

Correlating electric and structural properties in surface-layer of carbon nanotube composite

E. Pavlenko¹, V. Tishkova¹, P. Puech¹, E. Flahaut², W.S. Bacsa¹

¹CEMES-CNRS and University of Toulouse
29 Jeanne Marvig, 31055 Toulouse, France, wolfgang.bacsa@cemes.fr
²CIRIMAT, Insitiut Carnot, University of Toulouse
118 route de Narbonne, 31062 Toulouse, France

ABSTRACT

It has been recently observed that annealing of carbon nanotubes on the surface of a thermoplast polymer forms a composite surface-layer with uniform tube dispersions at scales of 10-100 micrometers. We examine cross sections of the surface composite layer using Raman imaging and transmission electron microscopy and correlate the structural information with electrical transport measurements. Annealing has the effect of increasing the electrical conductivity by one to two orders of magnitude. We estimate an electrical conductivity of 1.20 S/cm when annealing 3.5 $\mu\text{g} / \text{cm}^2$ double wall carbon nanotubes on polyether ether ketone polymer. The electrical conductivity increases up to two orders of magnitude after annealing and is linear up to an electric field of 10V/cm. The electrical current is found to saturate reversibly at higher applied electric fields.

Keywords: polymer composite, carbon nanotubes, Raman spectroscopy, electron microscopy, electronic transport

1 INTRODUCTION

The presence of carbon nanotubes in high performance thermoplast polymers can increase its electrical conductivity by more than five orders of magnitude [1]. To maintain the properties of the polymer and to reduce effects on crystallinity when introducing nanoparticles in a polymer matrix, one needs to keep the concentration of nanotubes as low as possible. Currently the percolation threshold is at around 0.3% by weight and the maximum conductivity is attained at 2% by weight for double wall carbon nanotubes [2]. We use double wall carbon nanotubes because they are particularly long and have a high crystallinity [3]. This maximum electrical conductivity depends much on how the tubes are dispersed. We explore here the cross section of the composite surface layer using Raman spectroscopy, transmission electron microscopy and electrical conductivity measurements as a function of amount of tubes deposited on the surface. Transmission electron microscopy turns out to be limited when observing small diameter nanotubes in a polymer matrix, Raman spectroscopy can be used to monitor the tube dispersion at different scales (> 0.5 micrometer). Raman spectroscopy gives access to the vibrational mode such as the in plane out phase vibrational

band of neighbouring atoms in carbon nanotubes located at 1600 cm^{-1} (G-band), a defect induced breathing mode at 1350 cm^{-1} (D-band). From the shifts of the G band one can deduce strain in the carbon nanotubes and charge transfer or the doping level of the tubes. From the D band one obtains information about the number of defects or the crystallinity of the tubes. The high absorption of the illuminating laser (Raman spectroscopy) by the nanotubes can lead to local temperature changes. This can be verified by comparing Stokes and Anti-Stokes spectra allowing determining the local temperature. Far from the electronic resonances the intensity of the band is proportional to the amount of CNTs sensed by the focal spot. The amorphous phase and luminescence give rise to a wide background signal.

2 EXPERIMENTAL

In order to obtain structural information of the composite surface layer we prepared first thin cross sectional slices. Sonicated suspensions of double wall carbon nanotubes with known concentration in NMP (3.5 mg/m^2 droplet) were dropped on the surface of PEEK (polyether ether ketone). From the surface spread by the droplet (1 cm^2) and the tube concentration we find 0.35 μg of nanotubes for each droplet. Double wall carbon nanotubes tubes (DW CNTs) were received from CIRIMAT Insitiut Carnot, University of Toulouse. The samples were annealed in a argon atmosphere at the melting temperature (380C) for 15 minutes [4,5]. Argon was pumped through the tube furnace (Argon flux=0,08 l/min, 1 m long, 2.5 cm wide quartz tube) to avoid oxidation of the samples when cooling down. An epoxy layer was then coated on the sample before cutting the sample perpendicular to the interface in slices, 100nm thick, with a diamond knife using the ultramicrotome technique. The slices were finally placed on Cu grid with a carbon holey film for TEM and Raman measurements to study the cross section of the composite surface layer.

Raman spectra were recorded using a Explora-Horiba spectrometer with a piezo electric displacement table from PI GmbH. Linear polarized 785 nm laser excitation with an optical objective x100 was used. The measurements were performed on polished surfaces and Raman line scans were taken with a steps size of 20 nm. We used a Philips CM20 instrument for transmission electron microscopy (acceleration voltage 120 kV). Electrical measurements

were performed using a programmable electrometer from Keithley 6517B/E and depositing two silver electrodes 12 mm apart. Temperature dependent transport measurements were made after the sample has been first brought to the maximum temperature.

3 DISCUSSION

Figure 1 shows the optical image of the composite surface layer. Figure 2 shows the Raman signal when scanning across the composite layer along the vertical line in figure 1. The two Raman spectral bands at 1300 cm^{-1} (D) and 1600 cm^{-1} (G) indicate the presence of carbon nanotubes in the composite layer. The constant Raman G band intensity shows that the nanotube concentration is uniform across the layer within the limits of the lateral resolution of the imaging optics which is larger than half the wavelength of the excitation wavelength ($>392.5\text{ nm}$). Figure 2 shows that the fluorescence background is clearly reduced in the composite layer. The percolating nanotubes in the composite have the effect of quenching the laser induced photoluminescence. From figure 2 we estimate that the thickness of the composite layer is around 1100 nm . The prologation of the G band into the PEEK at the lower half of figure 2 is attributed to contamination of the surface of PEEK with CNTs when cutting the 100 nm thick composite layer.

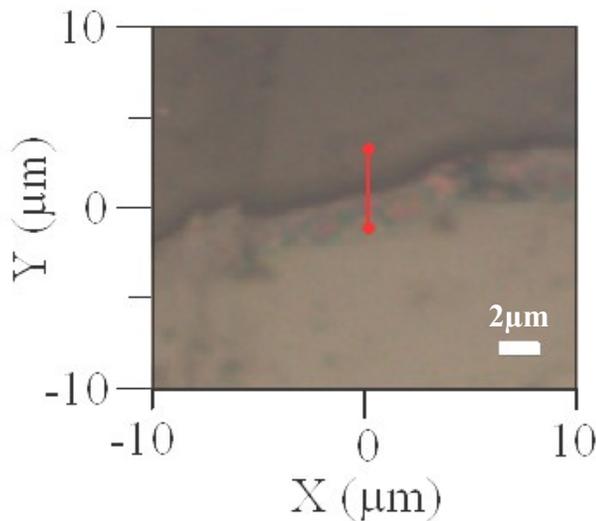


Fig. 1 Optical image (objective x100) of composite layer (dark horizontal band) at the interface of PEEK (below) and epoxy layer (above). The vertical line indicates the scan where Raman spectra were recorded.

The Raman D band which is due to defect induced scattering of sp^2 bonded carbon is less intense in the center of the composite film. At this point it is not clear why the D band is not uniform across the composite layer. It could be that the other forms of carbon present in the CNT sample

diffuse differently in PEEK and contribute to a larger extent to the D band.

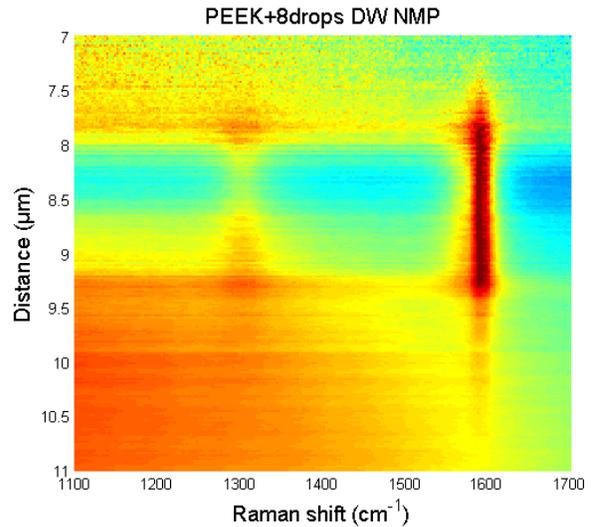


Fig 2. Raman signal when scanning across the composite layer, perpendicular to the interface. The two spectral bands correspond to the Raman G and D band indicating the presence of carbon nanotubes and their uniform distribution. Red indicates high intensity, blue low spectral intensity.

Figure 3 shows the cross section of the composite layer using transmission electron microscopy. We observe a 100 nm wide composite layer containing spherical particles. The particles are either disordered forms of carbon or remaining particles from the catalyst when growing the double wall carbon nanotubes. Double wall carbon nanotubes have a small diameter ($2\text{-}3\text{ nm}$) and give often not enough contrast against the polymer matrix at low concentration to make them visible. In figure 3 one can see that some tubes are extending into the upper part of the image. Clearly the observed apparent thickness of the composite layer as observed by TEM is much smaller than when using Raman imaging. This can be explained by the difficulty to make the tubes at low concentration visible using TEM. From figure 3 it is seen that the particles do not diffuse the same way into the PEEK. When depositing droplets of suspensions of nanotubes on the surface, the tube distribution is not uniform. Although it is known that the tubes disperse spontaneously in the PEEK matrix at scales of $10\text{-}100\text{ micrometers}$, the tube density fluctuates considerably over distance of several 100 micrometers . This also has the effect that the composite layer fluctuates in thickness when assuming that the thickness scales with the number of tubes present initially on the surface. This explains in part differences found in the Raman and TEM measurements.

Electrical measurements were performed as a function of the number of droplets evaporated on a given surface and

before and after annealing (3.5 mg/m^2 droplet). The annealing had the effect that the electrical conductivity increased by one or two orders of magnitude. This shows that the annealing process increased the number of conducting paths. This means annealing has the effect to spread larger agglomerates and increasing the amount of smaller agglomerates which multiplies the number of connecting paths.

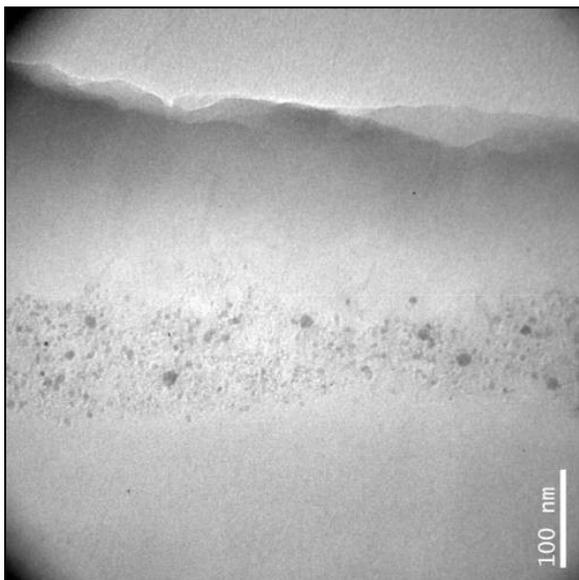


Fig. 3 Transmission electron microscop image of a composite layer. Lower side PEEK, upper side Epoxy. The particles are due to disordered forms of carbon or remaining particles from the catalyst when growing the double wall carbon nanotubes. The contrast from low density of double wall tubes is too low to make them visible in the PEEK matrix.

When increasing the number of droplets of the NMP carbon nanotube solution on the PEEK surface the resistivity did not necessarily increase before annealing. We assume that the drying process is agglomerating the tubes on the surface in a non uniform way. After annealing the conductivity increased by a factor of 20 when depositing a few droplets and to 150 times for 10-12 droplets. The electrical conductivity is estimated to vary between 0.04 S/cm and 1.20 S/cm for fields smaller than 10 V/cm . Due to the non uniform deposition of the nanotubes, the dispersion is not uniform at scales of 100 micrometers leading to variable thickness of the composite surface layer making it difficult to determine the electrical conductivity accurately. The conductivity is found to be linear up to a field of 10 V/cm and the current saturates reversibly for higher fields. The origin of this non linearity is not known. Possibly the junctions between the tubes where the resistance is highest heat up and this has the effect of reducing the conductivity. Temperature dependent electronic transport measurements

show that the conductivity increases when increasing temperature by 20-40% depending on the DW CNT concentration.

4 CONCLUSION

We studied the formation of double wall CNTs composite surface-layer on PEEK by annealing different amounts of CNTs deposited on the surface. Raman imaging showed that the tube distribution is uniform across the thickness of the composite layer. It is found that the width of the surface layer varies over distances of 100 micrometers due to variations of tube concentration on the surface when solutions of nanotubes are drying on the surface of the polymer. Transmission electron microscopy shows that other forms of carbon and catalytic particles diffuse differently in PEEK as compared to the longer DW CNTs. The electrical conductivity is found to increase up to two orders of magnitude after annealing and is linear up to a electric field of 10 V/cm . The electrical current is found to saturate reversibly at higher applied electric fields.

REFERENCES

- [1] M. Foygel, R.D. Morris, D. Anez, S. French, V.L. Sobolev, "Theoretical and computational studies of carbon nanotube composites and suspensions: Electrical and thermal conductivity", *Phys. Rev. B* 71, 104201, 2005.
- [2] V. Tishkova, P-I Raynal, P. Puech^a, A. Lonjon, M. Le Fournier, P. Demont, E. Flahaut, W. Bacsa, "Electrical conductivity and Raman imaging of double wall carbon nanotubes in a polymer matrix", *Composite Science and Technology* 71, 1326, 2011.
- [3] R.R. Bacsa, E. Flahaut, Ch. Laurent, A. Peigney, S. Aloni, P. Puech, W.S. Bacsa, "Narrow diameter double wall carbon nanotubes: synthesis and inelastic light scattering", *New Journal of Physics* 5, 131, 2003.
- [4] V. Tishkova, G. Bonnet, F. Pons, B. Gautier, PH Cadaux, P. Puech, W. Bacsa, "Uniform dispersion of nanotubes in thermoplastic polymers through thermal annealing", *Carbon* 53, 399, 2013.
- [5] V. Tishkova, E. Pavlenko, M. Legros, G. Bonnet, P. Puech and W.S. Bacsa, "Unusual thermal diffusion of carbon nanotubes in a thermoplastic polymer", *NSTI-Nanotech 2012*, Santa Clara, Technical Proceedings (ISBN 978-1-4665-6274-5) 1, 298, 2012.