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Characterization of Single Walled Carbon Nanotube–Nitrocellulose Composites

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Composites of nitrocellulose (NC) and single walled carbon nanotubes (SWNTs), as well as fluorinated SWNTs produced by evaporation of solutions of NC and suspended SWNTs (while being subjected to sonication) are characterized. Raman measurements of the NC/SWNT composites showed shifts of the radial breathing and sizable upward shifts of the tangential mode frequency of the SWNT indicative of interaction between the NC and the SWNT. Composites containing 12.5% SWNTs by weight showed a 21% increase in hardness and a resistance of 0.51 Ohm-cm. Composites of NC containing a similar number of fluorinated carbon nanotubes showed a down shift of the tangential mode frequency, a 23% increase in hardness, and were not conducting. Ferromagnetic resonance and magnetization measurements indicated that the composites were ferromagnetic due to the presence of iron nanoparticles used as catalysts in the synthesis of the carbon nanotubes.

Keywords carbon nanotubes, nitrocellulose, composites, hardness, electrical conductivity, magnetism, Raman spectroscopy

Introduction

The unique properties of single walled carbon nanotubes (SWNTs, such as high electrical conductivity, thermal conductivity, high strength and aspect ratio has motivated considerable research in incorporating SWNTs into polymers and metals in order to engineer their properties. There have been reports of enhanced yield strength of SWNT/polymer composites, as well as enhanced electrical and thermal conductivity (1–6). An essential requirement for the enhancement of properties is a good dispersion of the SWNTs in the composites which can be achieved to some extent by using sonication in the incorporation process. However, the SWNT bundles are not totally unraveled and there is some slippage of the SWNTs in the bundles meaning optimum enhancement of strength is not achieved. It is possible that functionalized tubes would allow better interaction between tubes in the bundles and be more effective in enhancing strength by reducing slippage in the bundles. For enhancement of strength, it is also necessary that there be interaction between the SWNTs and the polymer.

In this work, modification of the hardness, the electrical conductivity and magnetic properties of nitrocellulose (NC) is demonstrated by the addition of SWNTs to the

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polymer. The effect of the addition of fluorinated nanotubes on the properties of the composites is also investigated. Raman spectroscopy is used to examine the interaction between the SWNT and the NC matrix. Nitrocellulose has important technological applications as an energetic binder in propellant formulations but has a number of problems such as relatively low temperature thermal decomposition, which severely alters its properties. Enhancement of the thermal conductivity could contribute to reduction of the susceptibility to decompose by preventing the build up of localized regions of high temperature (hot spots) Enhancement of the yield strength of NC could contribute to increasing the mechanical integrity of propellant formulations.

Experimental

A typical fabrication of the NC/SWNT composite involved dissolving 0.0775 grams of NC in acetone and suspending 0.0094 grams of SWNTs in the acetone. The acetone containing the suspended SWNTs and dissolved NC was allowed to slowly evaporate while being subjected to sonication. The evaporated NC containing the SWNTs was dried for one hour at 50°C. A similar process was used to incorporate the fluorinated nanotubes in the NC. Both functionalized and unfunctionalized carbon nanotubes were obtained from Carbon Nanotechnologies Incorporated where they are grown by the HiPco process. The method of fluorination is described by Mickelson et al. (7). Examination of these pristine tubes by paramagnetic resonance indicates the presence of a ferromagnetic signal arising from the iron nanoparticles which serve as the catalyst for growth. No attempt was made to remove the iron particles bound to the tubes because of the possibility that the magnetic particles on different tubes would provide a magnetic binding between tubes in a bundle perhaps reducing slippage.

Hardness measurements were made using a type A model DD-3 REX digital durometer. The hardness is reported in durometers as described by the American Society for Testing and Materials specification ASTM D2240. Raman measurements were made using a J.Y. Horiba confocal micro Raman spectrometer employing a helium neon laser having a wavelength of 632.8 nm. The electrical properties were measured by the standard four-probe method where current is sent through two contacts and voltage is measured across two other contacts. Ferromagnetic resonance measurements were made using a Varian E-9 paramagnetic resonance spectrometer operating at 9.2 GHz with a 100 KHz modulation. The magnetization of the sample was obtained by measuring the dc magnetic field dependence of the ac susceptibility at 350 KHz using a method similar to that described by Clover and Wolf (8). The system consists of an HP204 LC oscillator modified to have an external coil. The sample is contained in the coil, which is located between the poles of an electromagnet. The change in the frequency of the coil, which is proportional to the susceptibility is measured as a function of DC magnetic field using a HP 5314 frequency counter.

Results and Discussion

For SWNTs to mechanically reinforce a polymer, it is necessary that there be some interaction between the composite and the nanotubes. Raman spectroscopy can be used to explore this interaction. Figure 1 (bottom) is the Raman spectrum of the tangential mode of the pristine SWNT and Figure 1 (top) is the spectra in the NC matrix. The mode in the polymer is shifted up from 1567 cm^{-1} in the pristine tube to 1587 cm^{-1}. It has been shown that when SWNTs are doped with bromine, an electron acceptor, the

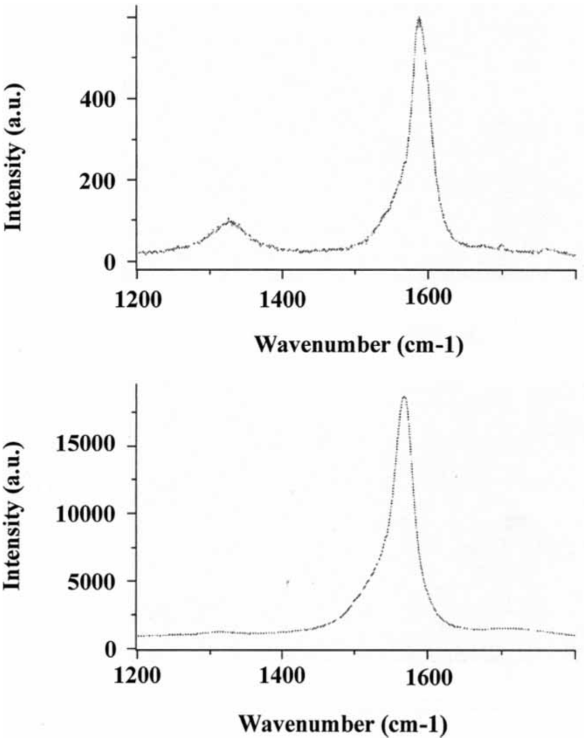

Figure 1. Raman spectra of the tangential mode of pristine SWNTs (bottom) and SWNTs in the NC composite (top).

tangential mode shifts up by 24 cm^{-1} (9). The large upward shift of the tangential mode of the SWNT in the nitrocellulose suggests some interaction between the NC and the SWNT most likely via the NO_2 group on the NC which is an electron acceptor. Changes are also observed in the frequencies of the radial breathing modes. Figure 2 shows the modes in the pristine SWNT (bottom) and the NC/SWNT composite (top). The modes at 255 cm^{-1} and 332 cm^{-1} have shifted to higher frequencies in the composite. Similar shifts were observed in the bromine doped SWNTs (9). These low frequency radial breathing modes are sensitive to the diameter of the tubes and the shifts reflect a small decrease in the diameter of the tube as a result of interaction with the NC.

The tangential mode frequency of the fluorinated SWNTs occurs at 1588 cm^{-1} representing a 21 cm^{-1} upward shift from the non-fluorinated SWNTs. The radial breathing modes are not observed in the fluorinated SWNTs. The mode in the NC/FSWNT composite is shifted down to 1581 cm^{-1} representing a shift of 7 cm^{-1}. There is also evident a shoulder on the low frequency side at approximately 1550 cm^{-1}. These results suggest that there is some interaction between the fluorinated SWNTs and the NC. It is interesting that the mode frequency shifts down in NC containing the fluorinated SWNT and up in the non-fluorinated NC composite.

Measurements of the sample hardness showed an increase from 80 durometers to 96.8 in the composite which contained 12.5% SWNTs by weight representing a 21% increase in hardness. The NC composite, having the same number of fluorinated tubes, did not show a

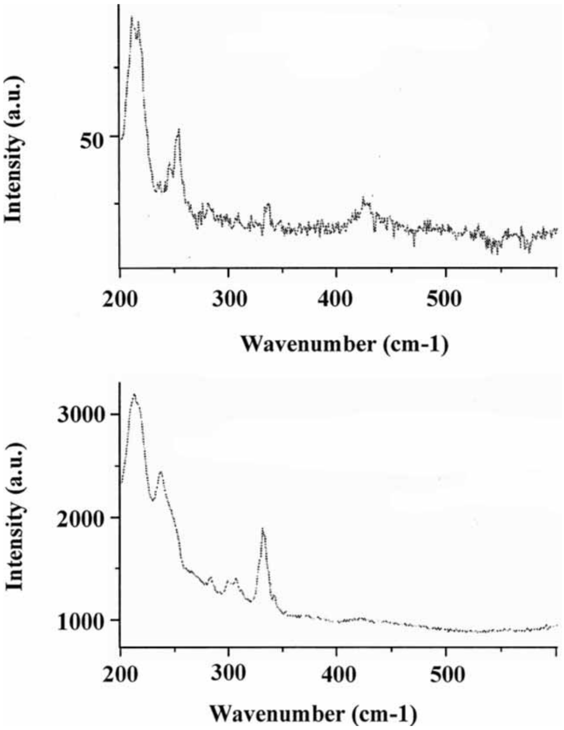

Figure 2. Raman spectra of the Radial breathing modes of pristine SWNTs (top) in the NC composite (bottom).

substantial increase in hardness compared to the unfluorinated SWNTs showing an increase of 23%.

Figure 3 shows the results of the measurement of the resistivity using the four probe method showing that the I–V relationship is linear and the sample is quite conducting.

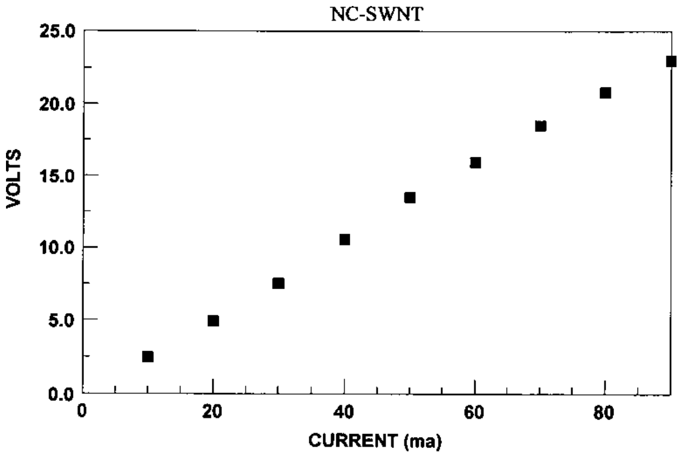

Figure 3. Plot of the voltage vs. current at room temperature in the NC/SWNT composite.

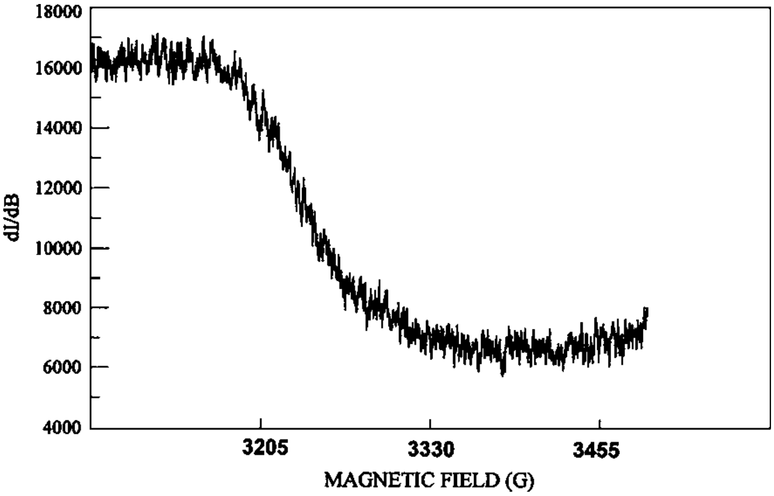

Figure 4. Ferromagnetic resonance spectrum of the NC/SWNT composite at room temperature.

The calculated resistivity of the sample is 0.51 Ohm-cm. The composites with the fluorinated SWNTs were not conducting because the fluorinated tubes are insulating. By incorporating SWNTs, which are bonded to iron nanoparticles arising from the growth process, the composite displays magnetic behavior. Figure 4 shows the ferromagnetic resonance spectra of the sample recorded at room temperature verifying the existence of ferromagnetism. The broadness and the fact it is centered at a field value well below that of the free electron value indicates it is a ferromagnetic signal, not a paramagnetic signal. The derivative of the absorption also shows a marked broadening and shift to lower field with decreasing temperature, which is characteristic of a ferromagnetic resonance spectra (10). Further verification is shown in Figure 5, which is a plot of the magnetization vs. dc magnetic field at room temperature normalized to the value at 3 kiloGauss.

Conclusions

Raman spectroscopy studies of the SWNT/NC composites show upward shifts of the frequencies of the radial breathing modes and the tangential mode suggesting some interaction between the NC and the SWNT which is a prerequisite for enhancement of strength. The composite shows a 21% increase in hardness compared to NC alone. However it should be possible to achieve larger increases in the hardness and yield strength by alignment of the tubes and use of tubes functionalized with other groups, which may prevent slippage of the tubes in the bundles. However incorporation of fluorinated SWNTS in NC did not contribute significantly to enhancing the strength. Interestingly the tangential mode frequency of the fluorinated SWNTs in NC shifted to a lower value compared to the pristine fluorinated SWNT, which is in contrast to the upward shift observed in NC containing the non-functionalized tubes. It is possible that adding other kinds of molecular groups to SWNTs may be more effective, however this issue needs further study. The SWNT/NC composite was shown to be both magnetic and electrically conducting, which may have technological implications. The high electrical conductivity implies high thermal conductivity, which could result in a higher thermal stability of the

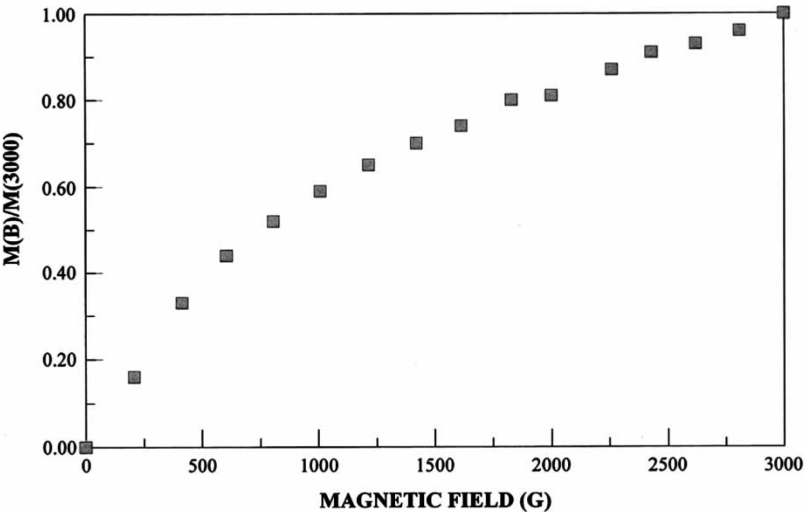

Figure 5. Magnetization of NC/SWNT composite vs. dc magnetic field normalized to a 3 kiloGauss field at room temperature.

NC by not allowing build up of localized regions of heat (hot spots). The thermal decomposition of NC is a serious problem in the use of NC in propellant formulations. The fact that energetic materials can be made magnetic could provide a labeling mechanism, which could be the basis of detection of energetic materials an important issue in the effort against terrorism.

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