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Effect of solvent solubility parameter on SWNT dispersion in PMMA

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Abstract

SWNT were dispersed in PMMA in eight different solvents with varying three dimensional solubility parameters. Results show that for achieving good dispersion, the polar component (δ_p) of the solubility parameter is most important, while the other components, namely dispersive and hydrogen bonding (δ_d and δ_h), or the total solubility parameter (δ_t) do not appear to be so critical. The best SWNT/PMMA dispersion was achieved in nitromethane, the most polar solvent used in this study. SWNT/PMMA samples exhibiting different degrees of dispersion have been studied using Raman spectroscopy. The intensity variations in the Raman radial breathing mode, as well as changes in the tangential (G) and overtone of the disorder (G′) band peak positions are consistent with the qualitative dispersion observations obtained from optical and scanning electron microscopy.

Keywords: Dispersion; Nanotube; PMMA

1. Introduction

Due to their exceptional electronic and mechanical properties [1], interest in single wall carbon nanotubes (SWNT's) has increased steadily since, their discovery in 1993 [2,3]. They are considered to be ideal candidates for developing functional and structural polymer/SWNT composites [4]. It has been shown that the incorporation of only a few percent of SWNT into many polymers leads to significant improvement in mechanical [5–8] and electrical [9,10] properties. To fully explore their reinforcing potential, uniform SWNT dispersion is necessary. In addition, SWNT exfoliation and orientation are also important [11].

Raman spectroscopy is a powerful and non-destructive method to characterize SWNT and SWNT based materials. The typical Raman spectrum of SWNT includes four main features: the tangential G band (near 1600 cm^{-1} and derived from the graphite-like in-plane vibration mode), the disorder induced D band (around 1300 cm^{-1}), the G′ band (at about 2600 cm^{-1} and it is generally considered to be the overtone of D band), and the low-frequency (generally in the 200–500 cm^{-1} range) radial breathing mode (RBM), which corresponds to the collective in-phase radial displacement of the carbon atoms [12]. The position of RBM is inversely proportional to the nanotube diameter and is frequently used to characterize the diameter distribution in a given SWNT sample. The intensity of the RBM bands depends on the laser excitation energy (E_{laser}) according to the resonance theory. It reaches its maximum intensity when E_{laser} matches the energy separation E_{ii} between the Van Hove singularities (VHS's) in the nanotube electronic density of states (DOS) [13]. Raman spectroscopy is also very effective for monitoring carbon nanotube deformation. The position of both G and G′ bands downshift under a tensile strain and up shift upon the application of compression or with pressure [14–17]. SWNT Raman modes shift to lower wave numbers with increasing temperature and G band has a larger temperature co-efficient than the RBM bands [18].

In this paper, we report a SWNT dispersion study in PMMA in eight different solvents with varying solubility parameters. The dispersion was characterized by optical and scanning electron microscopy. The solvents and their three-dimensional solubility parameter values are listed in Table 1. All the composite samples have been analyzed using Raman spectroscopy.

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Table 1
Solubility parameters of various solvents and PMMA [26]

Name	Molecular formula	δ_d (MPa$^{0.5}$)	δ_p (MPa$^{0.5}$)	δ_h (Mpa$^{0.5}$)	δ_t (MPa$^{0.5}$)
Toluene	C_7H_8	18.0	1.4	2.0	18.2
Methylene chloride	CH_2Cl_2	18.2	6.3	6.1	20.3
Methyl ethyl ketone	$CH_3COCH_2CH_3$	16.0	9.0	5.1	19.0
Acetone	CH_3COCH_3	15.5	10.4	7.0	20.1
Formic acid	HCOOH	14.3	11.9	16.6	25.0
N,*N*-Dimethylformamide	$HCON(CH_3)_2$	17.4	13.7	11.3	24.8
Acrylonitrile	H2C=CHCN	16.5	17.4	6.8	24.8
Nitromethane	CH_3NO_2	15.8	18.8	5.1	25.1
PMMA	$(CH_2C(CH_3)CO_2CH_3)_n$	18.6	10.5	7.5	22.7

δ_t: total solubility parameter, which is defined as: $\delta_t^2=\delta_d^2+\delta_p^2+\delta_h^2$, δ_d dispersive contribution, δ_p polar contribution, δ_h hydrogen bonding contribution.

2. Experimental

HiPCO™ nanotubes received from Carbon Nanotechnologies, Inc., were used without purification (Lot # R0231 and 35 wt% metal catalyst). PMMA ($\bar{M}_w = 95,000–150,000$ g/mol) was obtained from Cyro industries and was used as received. All solvents were purchased from Aldrich or from Fisher Scientific and were also used as received. SWNTs (10 mg) dispersed in 30 ml solvent were sonicated (the sonicator: Branson water bath sonicator by Smithkline Company, model B-22-4, power 125 W, frequency 43 KHz) for 70 h at room temperature (water circulation was used in the bath to maintain the bath temperature at 23 °C). PMMA (90 mg) was added to this dispersion, followed by sonication for another 5 h. The dispersion was poured on to a glass plate, and the solvent was allowed to evaporate in the hood over several days. The resulting SWNT weight fraction in PMMA was 10 wt%. LEO 1530 field emission scanning electron microscope was used to characterize the morphology of the SWNT/PMMA composite films, and all the samples were coated with gold. The Raman spectra were collected on Holoprobe Research Raman microscope made by Kaiser Optical Systems, Inc., using 785 nm excitation wavelength ($E_{laser}=1.58$ eV). The laser spot diameter was a few micrometers and the resolution of the Raman spectrometer was 1 cm^{-1}. For each composite film, Raman spectrum was collected at different positions using an exposure time of 1 min or exposure time of 1 s with 100 accumulations to minimize heating effect.

3. Results and discussion

SWNT/PMMA dispersions are optically homogeneous when processed from nitromethane, acrylonitrile, and *N*,*N*-dimethylformamide, while other five solvents (toluene, methylene chloride, methyl ethyl ketone, acetone, and formic acid) resulted in heterogeneous dispersion.

Optical micrographs of the PMMA/SWNT dispersions in nitromethane and in methyl ethyl ketone are given in Fig. 1 as examples of homogeneous and heterogeneous dispersions, respectively. Scanning electron micrographs in Fig. 2 show that composites processed from methyl ethyl ketone and methylene chloride are phase separated. However, the rope diameter of the pristine SWNT as well as in the composite samples processed from various solvents, measured from scanning electron micrographs using the Mat Lab software, were all the same (26 ± 3 nm).

Fig. 2 also shows that the composite processed from nitromethane is more homogeneous than the one from *N*,*N*-dimethylformamide, In fact, of all the eight solvents, the composite processed from nitromethane appear to be the most homogeneous. These observations clearly suggest that solvents do play an important role in obtaining uniform SWNT dispersion in PMMA. From the SWNT/PMMA dispersion study, it was observed that when solvent polar solubility parameter component (δ_p) was higher than the corresponding δ_p value of the polymer, dispersion tended to be more homogeneous. While the total solubility parameter (δ_t), as well as the dispersive component (δ_d) and hydrogen bonding component (δ_h) do not appear to play that significant role in SWNT dispersion.

SWNTs are hydrophobic non-polar rigid-rods. Molecular dynamics simulation suggests continuous and spontaneous filling of a non-polar carbon nanotube with a one-dimensionally ordered chain of water molecules [19]. There may be an ordered arrangement of polar solvents around non-polar SWNTs and the extent of solvent penetration in the interstices of the SWNT bundle may increase with solvent polarity. The presence of this solvent may become the driving force for the polymer penetration, resulting in good SWNT dispersion.

PMMA/SWNT composites have been studied using Raman spectroscopy to see if differences in SWNT dispersion give a Raman signature. For this purpose, two types of samples were prepared. The first type of samples was dried in the hood for several days. The second type of samples were prepared by heating the hood dried samples in differential scanning calorimetry (DSC) from 25 to 150 °C at 5 °C/min and then cooling at the same rate to room temperature, in order to relax any thermal strains in the sample as well as to ensure the removal of any residual solvent. G band shift as a function of $\Delta\delta_p(\delta_{p\text{-solvent}}-\delta_{p\text{-PMMA}})$ is