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Electrical and mechanical properties of nanocomposites of single wall carbon nanotubes with PMMA

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Abstract

The electrical conductivity and mechanical characteristics of nanocomposites from pristine and doped single wall carbon nanotubes (SWNT) with polymethylmethacrylate (PMMA) were measured. In highly purified HiPCO SWNT, a percolation threshold as low as 0.17 weight percent has been found. The conductivity value at saturation is about 17 S/cm. If the purified HiPCO SWNTs are doped with $SOCl_2$, the percolation threshold does not change but the saturation conductivity rises to about 100 S/cm. The mechanical properties were investigated for the PMMA composite mixed with $SOCl_2$-doped SWNT. A small content of doped nanotubes dramatically changed Young modulus, toughness and tensile strength as well.

Keywords: Carbon and related materials, solution processing, conductivity, insulating films, semiconducting films, Raman spectroscopy

1. Introduction

Carbon nanotubes, due to their extraordinary electrical, thermal and mechanical properties have become objects of intensive investigation for different applications. But because of the high aspect ratio (thousands) in addition to the mechanical strength and high electrical conductivity, carbon nanotubes have become very promising components for multifunctional composites [1, 2]. However, there are problems coming from poor dispersion in polymeric matrix as well as from the smooth surface of the single wall carbon nanotubes (SWNT) which causes slipping of the nanotubes in a host material under strain. In order to prevent slipping and increase solubility, instead of pristine nanotubes, various covalently and non-covalently functionalized SWNT are used [3-5].

In this paper, we study electrical and mechanical properties of composites made by mixing polymethylmethacrylate (PMMA) with either pristine or $SOCl_2$-doped SWNT.

2. Experimental

2.1. Preparation

Highly purified SWNTs produced by the high-pressure carbon monoxide (HiPCO) process were purchased from Carbon Nanotechnologies, Inc. (Texas).

Thionyl chloride, $SOCl_2$ (99% purity), used for the doping of nanotubes was purchased from Fluka, AG, Switzerland.

For composites, a suspension of nanotubes in chloroform was mixed thoroughly with in chloroform dissolved PMMA in requested mass ratios of up to 8 for pristine and 13.5 for doped SWNT. The suspended mixture was dried in air, forming thin layers.

2.2. Electrical conductivity measurements

Electrical measurements of the composite samples were performed using the four-probe method. Conductive contacts were fabricated by silver-paint.

2.3. Mechanical characteristics measurements

Stress-strain characteristics were measured using a tensile-testing machine (Zwick & Roell).

2.4. Raman spectroscopy

Raman spectra were measured using microscope laser Raman spectroscopy with a Jobin Yvon – LabRam spectrometer. The laser excitation wavelength was 632 nm with spectral resolution of 4 cm^{-1}.

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3. Results and Discussion

The dependences of electrical conductivity on nanotube concentration in the PMMA matrix for the pristine and the $SOCl_2$-doped SWNT are represented in Fig. 1 and Fig. 2, respectively. The values of electrical conductivity with increasing SWNT content rise by 12 orders of magnitude for pristine and 13 orders of magnitude for doped SWNT. The conductivity value at the highes used concentration of 10 wt% for the pristine SWNT composites is about 17 S/cm. If the SWNTs are doped with $SOCl_2$, at highest concentration of 13.5 wt%, the conductivity rises up to about 100 S/cm. In the case of SWNT paper (100% of SWNT), the values of electrical conductivity are about 25 times higher than the highest measured values of the composites; 500 S/cm for pristine and 2500 S/cm for $SOCl_2$-doped SWNT papers. The percolation threshold after doping does not change and for both sets of samples has been found to be as low as 0.17 weight percent. The threshold was estimated using the relation $\sigma \sim (f\text{-}f_c)^{\beta}$ where f is a volume fraction of the conductive component, f_c is the volume fraction at the percolation threshold and β is a critical exponent for the conductivity. In the case of our samples, we use the fact that the densities of PMMA (1200 kg/m^3) and SWNT are similar, therefore mass fractions are used instead. The extremely low percolation threshold results from the high purity of the SWNTs building the conductive network in the insulating matrix. The high aspect ratio (length to diameter ratio) allows to efficiently build conductive bridges through the sample. A similar value of percolation threshold was reported in PPE-functionalized HiPCO SWNT of high purity [6]. In the work of Benoit et al. [7], a slightly lower value of 0.33% was reported for a composite of PMMA and SWNT prepared by the arc discharge method. For comparison, the value of the percolation threshold for composites of polymers with graphite was found to be of two orders of magnitude higher because of the low aspect ratio of graphitic particles.

Insets in Fig. 1 and Fig. 2 show the reduced fraction $(f\text{-}f_c)/f_c$ plotted versus electrical conductivity in logarithmic scale. From there it was found that β = 1.3 for pristine and β = 2.2 for doped samples. The parameter β gives information about the dimensionality of the random connections forming the network [9]. β = 2.2 would be close to the 3D percolating network.

Our measurements of mechanical characteristics show that a very low concentration of nanotubes in the polymer matrix influences dramatically the mechanical properties of material, and this very differently for samples containing pristine versus with doped SWNT. In Fig. 3 we show stress vs. strain curves for composite samples of PMMA with pristine SWNT. There are three important characteristics we evaluate: Young modulus, toughness and tensile strength. In the case of pristine SWNT in PMMA (Fig. 3), with the content of SWNT increasing up to 1 weight % the toughness of the samples increases, the tensile strength reaches a maximum for 0.1 wt % of SWNT in the PMMA matrix and Young modulus decreases with increasing SWNT concentration in PMMA (Fig. 4). This behavior is in contrast with our expectations, since an enhancement of the mechanical performance of composites with SWNT is often reported. The quality of our samples prepared from the suspension in an organic solvent could be rather lower because of small bubbles formed at solvent evaporation. Such defects do not influence much the electrical conductivity but could have a crucial effect on the mechanical properties.

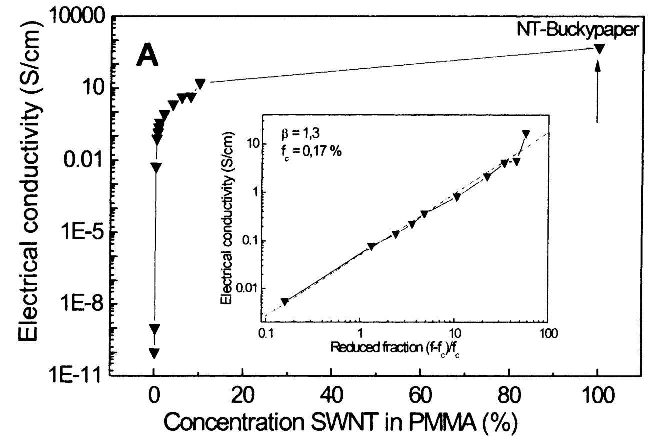

Fig. 1. Dependence of electrical conductivity on nanotube concentration in PMMA matrix for pristine SWNT. Inset: reduced fraction $(f\text{-}f_c)/f_c$ plotted versus electrical conductivity.

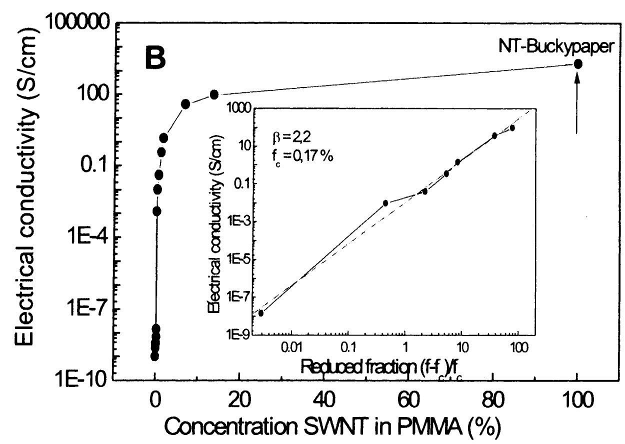

Fig. 2. Dependence of electrical conductivity on nanotube concentration in PMMA matrix for $SOCl_2$-doped SWNT. Inset: reduced fraction $(f\text{-}f_c)/f_c$ plotted versus electrical conductivity.