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The Significance of Percolation on the Dynamics of Polymer Chains Bound to Carbon Black

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INTRODUCTION

A critical need in the fundamental understanding of reinforcement in filled polymers is the characterization of the polymer-filler interface and the dynamics of the polymer in this interfacial regime. In carbon black filled polymers, one of the central themes in the mechanism of reinforcement is that of "bound" polymer. Understanding the dynamics of this bound polymer may be key to arriving at an understanding of reinforcement mechanisms in filled polymers. The interactions between polymers and filler surfaces are also key in the development of more advanced nanocomposite materials.

We have previously utilized inelastic neutron scattering methods to examine the variation of bound polymer dynamics as a function of carbon black type for a single, initial carbon black concentration.[1] An apparent change in the distribution in backbone motions was observed in the bound polymer compared with the pure polymer. In this study, we extend our prior work to examine the bound polymer dynamics as a function of the type of carbon black and the initial concentration of carbon black. The results suggest that two types of dynamic behavior are observed as a function of the initial carbon black concentration. This critical cutoff concentration may be related to the percolation threshold of the carbon black and suggests that quantifying the amount of bound polymer is insufficient for understanding the relationship between mechanical behavior and bound polymer content.

EXPERIMENTAL

We have compared the dynamics of bound polymer using inelastic neutron scattering measurements performed on a Fermi chopper time-of-flight (TOF) spectrometer. The data is presented in a "density of states" formalism, which gives the distribution of the vibrational energies, $g(\varepsilon)$, in the sample over the accessible energy range of the instrument. The vibrational energy range covered by the neutron method can reach very low energies (i.e. frequencies) which are lower than the range accessed by infrared or Raman techniques, hence, longer wavelength, lower energy motions can be probed. We examine samples containing only bound polymer by performing a Soxhlet extraction on all samples to remove all unbound polymer and compare all results to the pure, uncompounded polymer.

Materials

Three different types of carbon black were compounded into a synthetic, commercial polyisoprene (Natsyn 2200, Goodyear Tire and Rubber Co.).[2] Each carbon black is identified by

the specific grade (N299, G299, or N762). The G299 carbon black is the graphitized version of the N299 carbon black and was prepared by heating a sample of N299 carbon black under nitrogen atmosphere in an induction furnace at 2700 °C. Detailed characterization of the polymer, carbon blacks, compounding procedure, and Soxhlet extraction procedures have been described in a previous publication.[1] Three concentrations of carbon black filled samples were prepared: 20 parts (by mass) of carbon black per 100 parts of rubber (20 phr) (phr is defined as parts by mass of the component per one hundred parts by mass of the rubber) (nominal mass fraction of carbon black = 16.7 %), 30 phr (nominal mass fraction of carbon black = 23.1 %) and 50 phr (nominal mass fraction of carbon black = 33.3 %). We will refer to the samples by their initial carbon black concentration in phr.

Instrumentation

The unextracted 20 phr and 50 phr N299 filled polyisoprene and the extracted 50 phr N299 filled polyisoprene were cut into small squares and mounted directly on aluminum pins for the microtome. The extracted 20 phr N299 specimen was embedded in partially precured Epofix because it was too thin to be sectioned directly. Ultra-thin sections of nominal thickness 50-70 nm were cut cold (-100 °C) at 0.8 mm/s on Leica Ultracut UCT Microtome using a 45° dry cryo diamond knife. The sections were mounted dry on carbon substrate grids of 200 mesh (Ted Pella type B). Contrast of carbon black in the polymer was sufficient and no staining was necessary. Bright-field transmission electron microscopy (TEM) images were obtained on a Philips 400T at 120 kV under low-dose conditions.

The Fermi chopper time-of-flight spectrometer (TOF) instrument located at the NIST Center for Neutron Research (NCNR) was used for these experiments. Details of the experimental conditions have been published elsewhere.[1] The TOF technique measures $S(q,\omega)$, therefore, by integrating over all q at each ω, the so-called density of vibrational states, $g(\varepsilon)$, is obtained. All data presented have also been normalized over the entire energy range of the instrument so the area under the curve is unity.

RESULTS AND DISCUSSION

The morphologies of the unextracted 20 phr and 50 phr N299 filled polyisoprene are compared in Figures 1a-b. TEM images at low magnification show that the quality of carbon black dispersion is very good, at higher magnifications the size of the primary particles (~20 nm) is evident. After extraction, it is difficult to distinguish between the 20 phr and 50 phr N299 filled rubbers shown in Figures 1c-d, because the unbound rubber has been removed and the remaining bound rubber envelops the carbon black particles and collapses to fill some of the void space. By TEM, it appears that a very uneven surface is present, suggesting that some voids between aggregates remain after extraction. Because TEM is a transmission technique and the samples are very dense, however, it would be preferable to verify this observation with a technique that better characterizes topology, such as scanning electron microscopy or atomic force microscopy. Prior TEM characterization[3] of carbon black filled rubbers involve fixing the rubber with a stain, such as bromine, and then embedding in a methacrylate or epoxy resin, for room temperature microtomy. This is often because cryomicrotomy techniques are not always available to cut soft rubber samples in their native state.

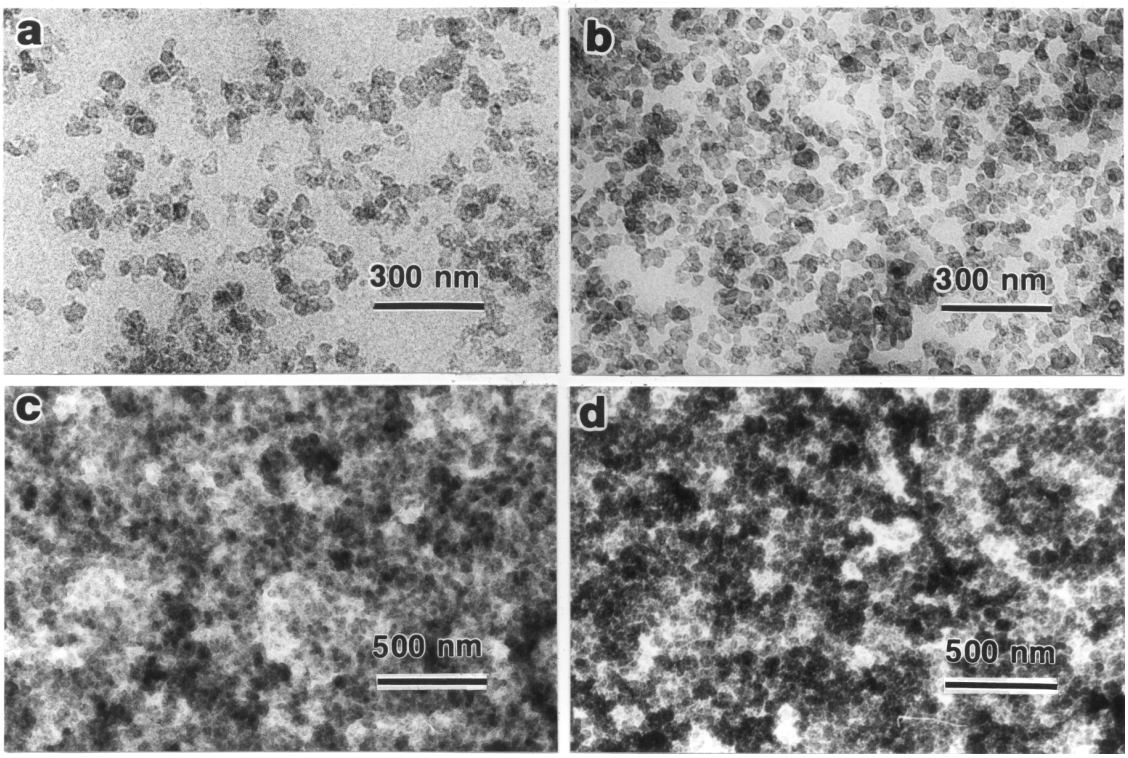

Figure 1. TEM of carbon black filled polyisoprene prepared by cryomicrotomy
a) 20 phr unextracted b) 50 phr unextracted c) 20 phr extracted d) 50 phr extracted

The concentration dependence of the density of states spectra for each of the grades of carbon black are shown in Figure 2. Due to difficulties in obtaining extracted N762 samples, data is only available for the N762 at an initial concentration of 30 phr. Estimates of the standard error are shown only for the pure polyisoprene spectra for clarity and are similar for the other data. In the data for the samples containing an initial concentration of 20 phr carbon black (Figure 2a), a broad peak at 25 meV is observed in all samples. Also turndown in the spectra around 10 meV is observed for all samples, but evidence for a peak at this position is weak. Within the statistics of our measurements, there appears to be no significant difference between the pure polyisoprene spectrum and the other two spectra of the bound polymer filled with carbon black (N299 and G299).

At initial carbon black concentrations of 30 phr, significant differences in the density of states spectra are observed as a function of the type of carbon black (Figure 2b). The N762 filled sample spectrum is closest to the spectrum of the pure polyisoprene, while the G299 sample spectrum has the largest differences from the pure polyisoprene. The peak at 25 meV in the G299 filled sample is higher in intensity, and narrower compared to the pure polyisoprene. The peak at 25 meV is slightly broader in the N299 filled sample and the peak at 25 meV in the N762 filled sample is nearly as broad as in the pure polymer case. An obvious peak around 8 meV to 10 meV is also observed in both the G299 and N299 filled samples compared to the pure polymer, while no peak at 8 meV to 10 meV is observed in the N762 spectrum. At initial carbon black concentrations of 50 phr, the spectra for the N299 and G299 samples appear to be identical, with relatively narrow peaks at 25 meV as well as peaks at ca. 8 meV (Figure 2c.)

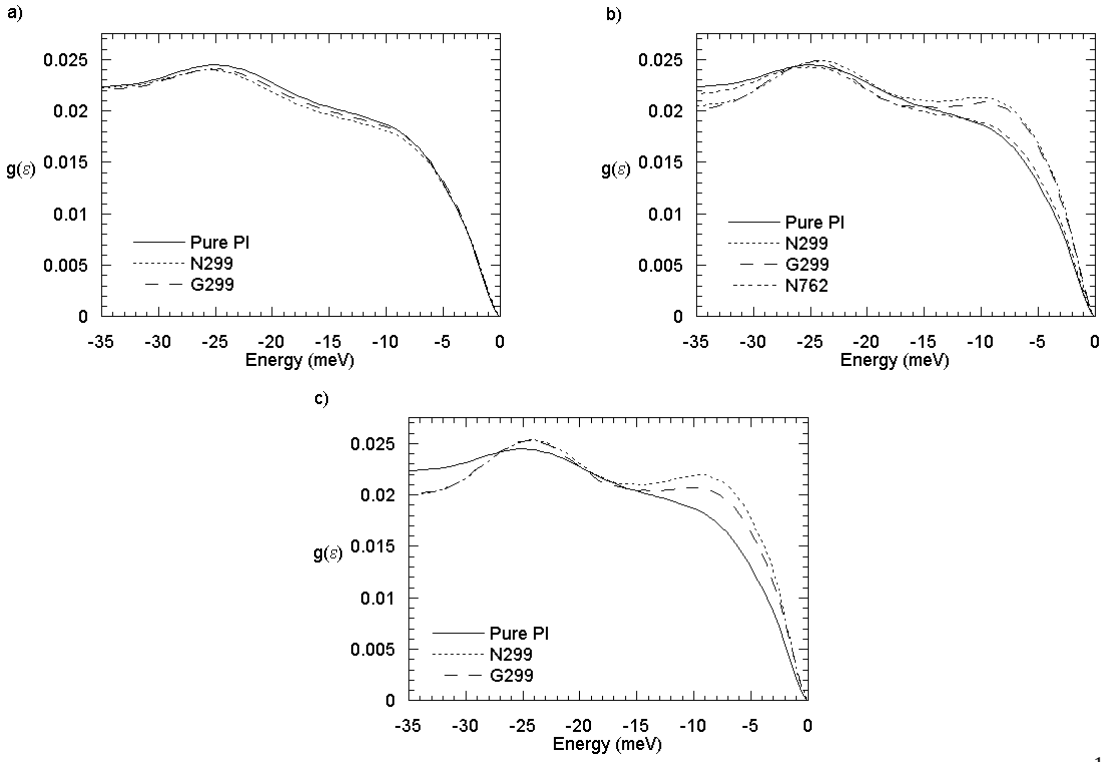

Figure 2. Density of vibrational states, g(ε), as a function of energy (1 meV = 8.07 cm^{-1}) for each of the initial carbon black concentrations: a) 20 phr; b) 30 phr; c) 50 phr.

Based on prior work by Frick and Fetters,[4] the peak at 25 meV is related to the first methyl group librational transition, while the feature at 8 meV to 10 meV is attributed to backbone oscillations. At 20 phr, there is no difference between the dynamics of the bound polymer and pure polymer. At the highest carbon black concentrations (50 phr), the bound polymer dynamics are very different from the pure polymer dynamics. Depending on the grade of carbon black, the 30 phr spectra resemble either the bulk polyisoprene (N762) or the bound polyisoprene spectra at higher carbon black concentrations. From the concentration dependence observed in this study, there appear to be two types of bound polymer vibrational dynamics.

Differences in the percolation values for each of the three grades of carbon black have been measured on the unextracted samples by electrical resistivity measurements (Figure 3). The resistivity of the G299 carbon black filled polymer decreases at low loading levels, while the N762 carbon black filled polymer resistivity decreases at much higher carbon black levels. The N299 carbon black filled material shows resistivity behavior that lies between the G299 and N762 carbon blacks. Coupled with the resistivity results, it appears that the local dynamics of the bound polyisoprene are strongly correlated to the percolation concentration of the carbon black. Our results suggest that while bound polymer may play a critical role in the reinforcement of polymers by fillers, the nature of the bound polymer dynamics as a function of the filler concentration may be a determining factor in the extent of reinforcement achieved by a particular filler.

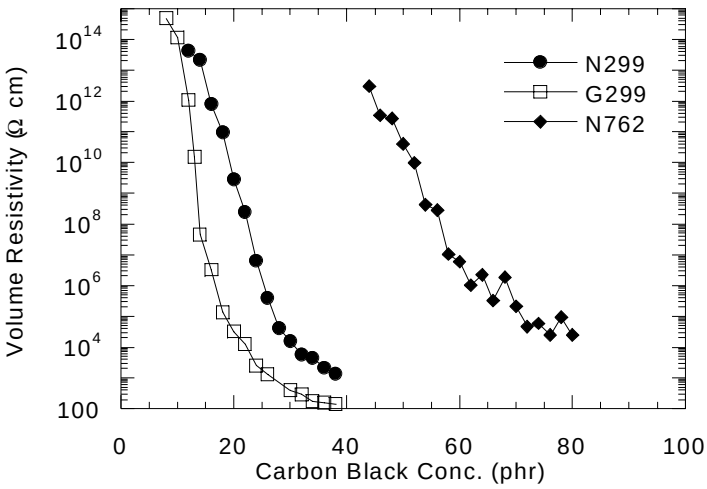

Figure 3. Volume resistivity of the unextracted carbon black filled polyisoprene compounds as a function of carbon black concentration for each grade of carbon black.

In our previous studies on carbon black filled polyisoprenes, the increase in the peak intensities due to methyl group librational motion as well as backbone motions was attributed to an apparent enhancement in local mobility of the bound polyisoprene. However, we have recently obtained results on silica filled poly(dimethyl siloxane) (PDMS) by neutron TOF methods to examine the influence of various surface chemistries on the local polymer dynamics as well as the influence of crosslinking.[5] The density of states spectrum for pure PDMS is similar to the pure polyisoprene spectrum, consisting of two peaks at similar energies. Based on prior work by Henry and Safford,[6] the high-energy peak in the pure PDMS at 22 meV is related to threefold methyl group rotation/vibration motions as well as librations of the entire chain that affect the methyl group. The low energy peak at 8 meV is attributed to unspecified low frequency skeletal and interchain vibrations which are sensitive to chain conformation.

Henry and Safford observed peak broadening and smearing, which they attribute to polymer adsorption counteracted by a decrease in chain flexibility due to chain adhesion to the filler surface. In contrast, we observe a sharpening of peaks upon the addition of filler to the PDMS, a result that is consistent with increased order of polymer at the filler interface compared to polymer in the bulk. In crosslinked samples, Henry and Safford observed that the high-energy peak narrowed and shifted to lower energies and the low energy peak became more prominent. When the crosslinked samples were stretched, the low energy peak was observed to sharpen and intensify, indicating the effect of chain ordering on the spectra. These changes were attributed to a reduction of the methyl group freedom, which is compensated by an enhancement of bending and torsional skeletal modes. The sharpening and shifting of peaks is similar to the behavior exhibited by the carbon black filled samples described above.

Based on the interpretation of the PDMS data as well as work comparing the inelastic neutron spectra of amorphous and crystalline ethylbenzene,[7] we believe a more plausible explanation for our results on polyisoprene bound to carbon black surfaces may be the ordering of the bound polymer chains on the surface of the carbon black. The presence of filler, and polymer interactions with the filler surface perturb both the methyl group rotation/vibration motions and the vibrational modes of the chain backbone. The statistical distribution of all vibrational modes narrows, suggesting each polymer chain, on average, experiences a more

similar environment with its neighbors, i.e., a greater degree of order, than in the bulk. This interpretation is consistent with recent molecular dynamics calculations of polymer chains near a filler surface,[8] and with numerous prior studies that indicate the bound chains are more rigid than the bulk polymer. The concentration dependence of the results is also consistent with data indicating that the amount of bound polymer decreases with increasing initial carbon black concentration. Further, for filler concentrations at or above percolation, we see clear evidence of chain ordering, whereas below percolation the polymer chains experience an environment that is similar to that of the bulk. Based on the available carbon black surface area, the bound polymer-layer thickness decreases with increasing initial carbon black concentration. This is consistent with a bound polymer chain lying down on the carbon black surface, occupying more interaction sites and bridging various carbon black aggregates in the sample above the percolation value for the carbon black. Below the percolation value for the carbon black, lack of bridging by polymer chains between the aggregates produces a thicker polymer layer, where the number of contacts per chain is decreased and the chains are not as constrained to the surface.

CONCLUSIONS

We have shown that the inelastic neutron scattering spectra of polyisoprene bound to various carbon blacks displays limiting behavior at low and high initial carbon black concentrations. At low carbon black concentrations (< 20 phr), the spectra of the bound polymer are no different from the pure polymer spectrum. However, at high carbon black concentrations (> 50 phr), the dynamics of the bound polymer are significantly different from the pure polymer, consistent with enhanced ordering of the polymer layer at the surface. These results suggest that the percolation value of the carbon black plays a role in the transition from one type of bound polymer dynamics to another.

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