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Vibrational Spectroscopic and Mechanical Investigation of Carbon Nanotube-Reinforced Styrene-Butadiene Rubbers

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Summary: This paper reports investigations carried out on elastomeric matrices based on a styrene-butadiene copolymer filled with multiwall carbon nanotubes. Stress-strain measurements of the composites demonstrate that carbon nanotubes bring significantly improvements in the mechanical properties with regard to the pure polymer. Raman spectroscopy, which is one of the most extensively employed methods for the characterization of carbon materials, has been applied for the analysis of the dependence of the Raman spectra on the nanotube content and on application of an uniaxial deformation. The results reveal a negligible stress transfer suggesting a weak interface between the tubes and the polymer chains.

Keywords: carbon nanotubes; elastomers; infrared spectroscopy; nanocomposites; Raman spectroscopy

Introduction

In practical applications, elastomers are usually reinforced with mineral fillers such as silica or carbon black to improve their physical and mechanical properties. The effectiveness of the reinforcing filler has been shown to depend on several parameters including the size of the particles, their aspect ratio (length/diameter), their state of dispersion and orientation in the matrix as well as their degree of interaction with the polymer chains.[1,2]

The last few years have seen the extensive use of nanoparticles because of the small size of the filler and the corresponding increase in the surface area, allowing to achieve the required mechanical properties at low filler loadings which is very attractive to industry. A reinforcement technique based on the incorporation of silica through a sol-gel in situ precipitation was developed by Mark et al.[3–8] for essentially silica filling of silicone rubbers. The sol-gel process prevents the formation of large silica aggregates frequently obtained by the usual blending of the filler into the polymer prior to its cross-linking into an elastomeric network and allows good control of the size and distribution of the particles within the matrix.[9] Other nanofillers, having large surface areas and aspect ratio, such as layered silicates or carbon nanotubes, are of prime interest as reinforcing agents for elastomeric matrices. If delamination of the stacked clay nanoplatelets or breaking down of bundles of aggregated carbon nanotubes are achieved, significantly enhanced properties are expected with regard to the unfilled polymers or conventional composites.

In the recent years, a considerable interest has been paid to the use of carbon nanotubes (CNTs) as electrical and thermal conducting inclusions and as a mechanical reinforcing agent for polymers. Carbon nanotubes consist of folded graphene layers with cylindrical hexagonal lattice structure. As a result of this unique arrangement, they display exceptional stiffness and strength and remarkable thermal and electrical

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properties, which make them ideal candidates for the design of advanced materials. These outstanding properties are expected to provide much higher property improvement than other nanofillers. In particular, the high aspect ratio of carbon nanotubes allows the formation of an interconnecting filler network called the percolation threshold at a much lower content than conventional conducting fillers like carbon blacks. The formation of a continuous network in the host medium has a strong impact on the electrical and mechanical response of the material. It results in a sharp drop of the electrical resistance of the nanocomposites and strongly contributes to the stress-strain behaviour of the resulting material.

The key parameters which determine the usefulness of carbon nanotubes as reinforcing fillers for elastomers are their effective dispersion within the matrix and the interfacial interactions between the polymer and the filler. Actually, one of the main problem with carbon nanotubes is their strong tendency to form agglomerates which act as defects in the composite and limit the mechanical performance of the resulting material. Despite the significant advances made on the processing of polymer composites, up to now poor dispersion and lack of interfacial adhesion between the tubes and the polymer matrix have been shown to limit the full realization of the filler properties for nanoscale reinforcement. Even if improvements in the composite tensile stiffness are observed, strain at break is often degraded as a result of the presence of bundles within the polymer matrix.[10–14] So, different processing methods have been used to optimize the dispersion of CNTs in the polymeric medium in order to fully exploit the potential of these materials.

This work presents some recent advances in processing and characterization of styrene-butadiene rubbers filled with multiwall carbon nanotubes (MWNTs). Mechanical measurements in addition to vibrational spectroscopic analyses, have been carried out in order to get molecular insights into the properties of nanotube based composites.

Experimental Part

Materials

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 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 $m^2.g^{-1}$. The average diameter as observed from the TEM micrographs is quite similar to that reported by the supplier (Figure 1).

The styrene-butadiene rubber (SBR) (Buna VSL 5025-0 from Bayer) was supplied by Formix (Orléans, France). It contains 25 wt% of styrene unit and a butadiene phase with cis (10%), trans (17%) and vinyl (73%) configurations. It was compounded with sulfur (1.1 phr), stearic acid (1.1 phr), cyclohexylbenzothiazole sulfenamide (1.3 phr), diphenylguanidine (1.45 phr) and zinc oxide (1.82 phr), ‘‘phr’’ means parts per hundred parts of rubber by weight.

Composite Processing

Different dispersion techniques are used to overcome the inter-tube van der Waals attraction without destroying the integrity of carbon nanotubes. One strategy that has been shown to preserve their intrinsic electronic and mechanical properties is to disperse them in a suitable solvent by ultrasonication before their incorporation

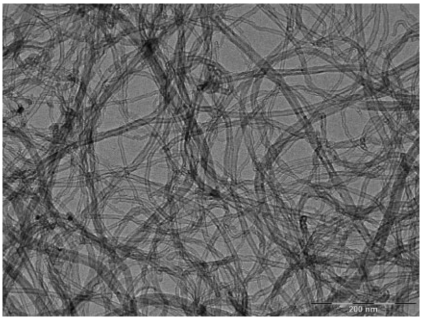

Figure 1.
TEM image of a suspension of MWNTs in cyclohexane.

into the polymer matrix. But sonication conditions have to be determined with great care to avoid tube damage.

In this work, an appropriate amount of MWNTs was dispersed into cyclohexane (in an approximate ratio 1:10 by weight) 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 seconds.

The gum containing the rubber (SBR or NR) and all the ingredients of formulation was mixed separately in cyclohexane under magnetic stirring until complete dissolution then mixed with the MWNTs dispersion.

The mixture may be submitted to a further sonication for 30 min if global examination by optical microscopy still reveals nanotube agglomeration on a micrometer scale. The sonication process is followed by agitation under magnetic stirring until evaporation of the solvent. Total removal of any remaining solvent is achieved under vacuum overnight at 50 °C before the cross-linking process and film formation.

The unfilled and filled samples were then cured into plaques at 170°C during 10 min under a pressure of 150 bar in a standard hot press. The resulting films were around 300 μm thick.

Characterization Techniques

The TEM image was obtained on a JEOL 100CXII. Carbon nanotubes at 0.01 wt% in cyclohexane were sonicated for 30 min and droplets of the suspension were placed onto copper grids for observation.

In order to evaluate the level of reinforcement provided by the MWNTs, strips of unfilled and filled elastomers were used in the uniaxial elongation experiments carried out to obtain the stress-strain curves at equilibrium.[15] The nominal stress σ, was calculated from $\sigma = f / A$, where f is the elastic force and A is the undeformed cross-sectional area.

The Raman spectra were recorded in the backscattering geometry on a Labram HR (Jobin-Yvon, Horiba Group, France) microspectrometer in conjunction with a confocal microscope. Most of the experiments were carried out with an excitation wavelength of 514 nm from a tunable Argon laser. A 100x objective of 0.9 numerical aperture was used.

Infrared spectra were obtained on a Tensor 27 from Bruker equipped with a Golden Gate single reflection attenuated total reflectance (ATR) system. ATR spectra were recorded with a resolution of 4 cm^{-1} and an accumulation of 32 scans.

Mechanical Characterization

The incorporation of reinforcing particles in an elastomeric matrix leads to an enhancement of the mechanical properties. Tensile tests are thus widely used to evaluate the extent of reinforcement imparted to the polymeric matrix by a filler. Representative stress-strain curves for pure SBR and for some SBR/ MWNTs composites are shown in Figure 2a (MWNTS). The stress at 100% deformation is seen to increase linearly with the MWNTs loading (Figure 2b). With regard to the pure polymer, 1 phr of MWNTs almost doubles the strain at 100% strain while a 1300% increase is observed for the 10 phr content. These observed improvements are higher than those previously obtained in the literature for the same polymer.[12,15–18] Such increases in stiffness are not observed for similar loading fractions of spherical carbon black or silica particles in the same matrix, thus highlighting the effect of the high aspect ratio (length/diameter) of the nanotubes.

Spectroscopic Investigations

Carbon nanotubes are now believed to be the ultimate filler for polymers. Good dispersion and high efficiency of stress transfer from the matrix to nanotubes are essential for mechanical reinforcement of polymers by nanotubes. Information at a molecular level are required to get a further insight into the properties of the composites.

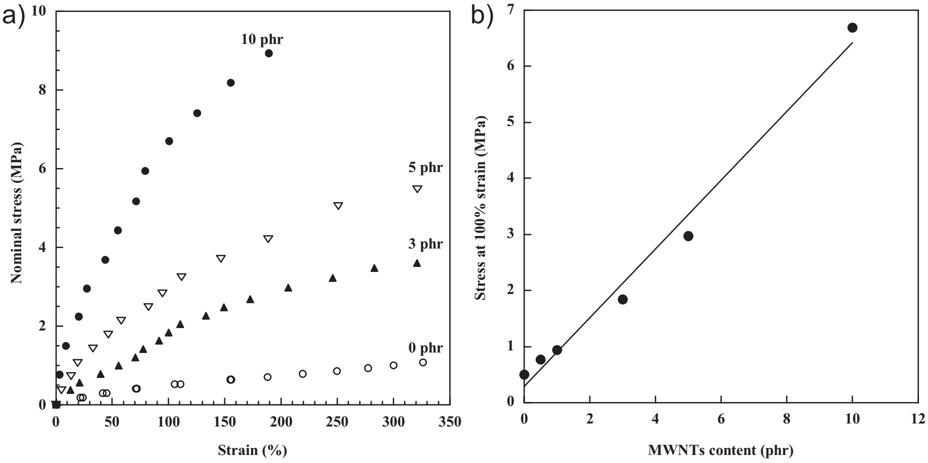

Figure 2.
Stress-strain curves (a) and stress at 100% (b) for pure SBR and SBR composites.

Raman spectroscopy has historically played an important role in the study and characterization of carbon materials.[19,20] A typical Raman spectrum of single-wall carbon nanotubes (SWNTs) displays four main features which are the radial breathing modes (RBMs), the D band (D from defect or disorder) and its associated overtone called G' band and the G band (G from graphite) which corresponds to the stretching of the C-C bond in graphitic materials.[21–23]

Although the D, G and G' modes are found in graphite, the radial breathing modes are specific to carbon nanotubes. These low frequency modes located between 150 and 350 cm^{-1} correspond to a mode where all atoms of the tube vibrate radially in phase as if the tube was breathing. The wavenumber of these modes are found to be inversely proportional to the tube diameter (d) according to this relation:

$$\omega(\mathrm{RBM}) = \mathrm{A}/\mathrm{d} + \mathrm{B}$$

where A and B depend on environment especially on the presence of nanotubes as individual cylinders or in the form of bundles.[24] This mode is an important feature to determine the diameter distribution in a sample.

The stretching of the C-C bond gives rise to the so-called G band. This mode which is located around 1580 wavenumbers is common to all sp^2 carbon systems. Unlike graphite, this mode in single-wall carbon nanotubes, gives rise to a multi-peak feature, also named the G band. However the two most intense G peaks correspond to atomic displacements along the tube axis and along the circumferential direction.[22]

The most discussed mode in the Raman spectrum of carbon nanotubes is probably the defect induced D-band which is observed between 1300–1400 cm^{-1}. This band has been associated with the presence of disorder in sp^2 carbon materials. The disorder can also be quantified by the analysis of the I_D/I_G ratio between the disorder-induced D-band and the Raman-allowed G-band. One important feature concerning this band is its strong dependence on the excitation laser energy which is unusual in Raman scattering. This fact is common to sp^2 carbon materials where it is seen that the position of the D band as well as its intensity depend linearly on the laser energy while the G-band is practically independent.[25–28] The D band dispersion has been explained by a resonant Raman process in which electronic transitions are linked to phonon modes that have the same wave vector as the π-π^* states involved in the absorption process.[25]

Finally the G' band located between 2600 – 2800 cm^{-1} is a second-order two-phonon process. This band which is a Raman signature of graphitic materials also shifts to higher wavenumbers with increasing laser excitation with a slope of about twice the slope of the D band.[28] This band is activated by double resonance processes which are responsible for its dispersive nature and cause a strong dependence on any perturbation occuring on the graphene structure. Recent studies have revealed that this band can be used to evaluate the strength of the interface between the nanotubes and the matrix in polymer composites because it is very sensitive to mechanical deformation. Strain-induced changes in peak positions and intensities have been observed for individual carbon nanotubes[29], nanotube bundles[30] and carbon nanotube-filled polymers.[31,32] For samples subjected to a tensile loading, a linear downshift as a function of the applied strain has often been observed in several studies and has been used to evaluate the stress transfer efficiency in composite materials.[33–36] This downshift is understood on the basis of an elongation of the carbon-carbon bonds, which makes the bond weaker and consequently lowers the vibrational frequency.[29]

The Raman spectrum of multiwall carbon nanotubes does not significantly differ from that of graphite. The radial breathing mode is usually too weak to be observable but we note the presence of the D band and its overtone as well as the classical G band which exhibits a shoulder around 1610 cm^{-1}. This shoulder is typical of defected graphite and can be smaller in better quality nanotube samples. As observed in single-wall carbon nanotubes, a strong dependence of the Raman bands on the laser frequency is observed especially for the D band that shifts, for pure nanotubes and for SBR composites, to lower wavenumbers with an increase in the excitation wavelength. The shift is also associated with an increase in the I_D/I_G ratio (Figure 3).

Figure 4 shows the Raman spectra of pure SBR, pure MWNTs and of two SBR/MWNTs composites. The spectra of the composites are seen to be almost dominated by the bands of the nanotubes.

Careful examination of the Raman spectra of the composites, shows that the bands of pure nanotubes are shifted to higher frequencies when carbon nanotubes are incorporated into the elastomeric matrix. For a laser wavelength of 514 nm, the D, G and G' bands are respectively

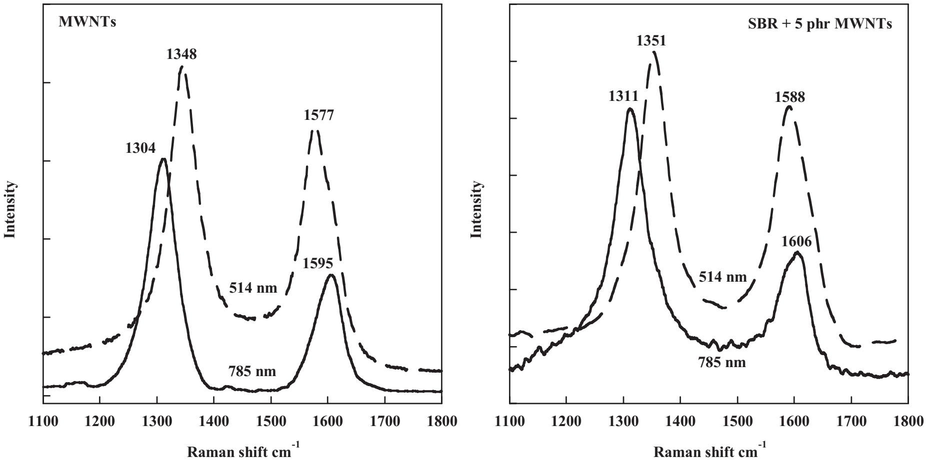

Figure 3.
Comparison of Raman spectra obtained at two different laser wavelengths (514 nm and 785 nm) for pure multiwall carbon nanotubes (MWNTs) and for a SBR composite filled with 5 phr of MWNTs.

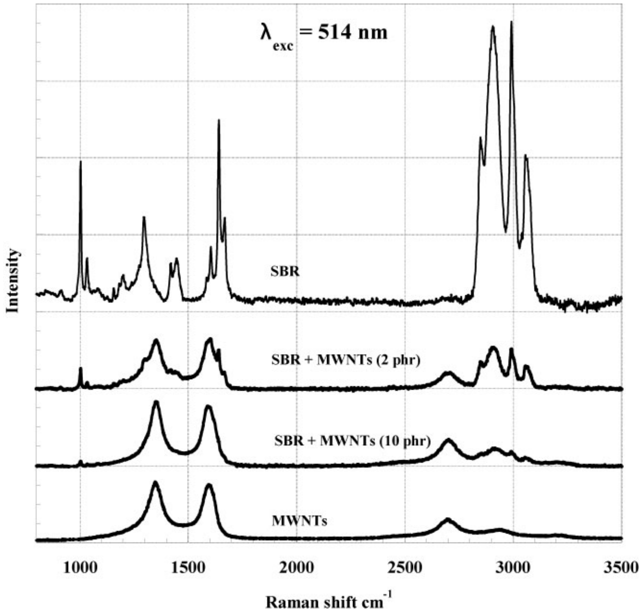

Figure 4.
Raman spectra of pure polymer, pure MWNTs and of two SBR/MWNTs composites using a laser wavelength of $\lambda_{exc} = 514$ nm.

located at 1348, 1577 and 2684 cm^{-1} in the Raman spectrum of MWNTs and at 1351, 1588 and 2700 cm^{-1} in the spectrum of the 5 phr MWNTs/SBR composite. This upshift is attributed to a disentanglement and dispersion of carbon nanotubes within the host matrix as a consequence of polymer penetration into the bundles during solution mixing.

The dependence of Raman spectra on the nanotube content is shown in Figure 5. A shift of the G band to lower wavenumbers with an increase in the nanotube loading is observed which could be considered as a sign of polymer-filler interactions. Nevertheless, it has to be pointed out that in the micrometer region probed, the Raman signal is the result of different contributions that could have opposite effects to the Raman band shift. These contributions include the strength of the interface between the nanotube and the polymer chains, the presence of nanotube bundles that cannot be avoided even with optimized dispersion conditions. On the other hand, especially at the highest filler loadings, embedded nanotubes can undergo mechanical compression during the polymer curing process. Compression will result in a positive shift of the Raman bands.

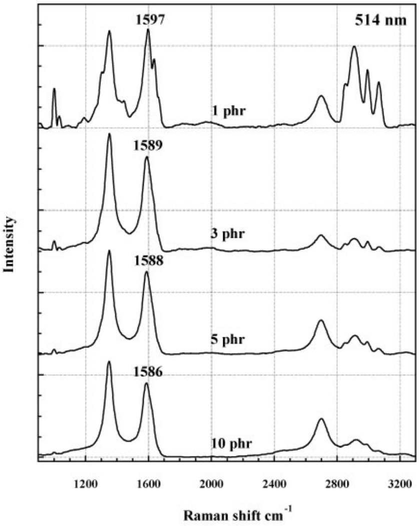

Figure 5.
Raman spectra of SBR/ MWNTs composites at different nanotube content obtained with an excitation wavelength of 514 nm.

As the Raman spectra of the composites are mostly dominated by the bands associated with the carbon nanotubes, it is difficult to detect Raman signals of the polymer chains. Infrared measurements with the use of an ATR accessory can yield information on bands associated with the chemical functional groups of the polymer chains. Only bands arising from the matrix are present in the infrared spectra. The ATR spectra of the unfilled SBR and of composites at different filler loadings are represented in Figure 6. The infrared spectra show a steeply rising baseline to the short wavenumbers but the spectral information is still present and shows that the bands of the pure polymer especially those associated with the stretching modes of the CH_2 group are shifted to lower wavenumbers in the composite spectra. These bands, respectively assigned to the asymmetric and symmetric stretch of the methylene group are both seen to decrease with the amount of filler. CH-π interactions were suggested to be involved between the π-electron–rich surface of the carbon nanotube and the methyl or methylene groups of polymer chains.[37]

Raman spectroscopy is expected to probe interactions between nanotubes and polymers in nanotube-based composites. If the nanotubes are carrying strain, the Raman peaks of carbon nanotubes will exhibit shifts upon application of a mechanical deformation to the composite. Large downshifts up to 20 cm^{-1} at about 1% strain have been observed for the G' band of SWNTs in stiff polymers such as epoxy resins.[33–35] In SWNTs/PMMA nanocomposite fibers, the frequency shift of the G band was used to probe the mechanism of load transfer from the polymer matrix to small SWNT bundles.[38] In rubbery composites like silicone rubbers, Frogley et al.[35] report a shift of the G' band of SWNTs of only 2 cm^{-1} over 50% strain which is much less than that observed in stiffer matrices. This small wavenumber strain shift, which is from our point of view, within the experimental uncertainty, reflects a weak interface between the two phases.

Upon stretching the composite filled with 5 parts of nanotubes, the strain-induced strain concerns essentially the G band which exhibits upshift with an increase in strain. But there is almost no significant shift of the G' band under tension which means that load transfer to the nanotubes is negligible (Figure 7a). The upshift in frequency of the G mode is not reversible because after total removal of

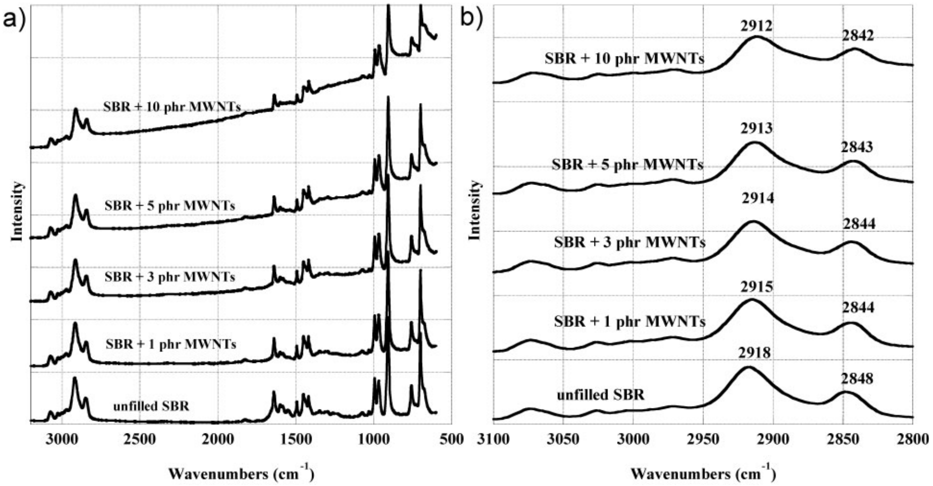

Figure 6.
ATR spectra of pure polymer (SBR) and of SBR/MWNTs composites.

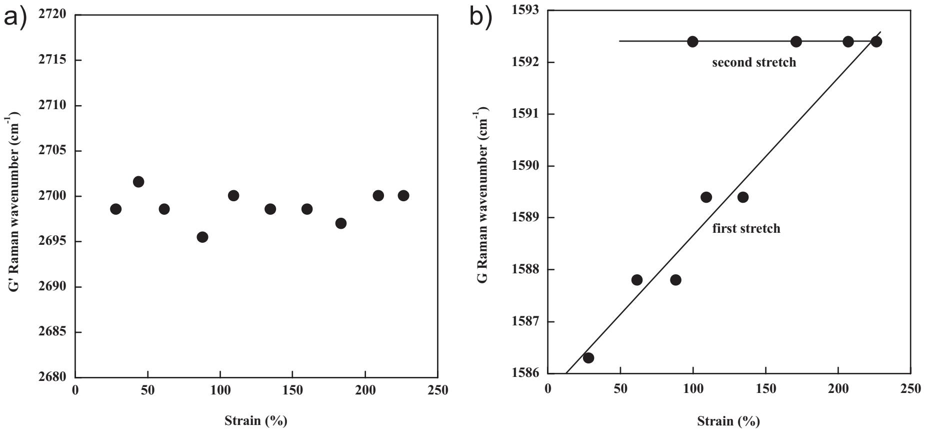

Figure 7.
Strain dependence of the G' band (a) and G band (b) for the SBR composite filled with 5 phr of MWNTs.

the stress and second stretching, we do not observe any shift with strain (Figure 7b). This leads to the belief that the main effect of the strain, in our case, is to debundle the nanotubes.

Conclusion

Carbon nanotubes really appear to be the ultimate filler for elastomers since they impart unprecedented levels of reinforcement to the rubbery matrices. It is due to the high aspect ratio and the relatively good state of dispersion. Another major attribute is to allow the formation of conductive polymers with tiny amounts of nanotubes. Raman spectroscopy, which has been widely used to investigate carbon nanotubes, shows, as in other sp^2 carbon materials, a strong dependence of the frequency of the disorder-induced D band in pure multiwall carbon nanotubes as well as in composites. Increasing the nanotube loading leads to a shift of the G Raman band to lower wavenumbers which could be seen as a sign of polymer-filler interactions. Raman spectroscopy has been also shown to provide extra insight into the interface of the polymer-filler system. Great promises are expected from the combination of Raman spectroscopy and AFM for an information at the nanoscale and an opening into the NanoRaman world.

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