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NMR and Raman spectroscopic characterization of single walled carbon nanotube composites of polybutadiene

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Abstract

Significant shifts of the frequency of the Raman spectra of the tangential mode of single walled carbon nanotubes (SWNTs) and fluorinated tubes (FSWNTs) in composites of polybutadiene (PB) were observed relative to the pristine SWNTs indicative of the interaction between the polymer and the SWNTs. Proton NMR line width measurements demonstrate partial suppression of polymer segmental motion for both types of nanotube composites and spin-lattice relaxation results indicate that short time-scale localized motions are also affected by SWNT inclusion, more so for FSWNTs. Hardness measurements as a function of wt% SWNTs and FSWNTs in the polymer show larger enhancements of hardness in the composite with the fluorinated tubes.

I. INTRODUCTION

Because single walled carbon nanotubes (SWNTs) have the largest aspect ratio of any known fiber and have tensile strength on the order of 45 GPa, they have the potential to be the ultimate reinforcing material. Enhancements of hardness and tensile strength have been observed in SWNT/polymer composites.¹ However, in most cases the increases have been considerably less than predicted. Typical enhancements range from 23–78% for polymers containing 5% by weight of SWNTs. For example a composite of poly(p-phenylene benzobisoxazole) containing 5% SWNTs shows a 23% increase in tensile strength compared to the undoped polymer, while a similar composition of an SWNT poly (vinyl alcohol) composite showed a 78% increase.^{2,3} Possible reasons for the less than optimum enhancements of strength are poor dispersion of the tubes, lack of alignment, and the existence of bundles of tubes. It is likely that the bundling of the tubes is the most serious obstacle, firstly because the aspect ratio is reduced, and secondly the weak van der Waals forces between the tubes in the bundles means the tubes can easily slip under stress, resulting in a shear modulus comparable to graphite. It has been shown that linking neighboring tubes in the bundles may result in a significant increase in the loading modulus by eliminating sliding between the nanotubes.⁴ This suggests that side walled functionalized tubes may be more effective in increasing the mechanical strength of composites.

It has been shown that side wall fluorinated nanotubes can produce a significant increase in hardness compared to unfunctionalized single walled tubes in polyacrylonitrile and polyisobutylene.^{5,6} However, the generality of this result and its applicability to other

polymer systems need to be examined. Enhancement of strength also requires interaction between the single walled nanotubes and the polymer. An objective of this work is to compare this interaction for nonfunctionalized SWNTs and fluorinated SWNTs using Raman spectroscopy and NMR. Also presented are hardness measurements which show that fluorinated SWNTs increase mechanical strength more than nonfunctionalized SWNTs.

II. EXPERIMENTAL

A typical fabrication of the PB/SWNT composite involved dissolving 0.10 g of PB in benzene and suspending 0.005 g of SWNTs in the liquid. The benzene containing the suspended SWNTs and dissolved PB was allowed to slowly evaporate while being subjected to sonication. The evaporated PB containing the SWNTs was then dried for two hours at 75 °C. Both the single walled and fluorinated carbon nanotubes were obtained from Carbon Nano-technologies Incorporated (Houston, TX) where they are grown by the HiPCO process. Examination of these pristine tubes by paramagnetic resonance indicates the presence of a ferromagnetic signal arising from the magnetic nanoparticles, which serve as the catalyst for growth.

Raman measurements were made using a J.Y. Horiba confocal micro Raman spectrometer (Edison, NJ) using He-Ne laser light with a wavelength of 632.8 nm. NMR measurements were conducted on a Chemagnetics CMX300 spectrometer (Ft. Collins, CO), operating at an ^1H NMR frequency of 301.0 MHz. Variable temperature NMR spectra were obtained by Fourier transformation of the transient signals following either single pulse or solid echo excitation, with approximately 2 μs pulse widths. Wide-line (static) rather than magic angle spinning NMR was deliberately used to better assess the effect of motional narrowing as a function of temperature. Spin-lattice relaxation times (T_1) were determined by the inversion recovery method. Spectral intensities shown later were not adjusted for differences in sample masses or gain settings.

Hardness measurements were made using a type A model DD-3 REX digital durometer (Grove, IL). The hardness is reported in durometers as described by the American Society for Testing and Materials specification ASTM D2240.

III. RESULTS AND DISCUSSION

A. Raman measurements

For SWNTs to mechanically reinforce a polymer, there must be some bonding between the polymer and the SWNT. Raman spectroscopy can be used to study this interaction. Figure 1 shows the tangential mode of the pristine SWNTs (bottom) and the SWNTs in the polymer composite (top). The mode has shifted up from 1574 cm^{-1} in pristine SWNT to 1579 cm^{-1} in the polymer composite. The lines are also broader in the composite. The modes observed here are from semiconducting carbon nanotubes which constitute approximately 2/3 of the total in a typical synthesis. Observation of the Raman spectra of metallic tubes requires excitation with a laser having a wavelength of 647.1 nm. This shift of the tangential mode for the SWNTs in the polymer indicates some interaction between the SWNTs and the polymer probably via the CH_2 side groups on the polymer. Note also that the D mode at 1320 cm^{-1} which is associated with defects on the tube surface has increased in intensity relative to the intensity of the tangential mode in the polymer matrix, indicating that the processing, likely the sonication, has introduced some defects onto the surface of the tubes.⁷ When SWNTs are suspended in benzene and subjected to sonication, Raman measurements on the SWNTs after the benzene has evaporated show an increase in the intensity of the D mode relative to the G mode, indicating that sonication can do damage to the SWNTs. The D mode has shifted from 1320 cm^{-1} in the pristine SWNT to 1340 cm^{-1} in the polymer

composite. This shift, however, could be due to the sonication induced damage of the tubes. The upward shift of the frequency of the tangential mode in the polymer could also be a result of stress on the SWNTs, perhaps arising from the pressure of the polymer matrix on the SWNTs. Measurements of the effect of pressure on the SWNTs show that the frequency of the tangential mode increases linearly up to 2 GPa with a slope of approximately $7.37 \text{ cm}^{-1}/\text{GPa}$.⁸ The 5 cm^{-1} upward shift observed here suggests the pressure would be about 0.7 GPa, which is considerably higher than what might be expected.

The two low frequency radial breathing modes (RBMs) observed in the pristine SWNTs at 211 cm^{-1} and 251 cm^{-1} shifted up in the polymer to 215 cm^{-1} and 253 cm^{-1} . The frequencies of these modes have been shown to relate to the radius of the tubes by

$$R(\text{\AA}) = 1119.53/\omega(\text{cm}^{-1}). \quad (1)$$

Thus the pristine tubes have two radii of 5.31 Å and 4.46 Å, whereas in the polymer they have smaller radii of 5.21 Å and 4.42 Å. This decrease of the radii of the tubes in the polymer provides further evidence of interaction between the SWNTs and the polymer.

It has been shown that composites of fluorinated SWNTs and polyacrylonitrile and polyisobutylene SWNTs have increased strength compared to composites of unfunctionalized SWNTs.^{5,6} It is of interest to see whether this holds for composites of other polymers. Figure 2 shows the Raman spectra of the tangential mode in the pristine fluorinated SWNTs (top) and the fluorinated SWNTs in the polymer composite (bottom). The frequency in the polymer composite shifted up from 1577 cm^{-1} to 1583 cm^{-1} . Interestingly, the defect mode shifted down from 1322 cm^{-1} to 1309 cm^{-1} in the composite. The shift of the G mode is indicative of interaction between the fluorinated SWNTs and the PB polymer. RBMs are not observed in the fluorinated tubes. Figure 3 shows the Raman spectra in the C-H vibration region of the undoped polymer (top) and the nonfluorinated SWNT-polymer composite (bottom), showing very marked differences. The undoped polymer was subjected to the same treatment, that is, dissolution in benzene, sonication while evaporating, and heating to dry the polymer to ensure the changes seen in the SWNT-polymer composite were not due to processing induced decomposition. The most notable change is the absence of the vibration at 3007 cm^{-1} in the composite. This suggests a significant role of the CH or CH_2 groups in the bonding to the SWNT. Further evidence for the involvement of the C-H entities in the bonding process will be shown from the NMR data discussed below.

B. NMR measurements

The wide line proton NMR spectra of PB without SWNT at several temperatures are shown in Fig. 4. There are two distinct ^1H sites corresponding to different chemical environments, namely the CH and CH_2 sites. A modest degree of motional narrowing, for both peaks, is observed above -30°C as well as discontinuities of both peaks between -20 and -10°C , as shown later. The spectra of the PB-SWNT and PB-FSWNT samples are displayed in Figs. 5(a) and 5(b) and their differences are more pronounced at the higher temperatures. The distinct CH and CH_2 sites are overshadowed by broadening as carbon nanotubes are added. In Fig. 5(a), the emergence of a peak characteristic of the CH site with an increase in temperature is attributed to motional narrowing even though the nanotubes add to the overall broadening as compared to the pure polymer sample. The PB SWNT composite CH peak is not suppressed at elevated temperature by the addition of the nanotubes, whereas in Fig. 5(b), PB with FSWNT does not exhibit a motionally narrowed CH peak at elevated temperature. The overall line widths of the pristine polymer and PB-SWNT and FSWNT

composites are plotted in Fig. 6. In addition to the broader line width of the composites, the transitional changes in the pristine polymer between $-20\text{ }^{\circ}\text{C}$ and $-10\text{ }^{\circ}\text{C}$, which resemble a glass transition but are significantly higher than the T_g value stated by the vendor (Aldrich, Milwaukee, WI), are eliminated. The FSWNT composite also demonstrated a significant increase in overall line width but less than that of the SWNT composite, not counting the narrowed CH peak in the latter. The addition of both kinds of SWNT causes a significant stiffening of the PB polymer as judged by the increase in line widths attributed to suppression of polymer segmental motion. An additional possible contribution to the line width in the composites could arise from the presence of the residual magnetic catalyst particles, but because there is no correspondingly large change in the spin-lattice relaxation times, we conclude that any such contribution comes only from the expected modest increase in the bulk magnetic susceptibility of the samples. The onset of motional narrowing in amorphous or partly amorphous polymers above the glass transition or other phase transitions is widely observed in a large variety of polymers and polymer complexes.⁹

The spin-lattice relaxation time, T_1 , for the pristine polymer and the two composites is plotted in Fig. 7. For the pure polymer, both proton resonances exhibit T_1 minima. For the composites, a single effective T_1 as evidenced by exponential recovery profiles is observed, indicating either a common relaxation mechanism for the two proton sites or efficient spin-diffusion between them. Despite the fact that adding SWNT causes more structural rigidity as evidenced by the line width increase described previously, the temperature at which the T_1 minimum occurs in the SWNT complex is not much higher than that of the pure polymer, indicating that the local segmental dynamics (i.e., sub-nanometer units with a corresponding timescale of $\sim 1\text{--}100\text{ ns}$) are only slightly affected by SWNT inclusion. However, fluorinated SWNT does cause a significant change in the local structural environment and thus shifts the minimum toward a higher temperature. The effect of FSWNT versus SWNT interactions with the polymer are manifested differently over the different timescales probed by line width and T_1 measurements but there is likely a relation between the T_1 minimum shift to higher temperature and the suppression of the CH motion in the FSWNT composite.

C. Mechanical properties

In this section the effect of SWNTs on the mechanical properties of the polymer are discussed. Hardness measurements were made on samples with various weight percentages of fluorinated and nonfluorinated SWNTs. Hardness has been shown to correlate with yield strength.¹⁰ The measurements were made on samples typically 5 mm thick and 2 cm in diameter. All of the hardness measurements show a slight time dependent increase in the hardness, which is indicative of work hardening. Figure 8 shows the hardness as a function of time for the polymer having no SWNTs (bottom curve), having 4% by weight SWNTs (middle curve), and 4% by weight of fluorinated SWNTs (top curve). The data shows clearly that the fluorinated SWNTs are considerably more effective in increasing the mechanical strength of the polymer compared to the nonfunctionalized SWNTs. The suppression of the CH group motion by FSWNT inclusion as evidenced by the NMR results is then suggested as a more relevant indicator of overall mechanical properties than the total line width in Fig. 6. The fluorinated SWNTs have one fluorine for every two carbons, meaning their molecular weight is 1.8 times larger than the nonfluorinated SWNTs. So in effect, there are $N/1.8$ fewer tubes in the 4% fluorinated SWNT, where N is the number of nonfunctionalized tubes in the 4% SWNT composite. The enhancement of the strength of the composite containing fluorinated SWNTs is likely because of reduced slippage of the tubes in the bundles and/or stronger bonding to the polymer.

The disappearance of the C-H vibration of the polymer at 3007 cm^{-1} in the composite suggests that the CH or CH_2 groups are involved in the bonding of the polymer to the SWNTs and the bonding is probably covalent as opposed to a van der Waals interaction.

Since there are no available carbon bonds on the walls of a perfect tube, there are only two possible ways a covalent bond can occur. One is that bonding is on the side walls near a vacancy where there would be an available carbon bond. The other possibility is that bonding is on the ends of open tubes where there are available carbon bonds. However, the data cannot be used to distinguish between either possibility. In the case of the fluorinated tubes, it is likely that the bonding is between the polymer H and fluorine on the functionalized tubes.

IV. SUMMARY

Composites of PB and SWNTs and FSWNTs have been fabricated. Significant shifts of the frequencies of the Raman spectra of the tangential mode compared to the pristine SWNTs have been observed, indicating interaction between the polymer and the SWNTs. Also, the frequencies of the radial breathing modes of the SWNTs shift to higher values in the composite, indicating a reduction of the radii of the tubes providing further evidence of interaction of the SWNTs with the polymer. Proton NMR spectra are broadened in both composites, indicating suppression of polymer segmental motion. Although the SWNT composite exhibits a greater overall line width, partial segmental mobility attributed to CH groups at elevated temperature is apparent and is not observed in the FSWNT composite. The latter sample also shows a more substantial shift in the T_1 minimum to higher temperature, reflecting localized interactions between the FSWNTs and the polymer. Measurements of the hardness as a function of wt% SWNTs in the polymer indicated that the fluorinated SWNTs were more effective in increasing the strength.

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REFERENCES

1. Thostenson T, Ren Z, Chou T. Multiscale modeling of compressive behavior of carbon nanotube/polymer composites. *Compos. Sci. Technol* 2001;61:1899.
2. Kumar S, Dang TD, Arnold FE, Bhattacharya AB, Min BG, Zhang X, Vaia RA, Park C, Adams WW, Hauge R, Smalley RE, Ramesh S, Willis PA. Synthesis, structure, and properties of PBO/SWNT composites. *Macromolecules* 2002;35:9039.
3. Zhang XT, Liu T, Sreekumar TV, Kumar S, Moore VC, Hauge RH, Smalley RE. Poly(vinyl alcohol)/SWNT composite film. *Nano Lett* 2003;3:1285.
4. Kis A, Csanyi G, Salvétat JP, Lee TN, Couteau E, Kulik AJ, Benoit W, Brugger J, Forro L. Reinforcement of single-walled carbon nanotube bundles by intertube bridging. *Nat. Mater* 2004;3:53. [PubMed: 14661017]
5. Owens FJ. Properties of composites of fluorinated single walled carbon nanotubes and polyacrylonitrile. *Mater. Lett* 2005;59:3720.
6. Owens FJ. Raman and mechanical properties measurements of single walled carbon nanotube composites of polyisobutylene. *J. Mater. Chem* 2006;16:505.
7. Cancado LG, Pimenta MA, Saito R, Jorio A, Ladeeiera LO, Grueneis A, Souza-Filho AG, Dresselhaus G, Dresselhaus MS. Stokes and anti-Stokes double resonance Raman scattering in two-dimensional graphite. *Phys. Rev. B* 2002;66:035415.
8. Venkateswaren UD, Rao AM, Richter E, Menon M, Rinzler A, Smalley RE, Eklund PC. Probing the single-wall carbon nanotube bundle: Raman scattering under high pressure. *Phys. Rev. B* 1999;59:10928.
9. McBrierty, VJ.; Packer, KJ. *Nuclear Magnetic Resonance in Solid Polymers*, Cambridge Solid State Science Series. Cambridge University Press; New York: 1993. Structure and motion in solid polymers. Chap. 5

10. Callister, WD. Materials Science and Engineering. 6th ed.. John Wiley and Sons; New York: 2003.

FIG. 1. Raman spectra of the tangential and defect mode of pristine SWNTs (bottom) and SWNTs in PB (top) showing a 7 cm^{-1} upward shift in the polymer indicative of bonding between SWNT and polymer.

FIG. 2. Raman spectra of tangential mode and defect mode in pristine fluorinated SWNTs (top) and in the fluorinated SWNTs in the polymer (bottom).

FIG. 3.
Raman spectra of the C-H vibrations in the undoped polymer (top) and the polymer containing SWNTs (bottom).

FIG. 4. Proton NMR spectra of pristine PB (polymer) at several temperatures from bottom to top, – 30, 0, 60, and 100 °C. Horizontal scale in kHz.

FIG. 5.

NMR spectra of PB-nanotube composites at several temperatures from bottom to top, -30, 0, 60, and 100 °C. (a) SWNT; (b) FSWNT. Horizontal scale in kHz.

FIG. 6. Arrhenius plot of proton NMR line widths for polymer and its SWNT and FSWNT composites. Lower set: neat polymer, CH₂ peak (dark symbol), CH peak (light symbols); Upper set: SWNT composite (dark symbol), FSWNT (light symbol).

FIG. 7.

Arrhenius plot of proton spin-lattice relaxation times for polymer and its SWNT and FSWNT composites. Neat polymer, CH_2 peak (filled circles), CH peak (open circles); SWNT composite (filled triangles); FSWNT (open triangles).

FIG. 8.

Time dependence of the hardness for undoped polymer [■], the polymer containing 4% by weight of SWNTs [◆] and the polymer containing 4% by weight of the fluorinated polymer [□]. The units of hardness are durometers as described in the text.