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Electrical conductivity and Raman imaging of double wall carbon nanotubes in a polymer matrix

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A. Carbon nanotubes
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A. Polymer–matrix composites (PMCs)
B. Electrical properties
D. Raman spectroscopy

A B S T R A C T

Raman spectroscopy is used to access the dispersion state of DWNTs in a PEEK polymer matrix. The interaction of the outer tube with the matrix can be determined from the line shape of the Raman G band. This allows us to distinguish regions where the nanotubes are well dispersed and regions where the nanotubes are agglomerated. The percolation threshold of the electrical conductivity of the double wall carbon nanotubes (DWNTs)/PEEK nanocomposites is found to be at 0.2–0.3 wt.%. We find a maximum electrical conductivity of 3×10^{-2} S/cm at 2 wt.% loading. We detect nanotube weight concentrations as low as 0.16 wt.% by Raman spectroscopy using a yellow excitation wavelength. We compare the Raman images with transmission electron microscopy images and electrical conductivity measurements. A statistical method is used to find a quantitative measure of the DWNTs dispersion in the polymer matrix from the Raman images.

1. Introduction

Carbon nanotubes (CNTs) have excellent mechanical, thermal and electrical properties, and are conductive and reinforcement fillers in thermoset or thermoplastic polymers. Using the thermoplastic polymer as a matrix opens the possibility to combine the unique thermal and solvent resistant properties of the polymer with the electrical properties of CNTs. Poly(ether ether ketone) (PEEK) is a high performance thermoplastic polymer with high thermal and chemical stability as well as excellent mechanical properties [1]. Making PEEK electrically conducting, the composite can be used in antistatic coatings to remove static charges [2] and can shield electromagnetic radiation [3]. Carbon black, carbon nanofibers (CNF), as well as single and multi wall carbon nanotubes (SWNTs and MWNTs) have been incorporated in a PEEK matrix in the past. Progress has been achieved in the dispersion of the SWNTs in the PEEK matrix by using polyetherimide (PEI) [4] and polysulfones [5]. However, functionalisation has the effect that the thermal and electrical properties are lower compared to the raw SWNTs/PEEK composites [6,7]. The wrapping or functionalisation of the SWNTs increases the tube–tube electrical resistance. Diez-Pascual et al. [7] measured an electrical conductivity for PEEK/SWNTs composites of 10^{-2} S cm^{-1} at 1 wt% of nanotube loading and a low percolation have been observed (less than 0.1 wt%). Using multi-wall CNTs (MWNTs) Bangarusampath et al. [8] has found a percolation threshold in the electrical conductivity for a MWNTs/PEEK composite at 1.3 wt%. The conductivity value of 1 S/cm, required for the electrostatic applications, has been achieved at 17 wt% loading [8].

Direct and alternating-current electrical properties of thermoplastic polymers including PEEK were also studied using carbon black, graphite, and CNF [9]. It has been shown that carbon black and graphite fillers have a lower electrical conductivity than CNF. To improve the electric performance of CNT polymer composites it is important to control the filler dispersion in the polymer matrix. Comparative analysis of different nanocomposites shows heterogeneity of the experimental percolation thresholds depending on the filler, polymer and preparation methods [10]. For example the effect of the stirring speed on the percolation threshold show that at lower speed percolation threshold value is lower [11].

To get a better understanding of how the nanotubes are dispersed in the polymer matrix, we have used Raman spectroscopy to characterize the distribution of the carbon nanotubes in the polymer matrix [12]. The Raman shift of the G band can be used to investigate the load-transfer in the nanocomposites [13] and their tensile properties [14,15]. The development of new methods for the characterization of the CNT dispersion in the polymer is of particular interest.

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To have a better insight and to learn about dispersions of nanotubes in a polymer matrix we incorporated DWNTs in PEEK because as we will see, double wall carbon nanotubes (DWNTs) can serve as a local sensor for the interaction of the carbon nanotubes with the matrix. The G band of DWNTs is broadened due to the contribution of the two walls. It has been shown how doping and high pressure influences the outer and inner tubes [16,17]. Recently it has been shown how bundling or agglomeration of DWNTs affects the G band [18]. The difference in the frequency shifts from insulated and bundled DWNTs gives the possibility to distinguish their agglomeration state. In the present work we use Raman spectroscopy as a sensitive tool to evaluate the distribution of the DWNTs and to quantify the dispersion of the nanotubes in the polymer matrix. The results obtained from the Raman imaging are compared with the electrical conductivity measurements.

2. Materials and methods

DWNTs were synthesized by catalytic chemical vapor deposition (CCVD) described elsewhere [19]. The catalyst particles are partially removed through chemical etching. According to statistical studies on HRTEM images of CNTs 12% are single-walled, 70% double-walled and 16% and triple-walled, and 1.5% quadruple-walled [19]. The outer average diameter is 2.8 nm and an average length of approximately 10 μm. The BET specific surface area of CNTs was 700 $m^2\,g^{-1}$. The aspect ratio (length/diameter) of an individual carbon nanotube was estimated at 3500. After extraction, CNTs were washed many times with distilled water and kept in acetone prior dispersion in PEEK.

Poly(aryl ether ether ketone) PEEK used was supplied by Victrex, UK (Victrex® PEEK™ 90P high flow unfilled powder). According to Victrex, the density at 25 °C of PEEK matrix is 1.3 g cm^{-1} and the melt viscosity is 90 Pa s at 400 °C. From differential scanning calorimetry (DSC) a PEEK melting temperature of 341 °C and crystallinity of 32% were determined. The PEEK powder was added to a CNTs/acetone suspension and then submitted to a short pulse of sonication probe for 10 s, corresponding to a dissipated power of 50 W. The PEEK/CNTs/acetone suspension was then heated to 50 °C to evaporate most of the acetone. The remaining paste was compression molded in a Carver hydraulic hot press at 400 °C for 30 min under about 0.01 MPa. With this process, composites containing 0.16, 0.3, 0.5, 0.8, 1.2, 1.5 and 2 wt% were prepared.

2.1. Electrical measurements

Electrical conductivity measurements were carried out by recording the complex conductivity $\sigma^*(\omega)$ using a Novocontrol broadband spectrometer. The measurements were carried out in the frequency range of 10^{-2}–10^6 Hz at room temperature. The real part, $\sigma'(\omega)$ of the complex conductivity $\sigma^*(\omega)$ was investigated. For all the nanocomposite samples considered in this study, the phase lag between the measured impedance and the applied alternating current (ac) voltage was negligible at low frequencies, so that the reported impedance at 0.01 Hz is equivalent to the direct current (dc) resistance with a threshold detection limit of $10^{14}\,\Omega$. The dc conductivity σ_{dc} of samples was determined from the independent frequency part of $\sigma'(\omega)$ i.e., the low frequency plateau.

2.2. Microscopy

Transmission electron microscopy (TEM) measurements were performed on a TEM microscope Phillips CM 20 at 150 kV. The composites samples were cut into thin (100 nm) slices at room temperature using Ultratome equipped with a diamond knife and deposited on copper TEM grid.

2.3. Raman imaging

Raman imaging was performed on a Jobin–Yvon Horiba T64000 spectrometer using 568 nm excitation wavelength (Krypton laser). The sample was placed on a XY mechanical or piezo-electric table; the measurements were done on areas of 50 by 50 μm with step of 1 μm and 200 by 200 μm with step 3.4 μm. Each Raman spectrum is fitted with a Lorentzian function, and then maps of the intensities and positions of the G band are plotted.

We have used TEM and Raman imaging as well as electrical conductivity measurements in function of CNTs weight fraction. The Raman signal from DWNTs gives the possibility to distinguish between tube agglomeration and the dispersion of individual tubes. The main advantage compared to SWNTs is that DWNTs have an outer tube which can interact with the matrix but leaving the inner tube pristine. DWNTs form long bundles favoring the network formation of DWNTs in the polymer matrix.

3. Results and discussion

A drastic increase in the direct current electrical conductivity of DWNTs/PEEK composite takes place when conductive CNTs form a network of connected paths through the insulating PEEK matrix. The conductivity of the composite, σ_{dc}, above the percolation threshold is treated with a power law according to the percolation theory:

$$\sigma_{dc} = \sigma_0 (p - p_c)^t \tag{1}$$

where σ_0 is the conductivity of the filler, p the filler weight fraction, p_c the percolation threshold (the onset of the insulate-conductor transition) and t is universal critical exponent, which depends on the dimensionality of the conductive network. t = 1.6–2 in three dimensions and $t > 2$ have been observed in anisotropic systems.

We find that the electrical percolation in DWNTs/PEEK composites occurs when p_c is in the range of 0.2–0.3 wt% as seen in Fig. 1. A low percolation threshold for a three dimensional isotropic case is expected because the high aspect ratio of DWNTs and their relative good dispersion in the composites. The room temperature maximum conductivity σ_{max} of composite at 2 wt% of CNTs is about 3×10^{-2} S cm^{-1}. Fitting the composite conductivity data with Eq. (1) yields a percolation threshold of 0.25 wt% (solid lines in Fig. 1 and its inset). The value of exponent t is extracted from the fitting which yields 2.3. This value is close to the theoretical value for the

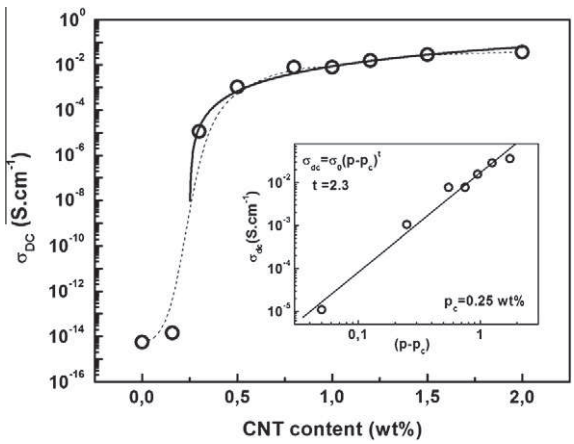

Fig. 1. Electrical dc conductivity of the DWNTs/PEEK composites as a function of CNTs weight fraction. Inset, log σ_{dc} plotted against log $(p - p_c)$, where φ_c is the percolation threshold. Solid lines in both graphs are calculated conductivities based on the fitting of the experimental data to the Eq. (1). Fitted parameters are: t = 2.3, σ_0 = S m^{-1} and p_c = 0. 25 wt%.

three dimensional conductive network. Extrapolation to $p = 1$ gives $\sigma_0 = 1.7 \times 10^{-2}$ S cm^{-1} which is five orders of magnitude lower than the conductivity measured in sintered DWNTs [20].

It is known that the percolation threshold and the conductivity depend strongly on the polymer type and synthesis method, aspect ratio of CNTs, disentanglement of CNT agglomerates, uniform spatial distribution of individual CNTs and degree of alignment. It is interesting to compare the physical parameters of DWNTs/PEEK composites such as p_c, t and σ_{max} obtained at room temperature with results observed in CNTs /PEEK or CNTs/semi-crystalline matrix. The same maximum conductivity of 10^{-2} S cm^{-1} was observed in SWNTs/PEEK composites [6]. In MWNTs/PEEK composites, a percolation was observed at 1.3 wt% with a low value of the critical exponent $t = 1.2$ and a conductivity of 10^{-2} S cm^{-1} for 0.2 wt% of MWNTs [8]. For a poly(ε-caprolactone)/polylactide semi-crystalline matrix filled by MWNTs, a percolation threshold of 0.2 wt% with a critical exponent of 2.2 and a conductivity of 10^{-4} S cm^{-1} for 4 wt% were observed [21]. The electrical conductivity of DWNTs/PVDF composites displayed a percolation behavior for only $p_c = 0.27$ wt% of DWNTs and $t = 1.91$ with a maximum conductivity of 10^{-1} S cm^{-1} for 2.6 wt% [22]. This shows that for DWNTs or MWNTs the percolation threshold is higher and often the electrical conductivity is smaller than when using SWNTs.

A percolation network needs to be formed in order to obtain a continuous path for the electrical conductivity. Dispersion of the CNTs in the polymer matrix plays a key role in the preparation of the conducting nanocomposites. TEM and Raman spectroscopy have been used to characterize the distribution of the DWNTs in the polymer matrix. Fig. 2 represents examples of the TEM images of 0.8 wt% DWNTs/PEEK composite. Fig. 2a shows a DWNTs agglomerate and the surrounding PEEK matrix. Fig. 2b is a higher magnification view of the same agglomerate. From the images one can see that the DWNTs contain residual catalyst particles (2–20 nm in diameter). The DWNTs diameter is 2–3 nm and the observation of individual nanotubes is found to be challenging made due to the presence and thickness of the polymer matrix which reduces the image contrast. The TEM images reveal an inhomogeneous dispersion of carbon nanotubes in the polymer matrix and most of nanotubes form large agglomerates.

Raman imaging analysis was used to determine the CNTs dispersion in PEEK at different concentrations (Fig. 3a–f). We have carried out several Raman maps at different scales and different regions. We show here results which are similar what we have found in several random regions of the sample. Fig. 3a–c shows the intensity map of the G band over an area of 200 by 200 μm for (a) 0.16 (a), 0.8 (b) and 1.2 wt% (c). Fig. 3d–f shows the spectral position map of the G band over the same area for the three weight

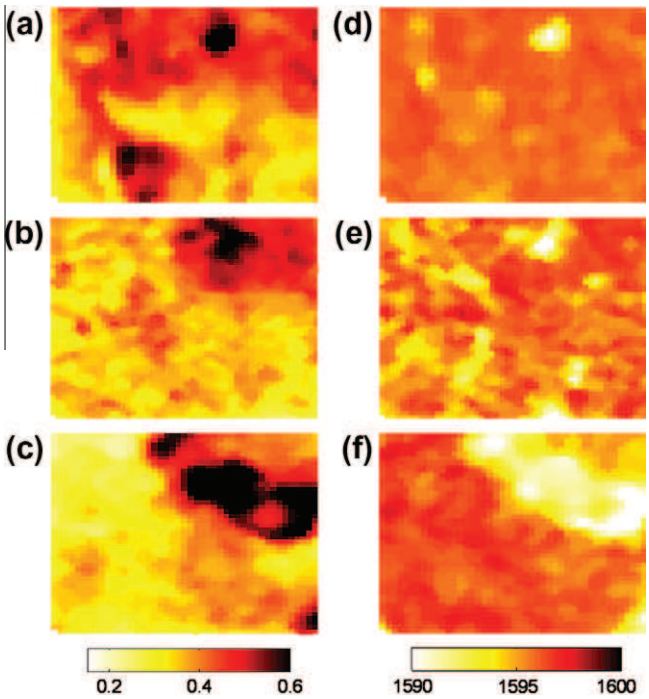

Fig. 3. Raman imaging of DWNTs/PEEK composites at different weight fraction. (a–c) From intensity of the G band. (d–f) From the position of the G band. (a and d) 0.16 wt%. (b and e) 0.8 wt%. (c and f) 1.2 wt%. The size of the maps is 200 × 200 μm.

fractions respectively. As a first approximation the intensity I_G of the G band is proportional to the density of tubes. At low concentration the G band is absent in some areas due to the lack of nanotubes. As the CNTs concentration increases, I_G increases and larger several micrometer sized CNTs agglomerates of nanotubes are visible. Fig. 3d–f shows that the G band is located at 1600–1605 cm^{-1} at low CNTs concentration for a large part of the image. At higher concentration the G band is downshifted in energy. At a weight fraction of 1.2 wt% (Fig. 3f), the G band is strongly downshifted to 1570 cm^{-1} at several positions on the nanocomposite sample.

Fig. 4a and b shows the G band Raman spectra of 0.8 wt% DWNTs/PEEK composite at two different locations of the sample. For regions with well dispersed CNTs, the G band is split into two peaks (Fig. 4b). It has been reported that the G band of DWNTs is composed of two peaks originating from the external and internal tubes [18]. The spectral position of the G band for the outer tubes was found to be sensitive to the chemical doping [23] and

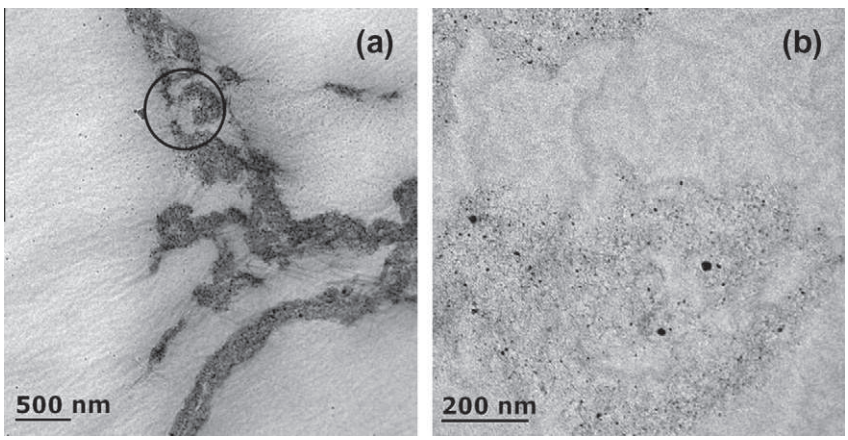

Fig. 2. (a) TEM image of 0.8 wt% DWNTs/PEEK composites. (b) Higher magnification view of (a) in the selected area.

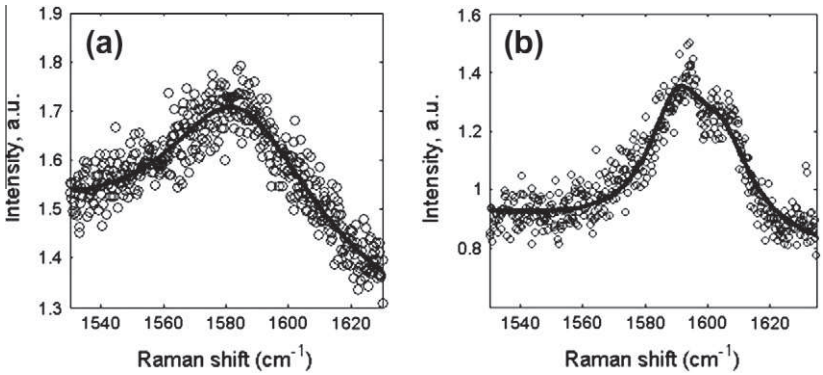

Fig. 4. High frequency Raman spectra of 0.8 wt% DWNTs/PEEK composite for: (a) agglomerated DWNTs, (b) well dispersed DWNTs. The red solid line is the Lorentzian fit to the G band of DWNTs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

to external pressure [24]. We assume that individual double wall tubes in a polymer matrix have a split G band like individual tubes on surfaces in air or in liquids. The splitting is explained by the interaction of the outer tubes with their environment. This means that the interaction of the outer tubes with the polymer matrix can be used as a local sensor for the dispersion of the DWNTs in the PEEK matrix: the splitting of G band indicates an interaction of outer tubes with the polymer matrix that is characteristic of a better dispersion. When the G band is observed at the same spectral position in pristine DWNTs and in composites, the nanotubes are organized in bundles or in agglomerates. The G band Raman spectrum in Fig. 4a is characteristic of DWNTs agglomerates because no splitting was observed. In Fig. 4b the upshift of the G band is associated with the interaction between the PEEK matrix and the outer tube and suggests that DWNTs are well dispersed in the polymer matrix. The obtained result is in agreement with observed radial breathing mode (RMB) of the DWNTs/PEDOT nanocomposites [25]. RBM band shifts associated with the outer tube diameter was observed in the composite compared to the pristine nanotubes. The position of the RBM band of the inner tube is not affected by the presence of the polymer [25].

Raman imaging has been performed for DWNTs weight fraction ranging from 0.16 to 1.5 wt%. In order to evaluate the quality of the DWNT distribution in the PEEK matrix the weighted mean w and the associated standard deviation σ of the G band position in the investigated composite sample has been determined:

$$W = \frac{\sum_i I_i P_i}{\sum_i I_i} \tag{2}$$

$$\sigma^2 = \frac{\sum_i I_i (P_i - \overline{P})^2}{\sum_i I_i} \tag{3}$$

where P, $\overline{P}$ and I are respectively the spectral position, the spectral position mean value and the intensity of the G band. Fig. 5 shows the weighted mean of the spectral position and its standard deviation as a function of DWNTs weight fraction. The weighted mean of the G band position below the percolation threshold displays the highest value while above 0.3 wt% the value is independent of the weight fraction and the standard deviation presents the same behavior. The weighted mean refers the interaction of the outer tube with the polymer. If the G band of the outer tube is up shifted, the DWNTs are in interaction with the polymer matrix. The standard deviation corresponds to the homogeneity of the dispersion. This means when the weighted mean is upshifted and the standard deviation is close to zero, the DWNTs are well dispersed in the polymer matrix. This is a simple method to quantify the quality of the dispersion using G band Raman images.

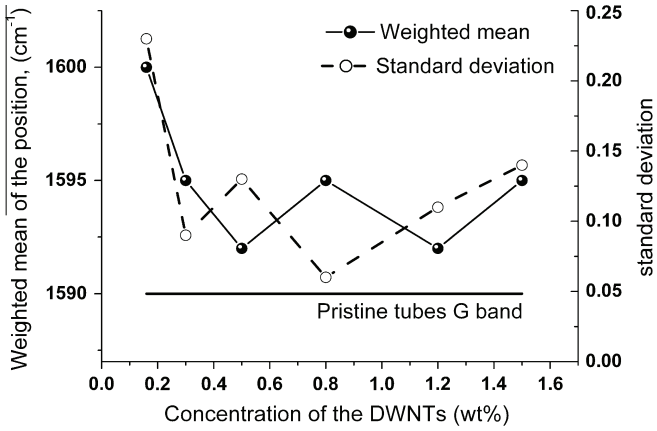

Fig. 5. Weighted mean and standard deviation of the G band position as a function of DWNTs/concentration in PEEK matrix. Solid line – position of the G band for the pristine DWNTs (from 1582 to 1600 cm^{-1}).

4. Conclusion

In this work we have studied the dispersion of DWNTs in a PEEK matrix. Electrical conductivity measurements show that the percolation is at 0.25 wt% of DWNTs and the maximum conductivity is 10^{-2} S cm^{-1}. We explored the DWNTs dispersion using G band Raman imaging. Difference in the G band position of inner and outer tubes in DWNTs are used as a local sensor, to distinguish areas where the tubes are well dispersed in the matrix and where the DWNTs are agglomerated. By optimizing the excitation wavelength we were able to detect DWNTs concentrations as low as 0.16 wt% using Raman spectroscopy. We find that DWNTs are difficult to detect in the polymer matrix at low concentrations due to their small diameter (1.8–3 nm) using electron microscopy. We find that the dispersion of individual tubes is better at low concentration but the overall dispersion is not homogeneous. We find that at DWNTs concentrations, where electrical percolation is observed in PEEK matrix, a uniform distribution of nanotube agglomerates is observed. Our experimental results confirm that the percolation threshold can be reduced by improving the nanotube dispersion.

Acknowledgments

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