Raman spectroscopy as a tool for the analysis of carbon-based materials (highly oriented pyrolitic graphite, multilayer graphene and multiwall carbon nanotubes) and of some of their elastomeric composites

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A B S T R A C T

Raman spectra of highly oriented pyrolitic graphite, multilayer graphene and multiwall carbon nanotubes are carried out at different laser powers and different excitation energies. The effects of the laser heating and the double resonance Raman scattering are investigated as a prerequisite for a correct interpretation of the Raman spectra of carbon materials-based composites. The Raman spectra of multilayer graphene and multiwall carbon nanotubes embedded in a silicone matrix are also analyzed in an attempt to get some insights into the polymer–filler interface.

1. Introduction

Carbon occurs in many forms and can be viewed as the building block of all other graphitic carbon allotropes of different dimensionality such as graphene, graphite or carbon nanotubes. Graphene is an atomically thick, two-dimensional (2-D) sheet composed of sp^2 carbon atoms arranged in a honeycomb structure, graphite (3-D carbon allotrope) is made of graphene sheets stacked on top of each other and separated by 3.37 Å and carbon nanotubes are one-dimensional systems formed by one or several graphene layers rolled up into cylinders. These carbon nanomaterials that possess unique nanostructures, have attracted considerable interest on account of their outstanding electrical, mechanical and thermal properties. Incorporated into polymeric media, they impart to the host matrix, considerable property enhancements at much lower loadings than conventional fillers [1–6]. The dispersion of the nanofillers in the polymer matrix as well as the interfacial bonding between the polymer–filler system are important parameters in the extent of property improvement.

Raman spectroscopy has become a key technique for the characterization of these materials ranging from highly oriented pyrolitic graphite (HOPG), graphene, carbon nanotubes, pyrocarbons or carbon black. Because their Raman scattering is resonantly enhanced, they give rise to strong well-defined bands even if they are used at very small amounts in a polymer matrix. Raman spectroscopy has been shown to yield detailed information on the different carbon nanostructures and on their degree of structural disorder [7] as well as on their state of dispersion [8] and orientation [9–11] in a host polymeric medium. Raman spectroscopy has also been used to probe the interactions between the polymer chains and the nanotubes in carbon nanomaterials-based composites. Carbon species are deformed under application of a mechanical deformation and some of their Raman bands shift linearly to lower frequency with increasing strain as a result of a change in the interatomic force constants [12]. In composites submitted to an uniaxial strain, shifts and hence reinforcement are observed if stress transfer takes place from the polymer matrix to the carbon material [13,14].

The aim of this work is to explore the potential of Raman spectroscopy for the analysis of carbon nanomaterials-based composites. But interpretation of the results requires first determination of the intrinsic spectroscopic properties of the carbon

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species. For this reason, we will discuss specific features of the Raman spectrum such as laser induced temperature effects and frequency dependence of some Raman bands on the laser excitation energy that may strongly affect the scattering signal. Highly oriented pyrolitic graphite considered as an almost perfect infinite stacking of graphene layers, multilayer graphene and multiwall carbon nanotubes as well as composites based on poly(dimethylsiloxane) (PDMS) filled with either carbon nanotubes or multilayer graphene, are examined with a special focus on the curious excitation energy dependence of some bands of the carbon species in order to get information on polymer–filler interactions.

2. Experimental

2.1. Materials

Graphene powder (N006-P), consisting in multilayer graphenes (MLG) with grain sizes of ~10–20 nm in thickness and approximate lateral dimensions of 14.0 μm, was supplied by Angstron Materials Inc., USA.

Multiwall carbon nanotubes (MWNTs) were purchased from Nanocyl S.A. (Belgium). In this study, we have used the Nanocyl 7000 series (purity: 90%) produced via the catalytic carbon vapor deposition (CVD) process without any further purification. Their average diameter and length are around 10 nm and 1.5 μm, respectively, and their surface area between 250 and 300 $m^2 g^{-1}$. HOPG is highly oriented pyrolitic graphite purchased from Carbone Lorraine France.

Hydroxyl-terminated PDMS (average molecular weight of 18,000 g mol^{-1}) was purchased from Gelest.

2.2. Preparation of the composites

The unfilled network was prepared from the hydroxyl-terminated PDMS by an endlinking reaction with tetraethoxysilane (TEOS) as the cross-linking agent and stannous-2-ethyl-hexanoate as the catalyst. Theoretically, a stoichiometric balance between ethoxy groups of the tetrafunctional alkoxysilane cross-linker and the hydroxyl chain ends of the PDMS precursor chain, should lead to model networks in that the molecular weight M_c between cross-links is predetermined as well as the functionality of the cross-links (specifically 4). In fact, as reported in the literature, the end-linking reaction requires larger amounts of TEOS than the stoichiometric equivalent. In this study, an excess of TEOS of 50% with regard to the stoichiometric conditions, is used to ensure correct modulus and reasonable soluble fraction.

As already mentioned, nanotube dispersion in a host medium is really a challenge on account of the tendency of pristine tubes to assemble into bundles. It has been observed that homogeneous distributions of CNTs in the resulting material can be achieved by sonicating CNTs in a suitable solvent before incorporating the solution in the polymer. For the preparation of the PDMS/MWCNTs composite, the adequate amount of MWCNTs is dispersed in iso-propyl alcohol by sonicating the suspension for 30 min using a Vibra-Cell VCX 500 operating at 40% amplitude with on and off cycles, respectively, equal to 4 and 2 s. After a rest of 30 min, the mixture is submitted to a further sonication for 30 min. PDMS is then mixed to the MWNTs suspension by agitation under magnetic stirring until total evaporation of the alcohol. The cross-linking agent and then the catalyst are incorporated and after further mixing for a few minutes, the mixture is slowly cast into a Teflon mold and left overnight at room temperature for complete curing.

For the composites prepared with MLG, no ultrasonic treatment is required as recommended by the supplier. MLG is directly dispersed in PDMS under magnetic stirring till obtaining a homogeneous mixture. Then curing reaction and film formation proceed as described above.

2.3. Characterization

The Raman spectra of pure carbon-based materials were measured using a LabRam HR Evolution Raman Spectrometer (Jobin-Yvon Horiba Scientific) with a Confocal Microscope at room temperature. The experiments were carried out with different excitation wavelengths 355 nm, 405 nm, 532 nm from laser diode modules and 633 nm from a He–Ne laser. Detection was achieved with an air cooled CCD detector and a grating 1800 grooves/mm, giving a spectral resolution of 4 cm^{-1} at 355 nm and 3 cm^{-1} at 405 nm. A second grating 600 grooves/mm has been used at 532 nm and 633 nm giving a spectral resolution, respectively, of 4 cm^{-1} and 3 cm^{-1}. The confocal aperture was adjusted to 150 μm and a 50× objective of 0.75 numerical aperture was used. After changing the excitation wavelength and before recording the spectrum of a new sample, the calibration of the spectrometer is checked by using the line at 521 cm^{-1} of the silicon sample.

The effects of the laser heating were investigated by using the 532 nm line as the excitation. The laser power ranged from 250 μW to 12.5 mW. The experiments were performed by initially submitting the sample to minimal laser power density. The power density was then increased, and spectra from the same sample area were recorded again.

3. Results and discussion

3.1. Graphitic carbon materials

The Raman signals arising from lattice vibrations (phonons) of graphitic materials consisting of stacked graphene layers, are very sensitive to the degree of structural disorder (defects). In the case of highly oriented pyrolitic graphite (HOPG), that is a grown graphite with a quasi-perfect infinite ABAB stacking of graphene layers, only two phonon modes with E_{2g} symmetry at the center of the first Brillouin zone are active in first-order Raman scattering. The first one is located at about 43 cm^{-1} and corresponds to anti-phase translational motions of successive layers perpendicular to their normal [15]. It is hardly observable because of its proximity with the Rayleigh line. Note that in a single layer (1L) graphene this mode does not exist. The second one, commonly called the G band, is located at 1581 cm^{-1} (Fig. 1) and corresponds to the zone center vibration of carbon atoms against each other's in the layer planes [15]. This is a common feature of all graphene and carbon graphitic materials. The Raman spectrum of HOPG recorded under the excitation wavelength of 532 nm also exhibits bands at 2442, 2718 and 3247 cm^{-1} (Fig. 1); they are assigned to second-order Raman scattering due to two-phonon processes [15].

The presence of disorder in the graphitic lattice is associated with the occurrence of two other features: the D band (D for defect) around 1350 cm^{-1} and a high frequency shoulder of the G band located around 1620 cm^{-1}, called D′ band [15,16]. The bands at 2718 and 3247 cm^{-1} have been attributed to the first overtones of the D and D′ bands, respectively (2D and 2D′ bands, respectively), while the band at 2442 cm^{-1}, denoted as D + D″, is related to a combination of a D phonon and a phonon belonging to the longitudinal acoustic branch (LA), seen at ~1100 cm^{-1} in very defective samples [15], and called the D″ peak [16].

In multilayer graphene (MLG), besides the G band and the multi phonon bands, the Raman spectrum displays the D and D′ bands accounting for edge-induced structural defects, respectively, located at 1349 and 1618 cm^{-1} (Fig. 1). Their low intensity reflects a small amount of defects in the sample.