

Diagnostics of carbon nanotube composites by Raman spectroscopy

P Puech, A. Bassil, S Barrau^{*}, P Demont^{*}, R R Bacsa^{**}, E Flahaut^{**}, W S Bacsa

LPST, UMR CNRS 5477, IRSAMC, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France, bacsa@lpst.ups-tlse.fr

^{*}LPP, CIRIMAT, UMR CNRS 5085, Université Paul Sabatier, 31062 Toulouse, France

^{**}LCMIE, CIRIMAT, UMR CNRS 5085, Université Paul Sabatier, 31062 Toulouse, France

ABSTRACT

We use Raman imaging as diagnostic tool to assess the degree of interaction of double wall carbon nanotubes with the composite matrix. The local environment of the carbon nanotube has a strong influence on the Raman G and D band shape, spectral position and relative intensity. Additional spectral lines are observed due to the interaction of amphiphilic molecules with carbon nanotubes. We use high pressure experiments on carbon nanotubes using different pressure transmitting media and correlations in the observed peak shifts to estimate the local pressure in carbon nanotubes composites.

Keywords: Carbon nanotubes, composites, Raman spectroscopy

1 INTRODUCTION

Carbon nanotube polymer composites are promising for applications due to their exceptional mechanical and electronic properties to improve the elastic properties of polymers or to make polymers conductive. The large surface of carbon nanotubes (CNTs) make them interact strongly with their environment. CNTs tend to agglomerate into bundles which are difficult to entangle. But the interaction of CNT with the polymer matrix so far is not sufficiently strong to improve their mechanical properties significantly. Functionalization of carbon CNTs can improve the interaction with the matrix but may reduce at the same time the intrinsic mechanical property of the CNT. Double wall carbon CNTs are believed to be an attractive alternative. Strong interaction through functional groups of the external wall can be combined with the unperturbed mechanical properties of the internal CNT. Functionalization is also a method to successfully untangle tube bundles and to improve the dispersion of the CNTs in the matrix.

Raman spectroscopy is particularly useful in characterizing the structural properties from macroscopic amounts to single and isolated CNTs [1]. Spectral images can be generated by mapping CNTs on surfaces. The Raman spectrum of CNT shows three main bands: the low frequency radial breathing mode (RBM, 100–500 cm^{-1}), the defect induced D band (1350 cm^{-1}) and the in-plane optical mode (G band 1585 cm^{-1}). In addition several overtone

bands ($D^*=2D$ band, $2D+G$ band) can be observed. The RBM energy is directly related to the tube diameter and the chirality (helicity) for small diameter tubes (<1 nm). Spectral position of the D band varies with excitation energy at a rate of 50 cm^{-1}/eV . Thomsen and Reich explained the D -mode frequency shift with excitation wavelength or the D band dispersion in graphite by considering disorder induced double resonance scattering processes [2]. The G band is due to the optical phonons of the honey comb lattice. For single wall CNTs the G band is split into two bands (G, G^+) due to the optical phonons perpendicular and parallel to the tube axis. For double wall CNTs the G band is broadened and the G band position is located at 1582-1596 cm^{-1} [3]. We investigate here the distribution of DWNTs in epoxy resin and their interaction with an amphiphilic molecule.

2 EXPERIMENTAL

The CNTs were prepared by the catalytic chemical vapor deposition method. Selective reduction at 1000 °C in a methane-hydrogen (18% CH_4) atmosphere of a solid solution of a transition metal oxide $\text{Mg}_{0.95}\text{Co}_{0.050}$ led to the formation of small diameter CNTs with one to three walls [4]. 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 CNTs were mainly single (SW) and double walled (DW) [4]. 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 (0.2-0.8%) and the suspension was sonicated for 1h 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. All Raman spectra were recorded at room temperature (MicroRaman, Renishaw Inc). The scattered light was collected in backscattering geometry using a microscope objective (x40) to focus the laser beam (514 nm, 2-5mW) on the sample.

3 RESULTS

Figure 1 shows Raman map of the spectral position of the G band on the surface of the composite. When scanning

distances of 60 μm over the surface and recording a spectrum in steps of 2 μm , we notice considerable shifts in the G band of up to 30 cm^{-1} (region 1 and 2 in figure 1) and a splitting of the G band at some places. Apart of the G band several bands in the 1000-1500 cm^{-1} spectral region are observed. These addition bands are attributed to the amphiphilic molecules interacting with the CNTs. The intensity of the most intense additional band at 1450 cm^{-1} is found to be directly correlated to the G band shift: higher spectral G band position corresponds to higher intensity of the band at 1450 cm^{-1} [5]. This band can be assigned to the CH bending mode in the CH_3 group [6]. This shows that the G band shift to higher energies is related to the interaction of the amphiphilic molecules with the CNT. In the case of DWNTs only the external wall is influenced by the amphiphilic molecules which results in a general broadening of the G band.

Shifts of the G band to higher energies are observed for CNTs in hydrostatic pressure experiments. Diameter reduction strains the chemical bonds in the cylindrical wall which results in an up-shift of the G band. The G band position is sensitive to the in-plane strain or compression. When applying an external hydrostatic pressure the G band of DWNTs shifts at a rate between 5.1-3.3 $\text{cm}^{-1}/\text{GPa}$ and for the external tubes between 5.8-8.6 $\text{cm}^{-1}/\text{GPa}$ depending on the pressure media [7]. The different pressure coefficients for internal and external tubes are explained by the fact that the pressure condition is different for the internal and external tubes. The internal tube is not exposed to any pressure from the inside when assuming the tubes are not filled. This has the effect that the G band splits with applied external pressure.

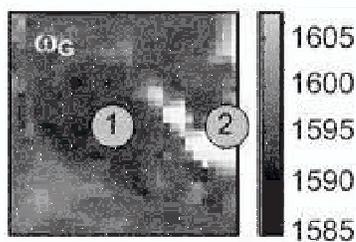


Fig.1: Raman map of G band energy, image size 60x60 μm . Region 1 and 2 explained in text.

We observe that the spectral position of the D band and D^* band shift the same way as the G band and disappears on some locations on the polymer composite surface. There is a clear correlation between the D and G band spectral position when comparing the D and G band across the surface. Interestingly the intensity of the D band is reduced considerably when shifting to higher energies [8]. This indicates that the disorder induced double resonance scattering process is less efficient when the CNT is under

compression. The D band cannot be observed in hydrostatic high pressure experiments due the pressure marker signal. The correlation of the D and G band position can be used here to determine the pressure coefficient for the D band ($\delta\omega_D/\delta\omega_G = 0.51$).

By changing the concentration of the amphiphilic molecules we expect to influence the dispersion of CNTs in the composite. Figure 2 shows two Raman maps of the G band energy when changing the concentration of palmitic acid. The G band shift distribution across the surface is different for the two concentrations. The spectral map of the G-band position from the sample with 0.2% of palmitic acid (2.a) shows areas which are connected and show a continuous transition. The brighter areas correspond to larger G-band shifts indicating the presence of DWNTs surrounded by amphiphilic molecules. Variations of the G band shift on the scale of 10 μm meters are observed. For the sample with 0.8% of palmitic acid (2.b), we observe isolated spots corresponding to large G band shifts.

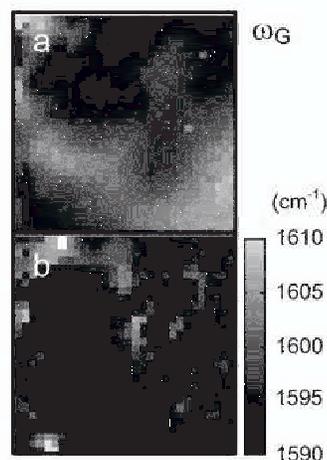


Fig. 2: Raman map of G band energy, image size 60x60 μm for two different concentrations of palmitic acid (2.a): 0.2%, 2.b): 0.8%)

This observation suggests that the CNTs agglomerate when the concentration of the amphiphilic molecules is too large. From the Raman analysis, we conclude that for lower concentration of palmitic acid, the amphiphilic molecules are interacting with the CNTs and help to disperse the CNTs in the polymer matrix. The shift of the G band, due to the interaction with the palmitic acid is as high as 30 cm^{-1} and is correlated with the intensity of the band at 1450 cm^{-1} .

The Raman maps show that even in the best case there is considerable heterogeneity in the dispersion of the CNTs in the epoxy matrix at the length scale of 2-10 μm . The actual shift of the G band can in principle be correlated with the hydrostatic high pressure experiments which would give

the possibility to convert the G-band to a specific local effective pressure. By changing the pressure medium in hydrostatic pressure experiments, however, we find that the pressure coefficient depends on the pressure medium [7]. This indicates that the interaction on the local level such as the organization of the molecules of the pressure medium around the CNT influence the pressure coefficient of the Raman bands.

4 CONCLUSION

Raman maps of CNT epoxy composites show a considerable variation of the G band and D band position. The appearance of an additional band at 1450cm^{-1} is attributed to the interaction of amphiphilic molecules with the CNTs. The band shift of this additional band is correlated with the G band shift. The G band variation at the length scale of $2\text{-}10\mu\text{m}$ is then used as an indication of the degree of interaction and dispersion of the DWNTs in the epoxy matrix. We find considerable variation in the dispersion of the DWNT in the epoxy matrix in the $2\text{-}10\mu\text{m}$ length scale. Variation of the pressure coefficient in hydrostatic pressure experiments observed from different pressure media indicate variations of the local pressure experienced by the DWNTs possibly related to organization of the molecules of the pressure medium on the DWNT surface.

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