Evaluation of the MWCNTs concentration in polymer nanocomposites by Raman spectroscopy

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ABSTRACT

A new Raman spectroscopic methodology is proposed to monitor the weight fraction of Multi-Walled Carbon Nanotubes (MWCNTs) in polymeric nanocomposites. In order to disentangle the parameters affecting the frequency of the Raman bands and their intensity, this methodology involves the acquisition of sets of Raman spectra as a function of MWCNTs loading, excitation laser power and temperature. In the specific case of isotactic polypropylene (iPP), any interaction of the carbon nanotubes with the polymeric host has minimal effect on the frequency of the MWCNTs G band ($\sim$1584 cm^{-1}); the same holds for the influence of residual stresses acting on the MWCNTs. The parameter that primarily alters the CNTs Raman bands frequency is temperature, determined by the excitation laser intensity, the MWCNTs concentration and the thermal properties of the polymer matrix. This is demonstrated by confocal micro-Raman spectra collected from agglomerates and from micro-Raman spectra of samples containing either poorly or well dispersed MWCNTs. A direct correlation of the G band frequency with the effective MWCNT wt% loading in the nanocomposites is confirmed after careful and systematic experiments performed on prototype well-dispersed samples.

1. Introduction

Last decade many scientific efforts have been undertaken for the fabrication of multifunctional polymer nanocomposites that take advantage of the unique combination of mechanical, electrical and thermal properties of carbon nanotubes (CNTs) [1,2]. Additionally, in CNTs incorporated polymeric membranes, the challenging issue of the immanent limitation of counterbalance between flux and selectivity is anticipated to be overcome [3–6] due to the CNTs high aspect ratio, their frictionless graphitic walls and the internal diameters of nano-scale range, acting as novel transport media by introducing channels in the polymer matrix.

One of the major parameters that influence the properties of the polymer–CNTs composite is the distribution/dispersion of the CNTs in conjunction with their weight percentage loading in the polymer matrix [1,7,8]. To this end, substantial preparation methods, like solution blending, melt blending

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and in situ polymerization, have been applied to improve the properties of the composites by achieving effective dispersion of the CNTs in polymer matrices. Optimized dispersion has been achieved by high power ultrasonication of the CNTs; this leads to metastable suspensions of CNTs (or their mixtures with polymers) in different solvents. Moreover, covalent or noncovalent (by use of surfactants) functionalization of CNTs offers the potential to tailor their interfacial properties [9,10].

In order to characterize the degree of the CNTs dispersion, or else their weight fraction within a medium, e.g. in a polymer matrix, several experimental techniques have been adopted. These include optical transmission microscopy, Scanning Electron (SEM) or Transmission Electron Microscopy (TEM), UV–Vis spectroscopy [11] and Raman spectroscopy. Raman imaging [12] offers a unique tool for direct characterization of the CNTs dispersion and loading in the polymer matrix by observation of the distribution of the intensity of CNTs bands on the composite's surface; however, it requires long time recordings and is more appropriate for characterization of surfaces in the order of ~100 μm^2. Raman spectroscopy is also known to provide information on the structure, crystallinity and ageing of both components of a composite material by evaluation of the associated vibrational features (band frequencies and widths). Alterations in CNTs band spectral features have been also proposed as indicators of their dispersion/loading characterization [13]. The parameters considered to affect the spectral features of carbon based materials are mainly temperature, pressure and intermolecular interactions and are briefly discussed in the next paragraphs.

In most cases, the Raman bands of carbon based materials experience softening with increasing sample's temperature. In their early work Everall et al. [14] stressed that the temperature shift of the vibrational bands of graphites and carbon fibres depends upon the excitation laser power, sample absorptivity (primarily determined by the carbon based materials absorptivity and their concentration in the polymer matrix), thermal conductivity and the efficiency of heat dissipation through the surrounding medium. The same parameters may also be considered for other carbon based materials such as CNTs, graphenes etc.

There have been several works studying different types of carbon based materials under external pressure [15–17]; in principle, pressure increase causes vibrational bands to shift to higher frequencies (blue shift). Pressure has been also proposed as a parameter that induces shifts of the Raman bands of CNTs composites mainly due to residual stresses (imposed by sample crystallinity and/or laser heating) [18,19].

Intermolecular interactions such as tube-tube and/or tube-matrix interactions depend on the strength of the interactions at molecular level between the polymer and the outer layers of the CNTs and could also result in vibrational band shifts [20,21].

Several studies deal with the characterization of CNT–polymer composites by Raman spectroscopy using various approaches in order to explain the alterations of spectral features some of which ascribe them to the dispersion state of the sample. For example, Kao et al. [13] reported

difference on the laser power dependence (up to a maximum of 2 mW) of the pristine SWCNTs Raman bands and the corresponding bands of the epoxy composite material, for the single case of 0.1 wt% loading. They observed a shift of G′ overtone of up to ~5 cm^{-1} between pristine and 0.1 wt% composite, attributed to either the dispersion of the nanotubes in the epoxy matrix or to the epoxy matrix limiting the thermal expansion of nanotubes due to heating (internal stress effect). Similar differences in the laser power dependence between frequencies of pristine MWCNTs Raman bands and the corresponding of composite materials have been reported for the styrene-butadiene/MWCNTs (SBR/MWCNT) system [20]. Relevant composites (3, 5 and 10 wt%) were illuminated with four different laser power values (up to 7 mW) and the G band appeared to sustain only slight shifts with laser power increase, the most intense of which was for the case of pristine CNTs. The authors attributed this phenomenon on either the MWCNTs rearranging in the SBR/MWCNT composites or the induced mechanical compression on the MWCNTs fillers by the SBR matrix. For the case of the binary system of amorphous carbon and single wall carbon nanotubes a method has been proposed, [22,23] that estimates the nanotube fraction percentage through the tangential mode shift under laser irradiation with different power densities.

From the above brief discussion, it is clear that there is need of further methodical work to evaluate appropriate Raman spectral features of CNTs and associate them with their dispersion characteristics or alternatively their respective concentration in polymer/CNT nano-composites.

The main concept of the current study is to establish a firm framework that correlates Raman spectral features with the dispersion state along with the concentration of the CNTs in a nano-composite material and (eventually to) provide pathways of experimental methodologies that interpret Raman spectral alterations.

2. Experimental section

2.1. Materials

MWCNTs with 97% purity over catalyst, external diameter between 15 and 35 nm and nominal length of ⩾10 μm were synthesized by Nanothinx (Patras, Greece) via chemical vapor deposition (CVD) [24]. The isotactic polypropylene (iPP) used for the preparation of the composite films was supplied from Ega-Chemie (T_m = 161 °C). Nanocomposites containing 0.25, 0.5, 1, and 4 wt% MWCNTs were prepared by melt mixing, using a home-made batch mixer [25]. In order to achieve better dispersion, the components of each film were physically premixed before being fed into the mixer. Melt blending was performed in the mixer at 190 °C and 40 rpm for 30 min under N_2 atmosphere. For one of the samples the blending time was intentionally set to less than 5 min. Prior to the melt mixing, the pristine nanotubes were sonicated for 15 min in ethanol and then dried in hood for 48 h; their typical length after the sonication was approximately 1.5 μm. The master-batches received after the mixing were melt-pressed (at 190 °C and 90 bar) into films using a hydraulic thermopress.