lack of theoretical and computational means for this type of problem necessitates direct experimental observation. In this work, we use neutron scattering spectroscopy to look into the dynamical properties of polymers in such nanocomposites. The advantage of this approach is the ability to access and resolve a hierarchy of dynamics, from atomic motions to mesoscale chain relaxations. Here, we focus on composites of carbon nanotubes and poly(methyl methacrylate) (PMMA), which are known for their mutual affinity and which have been used in earlier load-transfer studies [12]. The results provide a clear picture of the molecular origin of polymer relaxations in such systems.

2 EXPERIMENTAL METHODS

2.1 Samples

The nanocomposites used in this work were prepared with PMMA (Pressure Chemicals) of $M_w = 254.7$ kg/mole,

$M_w/M_n = 1.15$ and three different volume fractions (1, 8 and 15%) of single-wall carbon nanotubes (SWNT) (purchased from Nano-C Inc.) [13], all of which are above the percolation threshold of slender rods. An additional sample (which is only briefly discussed here) was prepared with C60 nanoparticles at a volume fraction of 50%, that is above the percolation threshold of spherical nanoparticles (~35%). The detailed procedure of the sample preparation can be found elsewhere [14, 15]. This procedure does not involve any surface functionalization or dispersion aids that can alter the dynamics and complicate the data interpretation.

2.2 Neutron backscattering Spectroscopy

Backscattering measurements were performed at the high-flux backscattering spectrometer (HFBS) at the NIST Center for Neutron Research. The measurements were carried out on the fully hydrogenated samples in two modes: fixed-window scan (FWS) mode and quasi-elastic neutron scattering (QENS) mode. The first probes atomic mean-square displacements, which we recorded as a function of temperature, T , from 50 K to 460 K in increments of 1K at a rate of 1 K/min. The second measures relaxations over a dynamic range of $\pm 11 \mu\text{eV}$, which we detected at select temperatures. It is important to mention that the neutron incoherent scattering cross-section of hydrogen is an order of magnitude larger than its coherent cross-section and the total scattering cross-section of C and O. The incoherent scattering from the H-atoms in the polymer thus dominates the signal and provides exclusive measurement of the matrix dynamics. The data reduction was done using the Data Analysis and Visualization Environment (DAVE) software [16] developed by NIST.

2.3 Microscopy

Transmission Electron Microscopy (TEM) measurements were performed on microtomed slabs of the composites to test the dispersion of the nanotubes and assess the network properties. Image analysis on several micrographs yielded the average bundle diameter, which we then used to estimate the average mesh size of the tube network [17]. For example, the average bundle diameter was found to be $\approx 8 \text{ nm}$ in the composite with 8 v% SWNT loading, yielding an average mesh size of $\approx 14 \text{ nm}$.

3 RESULTS AND DISCUSSION

We first discuss the local polymer dynamics, as determined from backscattering FWS measurements over a wide range of temperatures, T . This type of measurement yields the incoherent elastic scattering intensity, $I_{el}(Q)$, over an array of detectors with access to different length scales or wavevector transfers, Q . The sum of intensities over the entire Q range is a measure of the fraction of

effectively static entities within the sample. Motions that are slower than the instrumental resolution, i.e. $\approx 2 \text{ ns}$, appear immobile while motions faster than this time frame contribute to non-elastic scattering and decrease the elastic intensity. The elastic intensities from PMMA and the PMMA/SWNT composites were reported in a previous publication [15] over a temperature range of 50K to 460K. The obtained trends are consistent with a picture of transient pinning of polymer segments at the SWNT interface, in agreement with the results of recent molecular dynamics simulations [18]. The Q -dependence of the elastic intensities provides a direct measure of the local polymer mobility. The mean square displacements, $\langle u^2 \rangle$, of the polymer segments are evaluated from $I_{el}(Q)$ using the Debye-Waller approximation [19]:

$$\ln[I_{el}(Q)] \propto -\frac{1}{3}Q^2 \langle u^2 \rangle \quad (1)$$

The resulting mean-square displacements (MSD) indicate a remarkable suppression of the local polymer mobility in the composites relative to pure PMMA (see Fig. 1). It is important to keep in mind that, in the composites, the MSDs correspond to the non-interfacial mobile polymer segments. One would expect these non-interfacial segments to get increasingly constrained with increasing SWNT loading. On the contrary, the MSDs in the composites do not show any significant variation with SWNT loading despite the wide concentration range considered here. An assessment of the SWNT network yields mesh sizes of 7–28 nm for the current concentrations. In comparison, the average coil dimension of the polymer is $2R_g \approx 29 \text{ nm}$, where R_g is the polymer radius of gyration. The mesh size, thus, goes from being on the same order as $2R_g$ for the lowest loading to being much smaller than $2R_g$ for the highest loading. This invariability of the MSD patterns with the compactness of the SWNT network suggests that the fast non-interfacial segments are now kinetically caged by the slow polymer domains around the nanotubes.

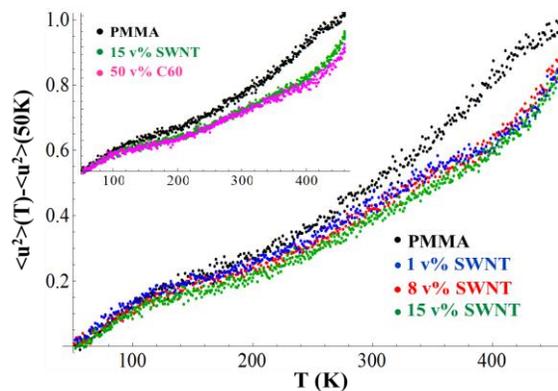


Figure 1: Thermal variations of the MSDs in PMMA and the SWNT composites, showing a significant suppression of local polymer mobility in the composites. The inset shows the overlap of the MSDs in composites with percolated C60 and percolated SWNT networks.

Interestingly, measurements on a similarly prepared nanocomposite with a network of percolated C60 particles show an MSD pattern that is almost identical to those of the percolated SWNT composites (see inset in Fig. 1). A more detailed discussion of the C60 composites will be presented elsewhere. Combined with previous reports on PMMA/C60 composites with much lower loadings [20], this starts to suggest a gradual suppression of the polymer mobility with increasing C60 loading up to the percolation threshold, beyond which the dynamics of the non-interfacial segments get kinetically trapped. The significance of the current result is in the generalization it offers on the behavior of polymers in percolated particle networks, regardless of the particle topology or the compactness of the nanoparticle network. Additional information about the dynamical transitions can be obtained from the MSD patterns by using basic thermodynamic principles. This approach allows the identification of the glass transition temperatures, T_g , in the different samples [15]. We find that T_g in the composites is shifted by $\sim 20\text{K}$ relative to pure PMMA, and is consistent with the picture of two dynamic polymer populations, where the connectedness of the slow domains raises the kinetic barrier of the glassy state and results in higher T_g .

Though the MSD patterns provide a lot of insight into the local mobility within the sample, they lack a quantitative description of the relaxation times and timescales of the associated motions. This information can be obtained from complimentary QENS measurements that access a wider energy window. An example on the QENS spectra on PMMA is shown in Fig. 2 at various melt temperatures. The broadening of the energy spectra, relative to the instrument resolution, is associated with the structural relaxations of the polymer dynamics within the accessed energy window, such that faster dynamics cause stronger broadening. This behavior is evident in the PMMA data shown in Fig. 2 as a function of increasing temperature. The QENS spectrum is described by the Fourier transform of a KWW function in the time domain that has the expression [21]:

$$S_s(Q, t) = A(Q) \exp[-(t / \tau_R)^\beta] \quad (2)$$

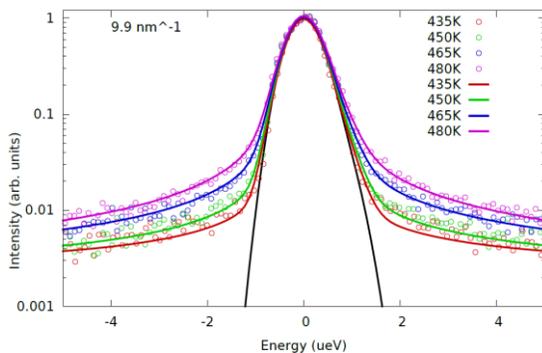


Figure 2: Quasi-elastic neutron scattering data on PMMA at $Q = 0.99 \text{ \AA}^{-1}$ at various melt temperatures along with the corresponding stretched exponential fits (colored lines). The black solid line represents the instrumental resolution.

where $A(Q)$ is the Debye-Waller factor, τ_R is the relaxation time of the measured dynamics and β is the stretching exponent. Fits of the QENS data are performed using eq. 2 and a stretching exponent of $\beta = 0.3$ over each of the detectors, i.e. for Q values between 0.25 \AA^{-1} and 1.75 \AA^{-1} . The fits yield the relaxation times of the polymer, which are plotted in Fig. 3 as $\tau_{av} = \frac{1}{\beta} \Gamma(\frac{1}{\beta}) \tau_R$, for $T = 480 \text{ K}$.

The calculated relaxation times show identical relaxation patterns in the composites at different SWNT loading. The relaxation times exhibit a Q -dependence that is typical of polymeric systems [21]. At high Q (small length scales), the dynamics are relatively fast, as expected for local atomic relaxations, whereas the relaxations become slower at smaller Q values (larger length scales) as we start to probe longer correlations within the system. But more importantly, the τ_{av} patterns indicate an order of magnitude slowdown in the polymer dynamics in the composites compared to pure PMMA over the entire accessed Q range (corresponding to length scales of $\sim 3 \text{ \AA}$ to 30 \AA). This result is consistent with previous neutron spin-echo (NSE) observations on a similar system [15]. Those measurements were performed at $Q = 0.9 \text{ \AA}^{-1}$, at which backbone relaxations are selectively studied. The extracted relaxation times also showed an order of magnitude slowdown in the polymer backbone dynamics in the SWNT composites relative to PMMA. It is important to point out that the dynamics probed by QENS are the self relaxations of the hydrogen atoms of the polymer, whereas those probed by NSE represent collective polymer relaxations at a well-defined length scale determined by the choice of Q -value at which the measurements are performed. Altogether, the results show a clear dynamical hierarchy within the composites, starting from transient pinning of local polymer segments at the nanoparticle interface to suppressed structural relaxations at longer length scales.

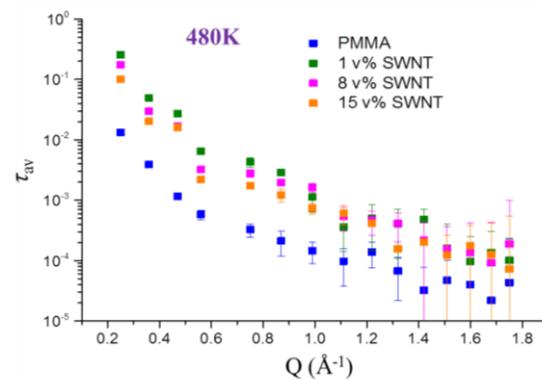


Figure 3: Q -dependence of the average relaxation times of the polymer at $T = 480\text{K}$, in the pristine matrix and in the composites. The SWNT composites show an order of magnitude slowdown in the polymer relaxations relative to pristine PMMA over the entire accessed Q -range. Error bars represent ± 1 standard deviation.

4 CONCLUSIONS

Using neutron scattering spectroscopy on PMMA and PMMA-carbon composites, we were able to get insights into the spatial and temporal hierarchy of polymer dynamics in a unique class of polymer nanocomposites with percolated nanoparticle networks and strong polymer-nanoparticle attractions. The measurements reveal a picture of transiently pinned polymer segments near the nanoparticle interface due to strong interfacial binding. These pinning events generate slow interfacial polymer domains, which upon nanoparticle percolation, interconnect and kinetically trap the faster non-interfacial polymer domains. By combining elastic incoherent backscattering scans with quasi-elastic neutron scattering measurements, we evaluated the effect of those local dynamic modes on the mobility of the non-interfacial polymer segments and their longer length-scale relaxations. The results showed a remarkable suppression in the local mean-square displacement patterns in the composites relative to pure PMMA. This observation was corroborated by an order of magnitude slowdown in the polymer relaxations in the percolated SWNT composites compared to PMMA over the entire Q -range accessed in the experiments. Moreover, complementary measurements on PMMA nanocomposites with percolated C60 networks show almost identical mean-square displacement patterns of the polymer as nanocomposites with percolated SWNT networks. This suggests a general dynamical behavior of polymers in percolated particle networks with strong interfacial attractions, where the connectivity of the polymer chains causes local dynamical modes to propagate to longer length- and time-scale dynamics.

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