

Spectroscopic detection of carbon nanotube interaction with amphiphilic molecules in epoxy resin composites

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Abstract

Incorporation of carbon nanotubes into epoxy resin composites has the effect of increasing electrical conductivity at low percolation levels. An amphiphilic molecule such as palmitic acid has been used to increase the surface contact area and improve the dispersion of the carbon nanotube bundles in the prepolymer. The chemical environment of the dispersed nanotubes has been probed using vibrational Raman spectroscopy. Spectroscopic Raman maps, on sample surfaces ($60 \times 60 \mu\text{m}^2$) with ratios of nanotubes to palmitic acid varying from 1:2 to 2:1 by weight, have been recorded to test the uniformity of the dispersion. Substantial spatial inhomogeneities have been observed in the G-band shift and an additional spectral band at 1450 cm^{-1} . The 1450 cm^{-1} band has been attributed to the CH_3 group of the amphiphilic molecules adsorbed onto the nanotube surface. The maps are correlated with the measured electrical conductivity values. The highest conductivity has been observed for the best dispersed nanotubes and nanotubes with the highest degree of interaction.

Introduction

The remarkable physical properties of carbon nanotubes (CNTs), which combine high strength and low weight have lead to potential applications in composites which incorporate CNTs into polymers. It is expected that both electrical and mechanical characteristics can be improved by adding CNTs (Kearns2002, Kumar2002, shi2003, sandler2003, Yang2002, Cadek2004) into suitable polymer matrices. The high aspect ratio of CNTs allows to obtain conducting composites at low percolation thresholds. Agglomerated single-walled CNTs (SWCNTs) in the form of randomly oriented nanotube ropes form a pseudo-metal with conductivity values in the 10^3 S.cm^{-1} range (Tans1997). CNTs as colloidal material are not spontaneously suspended in polymers. The chemistry and physics of the dispersion of CNTs is complicated due to the dependence of their electronic properties on helicity which can influence their properties in a solvent. Several methods have been reported where CNTs have been dispersed through functionalization, strong acids, solvents and surfactants or by the addition of amphiphilic molecules (velasco2003, gong2000, vigolo2000, cui2003). The hydrophobic part of the amphiphilic molecule interacts preferentially with the CNT surface and helps to disperse the CNTs in the polymer matrix (chen2001).

Interfacial interactions between the nanotube and the polymer are usually investigated using XPS (photoelectron emission spectroscopy) and direct information about the arrangement of the nanotubes in the polymer matrix is obtained by scanning electron microscopy (SEM). Inelastic light scattering provides information about the vibrational properties of the composite, which depend in turn on local chemical bonds averaged over the diffraction limited focal point of one micrometer. Strain can be estimated through the observation of spectral shifts of the in plane optical modes (G-band) of CNTs or the disorder induced second order D^* band (cooper2002, zhang2003). But absolute strain determination is more complicated due to the cylindrical structure of CNT and diameter dependence. For single wall carbon nanotubes (SWCNTs), all the atoms are located on the surface; as a result, the vibrational properties of SWCNTs depend strongly on their environment. Wood et al. [wood2000a, wood2000b] have shown that CNTs can in fact be considered as molecular sensors due to their high sensitivity to their immediate chemical environment. For instance, the phonon band of the D^* band at 2700 cm^{-1} is upshifted by 20 cm^{-1} when the tube is placed in water as compared to in air. The first order G-band shows similar sensitivity to its environment (Schadler1998). Similarly it is found that the fluorescence of SWCNTs depends on the surrounding medium and the surfactant molecule (Moore2003). The pressure coefficient of vibrational bands have recently been found to depend on the pressure transmitting medium which suggests that the molecular packing around the nanotube influences the effective pressure experienced by the tubes (Puech2004, Teredesai2001). We report here Raman spectroscopic and electrical conductivity measurements on CNTs–epoxy resin composites wherein amphiphilic molecules have been added to facilitate dispersion. The interaction between these surfactant molecules with CNTs influences the electrical properties of the composite.

Experimental details

The CNTs were prepared by the catalytic chemical vapour deposition method (CCVD). Selective reduction at 1000°C in a methane-hydrogen (18% CH_4) atmosphere of a solid solution of a transition metal oxide ($\text{Mg}_{0.95}\text{Co}_{0.05}\text{O}$) led to the formation of small diameter CNTs with one to

three walls; for more details see reference [Flahaut2000], [Bacsa 2001]. After the reaction, the unreacted catalytic particles were dissolved in dilute (3.7%) hydrochloric acid and CNTs were recovered. High-resolution electron microscopy images show the presence of individual CNTs and small bundles of CNTs with an average diameter of 2.4 nm. The nanotubes were mainly single- and double-walled. A dispersion of CNTs in water was first sonicated for 1 h before addition of epoxy resin which was dried in a vacuum oven at 100°C. Palmitic acid was added and the suspension was sonicated for 1 h at room temperature. After the addition of the hardener, the final mixture was cured at 120°C for 20 min and 145°C for 4 h [barrau2003a, barrau2003b]. Polymer composite samples A, B and C contain 0.2, 0.4 and 0.8 wt % of palmitic acid respectively. The CNT content in the polymer for all these samples is 0.4%wt. SEM image of CNTs dispersed in epoxy with the addition of palmitic acid is shown in Fig. 1.

The ac conductivity was measured in the frequency range between 10^{-2} and 10^6 Hz at room temperature using a Novocontrol dielectric spectrometer. The dc conductivity σ_{dc} was approximated to the value of ac conductivity at the lowest frequency (10^{-2} Hz).

The samples were successively polished with alumina powder of 10, 1, and 0.01 μm in size in order to have a flat surface for Raman mapping. We assume that the CNTs concentration is sufficiently low so that the polishing process does not influence the Raman measurement. All Raman spectra were recorded at room temperature using the MicroRaman instrument from Renishaw Inc. The scattered light was collected in backscattering geometry using a microscope objective (x100) to focus the laser beam (514 nm) on the sample.

Results and discussion

Figure 2 shows two representative Raman spectra recorded on sample B. Spectrum a.1 is similar to the Raman spectrum of CNTs in air. No additional spectral bands are seen. In spectrum a.2 splitting of the G-band is observed. We attribute the modification and shift of the G band to the interaction of the amphiphilic molecules with the CNTs. The appearance of a shoulder or second band can be attributed to the internal tubes of double walled tubes, which are not in contact with amphiphilic molecules or tubes within a bundle which are shielded from the amphiphilic molecules. From the reported behaviour of the G-band of DWCNTs under hydrostatic pressure (Puech2004b), we estimate that for DWNTs, the G-band shift for the internal tubes, is only half of that observed for the external tubes. In the case where bundles are present, only the tubes on the outer surface of the bundle will be in contact with the amphiphilic molecules and the local pressure experienced by the non contacting tubes in the bundle will be reduced and we expect to see a broadening of the G-band. The differences between the two spectra in fig. 2a shows that insufficiently dispersed bundles may be present in the sample leading to inhomogeneous contact with the surfactant. Figure 2b shows the mapping of the G-band in steps of one micrometer across a surface area of $60 \times 60 \mu\text{m}^2$. We have fitted the G-band to a single Lorentzian curve and found a considerable variation of the spectral position across the surface of the sample. The bright regions are those where the CNTs are in contact with the amphiphilic molecules. Thus the G band mapping can be effectively used to assess the quality of the dispersion in a polymer-CNT composite.

In addition to the change in the G-band frequency, we have observed an additional band at 1450 cm^{-1} . We note that the same band has been observed for CNTs under hydrostatic pressure using a methanol-ethanol mixture as pressure transmitting medium. The amphiphilic molecule has a non-polar hydrophobic tail ($\text{CH}_3\text{-(CH}_2\text{)}_{14}\text{-}$) and a polar hydrophilic headgroup (-CO-OH). From the literature we know that the CH bending mode in the CH_3 group is observed at 1450 cm^{-1} for organic compounds such as heptane [Koleman1974] and confirm by a pressure medium study of

Wang et al [Wang1999]. Based on these informations, we conclude that the band at 1450 cm^{-1} corresponds to the non-polar CH_3 group in contact with CNT surface. It appears that the Raman signal of this group is enhanced by the presence of the nanotubes. Figure 1c shows the spatial distribution of the 1450 cm^{-1} band which correlates with the map in figure 1b and which is characteristic of the G-band position. The intensity of the additional band at 1450 cm^{-1} increases in regions where the CNTs have a shifted G-band. Hence the binding of the nanotube to the amphiphilic molecule perturbs this vibrational mode makes it more Raman active. We note that the Raman spectra of CNTs functionalized with palmitic acid under different conditions (Al^{3+} , clay) by the COOH group shows no signature in the $1400\text{-}1500\text{cm}^{-1}$ range [Georgakilas2004]. The spectrum 2 in figure 2a shows three additional bands below the D-band which we believe are related to the hydrophobic chain of the amphiphilic molecule.

Figure 3 shows Raman maps of the G-band position for the three samples A, B and C, using the same scale. The spectral map of the G band position from sample A and B show large and continuous area with large G-band shifts corresponding to nanotubes surrounded by amphiphilic molecules. When the CNTs to palmitic acid weight ratio is 1:1 as in sample B, the shift of the G-band is higher, indicating an improvement compared to sample A (ratio 2:1). For sample C (ratio 1:2), some scattered spots are seen. This observation suggests that the amphiphilic molecules agglomerate when their concentration becomes too high. The CNTs are not necessarily completely covered by amphiphilic molecules. From the Raman analysis, we conclude that for sample B and to a lesser extent for sample A the amphiphilic molecules are strongly interacting with the CNTs. The shift of the G-band, due to the interaction with the palmitic acid, is as high as 30 cm^{-1} and correlates with the intensity of a band at 1450 cm^{-1} , which is associated to the interacting CH_3 functional group.

The conclusions drawn from the Raman maps are in agreement with the low frequency ac conductivity measurements. The conductivity values are 1.4, 11 and $8.2 \cdot 10^{-6}\text{ S.cm}^{-1}$ for the samples A, B and C respectively. The sample B displays the highest conductivity value which is in accordance with the conclusions drawn from the Raman maps. Since the observed conductivity value is lower than the pseudo metallic conductivity of pure CNTs, more experiments need to be done to improve the quality of the dispersion.

Conclusions

We find that the Raman G-band of CNTs is highly sensitive to its chemical environment. The use of polymer-CNT composites containing palmitic acid gives us the possibility to spatially visualize the influence of the interaction of the amphiphilic molecules with the CNTs. The scale of observation with this technique being micrometric gives complementary information to that obtained by SEM and macroscopic conductivity measurements. Hence, spectroscopic Raman mapping can be used to check the uniformity of samples and the conclusions are in accordance with the observed conductivity data. This study shows that Raman spectroscopy is a useful technique to study CNTs – polymer composites to improve their performance.

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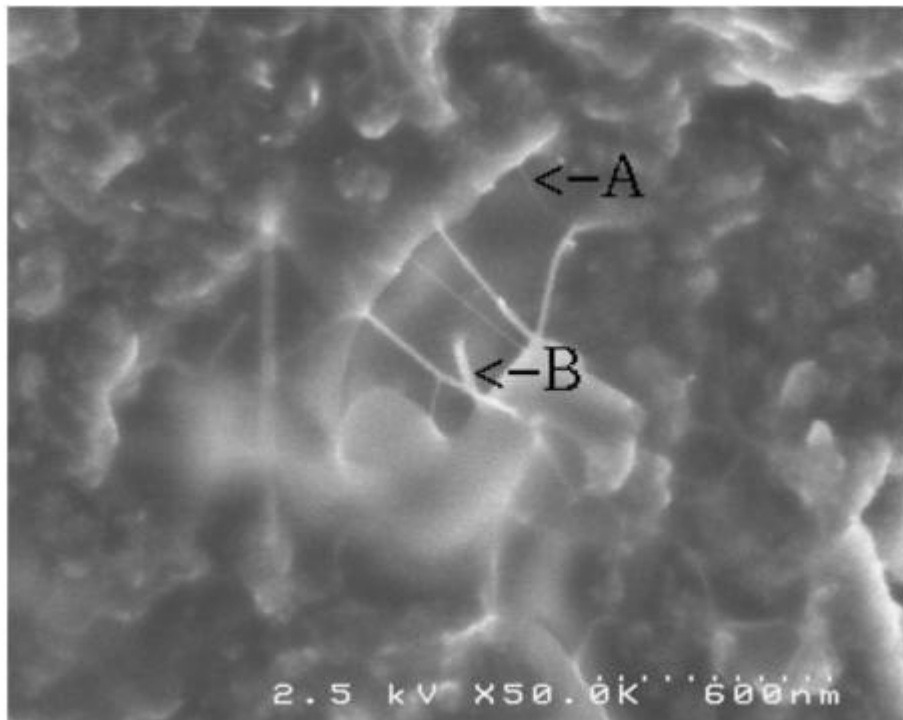


Figure 1 : SEM images of CNT's free (A) of and embedded by (B) palmitic acid.

Figure 2 : From left to right : two typical Raman spectra obtained on the same heterogeneous sample, map of the frequency of the G-band and map of the intensity of the 1450 cm^{-1} band.

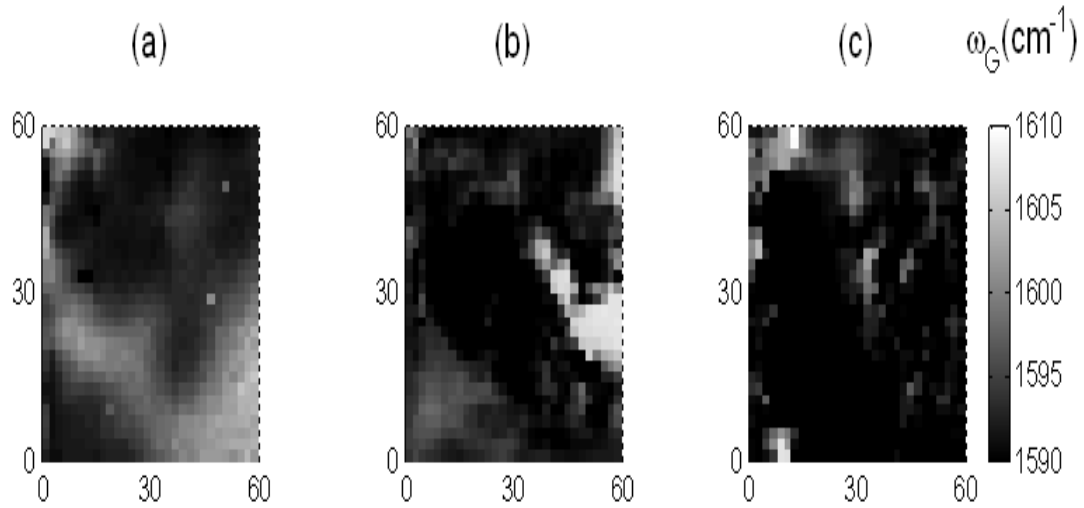


Figure 3 : $60 \times 60 \mu\text{m}^2$ maps with $2 \mu\text{m}$ resolution of the G-band frequency with (a) 0.2%, (b) 0.4% and (c) 0.8% of amphiphilic molecules (sample A, B and C respectively). The percentage in weight of CNTs is kept constant at 0.4%.