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Correlation between manufacturing processes and anisotropic magnetic and electromagnetic properties of carbon nanotube/polystyrene composites

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ABSTRACT

We present an original, easy to implement, reliable method of non-destructive testing of the orientation of carbon nanotubes by magnetic moment measurements performed in three perpendicular directions of magnetic field. Multi-wall carbon nanotubes/polystyrene composites were prepared by stretching and forge-rolling methods with the same nanotube loading. Unusually strong diamagnetic anisotropy in the composites prepared by the stretching method was observed and attributed to an additional diamagnetic response from the polystyrene aromatic rings wrapping the nanotubes. Strong anisotropy of diamagnetic susceptibility of the composites with highly aligned nanotubes correlates with anisotropic electromagnetic response and with improved microwave absorption properties. Both magnetic anisotropy and microwave absorbance is considerably lower in the composites prepared by the forge-rolled method. The magnetic results correlate well with polarized Raman spectroscopy. The research findings contribute to a better understanding of nanotube-polymer interface, alignment mechanisms, and ultimately the optimal design and performance of functional nanotube - aromatic polymer nanocomposites.

1. Introduction

Extraordinary mechanical, thermal and electronic properties of carbon nanotubes (CNTs) make them ideal fillers for composites used in many practical areas. One of areas is electromagnetic shielding, which is often an unavoidable necessity, especially in military and biomedical applications due to the interaction of electromagnetic fields and biological tissues. CNT composites are highly attractive in shielding due to their light weight, low cost, high strength and simple processing. One of the most important aspects is the CNTs alignment in the composites: cooperative interactions between the components can produce novel properties that do not occur individually. It was shown that the better the orientation, the higher the polymer composites' mechanical strength and shielding effectiveness (SE). Moreover, orientation of CNTs in matrix resulted in an anisotropic response of polymer composite relative to low frequency [1] and terahertz radiation [2] where it was demonstrated that the SE of polymer composites could be improved by controlling the orientation of MWCNTs. The magnetic catalytic particles embedded into the carbon nanotubes during the synthesis can lead to novel magnetic properties of the nonmagnetic polymer matrix. Many recent experiments and simulations investigated the role of catalytic particles in composite properties; SE of composites with nanotubes grown by catalytic chemical vapour deposition (CCVD) is higher than that for purified nanotubes, without contribution from the nanotube-enclosed metal catalysts. This effect was attributed to the contributions of

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magnetic losses and impedance match. Alternatively, the effect was attributed to increased dielectric losses because the magnetic particles content is so small that the magnetic effects are weak.

In the traditional chain "Synthesis – Characterization – Properties", the weakest link is "Characterization". The alignment of CNTs is mostly evaluated by the microscopy techniques like atomic force microscopy (AFM) and transmission electron microscopy (TEM) which provide surface information. Another approach is the use of spectroscopic techniques including polarized Raman spectroscopy, which provides quantitative but local judgements. In this work, multi-wall CNTs (MWCNTs) filled with iron nanoparticles were combined with polystyrene (PS) to evaluate interface interactions and MWCNT orientation in composite using magnetic susceptibility measurements. The measurements of magnetic moment versus field and versus temperature performed in the different directions of magnetic field produced valuable information about the orientation of MWCNTs, the arrangement of the macromolecules around them and the behaviour of catalyst nanoparticles. Comparison of the properties of anisotropic composites containing the same MWCNT amount but prepared by different methods showed that the samples with strongly anisotropic diamagnetic properties provide anisotropic electromagnetic response and show high SE in gigahertz range.

2. Materials and methods

2.1. MWCNT synthesis

MWCNTs were produced using aerosol-assisted CCVD method in a horizontal tubular reactor, which is described in detail elsewhere [3]. Silicon substrates with a size of 10 × 10 mm^2 were located in the central part of the reactor, then the reactor was pumped, filled with argon gas and heated up to 800 °C. Ferrocene (2 wt. %) was dissolved in toluene and the reaction mixture was injected into the reactor with a rate of 0.14 ml/min. The pyrolysis was performed at atmospheric pressure in an argon flow (250 cm^3/min) for an hour. Mössbauer spectroscopy study of MWCNTs synthesized by the same method detected three forms of iron nanoparticles, namely, two magnetic phases α-Fe and Fe_3C and one non-magnetic γ-Fe phase [4]. From the results obtained after the sample treatment with a diluted sulphuric acid, it was supposed that the α-Fe phase is mainly located close to the nanotube ends, while the γ-Fe and Fe_3C phases are inside of the channels [5].

2.2. Composite preparation

Polystyrene plates with 5 wt. % MWCNT loading were prepared using forge-rolling and stretching methods [6]. A required amount of MWCNTs separated from the silicon substrate was put into a toluene solution of polystyrene and the mixture was mechanically stirred until complete polymer dissolving. Then, the suspension was sonicated for ~2 min using a high-power sonic tip (200 W) with the purpose to improve the MWCNT dispersion. As produced slush was cast onto metallic substrate and dried to a viscous state at ambient conditions.

In the first batch of samples, a forge-rolling procedure was used. A composite plate was repeatedly forge-rolled along a certain direction at a linear speed of the rolls of ~10–15 cm/s. In the second batch, a stretching procedure was used. A soft composite plate was uniaxially stretched at a heating (~70 °C), which was provided by a hot air gun. A microscrew setup led to stretching of the plate in half. Finally, the composites were dried under a light load at room temperature. All the prepared plates had visually homogeneous grey colour. Investigation of the electromagnetic response of the composites prepared by the above-described techniques detected that the nanotubes have a predominant orientation in the plates [7].

3. Results and discussion

3.1. Electron and atomic force microscopy

Examination of product by scanning electron microscopy (SEM) on a Hitachi S-3400N microscope revealed covering of silicon substrate by a MWCNT array (Fig. 1a). In the array, nanotubes are well aligned and oriented normally to the substrate surface (so-called nanotube forest). Cleavage of the sample for SEM study resulted in a gap between array and substrate. This is indicative of weak interaction of the constituents, which allowed separating the CNTs easily.

For high-resolution transmission electron microscopy (HRTEM) investigation, the MWCNTs were mixed with ethanol, and after ultrasonication the suspension was deposited on a colloidal carbon film grid. TEM images obtained on a Jeol JEM 2010 microscope showed that the CCVD product consists of MWCNTs with an outer diameter of ~20 nm (Fig. 1 b).

These processing conditions ensure a good dispersion of the MWCNTs in the polystyrene matrix as revealed by the images obtained by SEM of the composites (Fig. 1 c, d). The images were obtained from a Jeol JSM-7001F microscope.

The polystyrene/MWCNT composites were investigated in PeakForce Tapping and Semicontact Tapping modes of Scanning Probe Microscope "BRUKER Multimode 8". AFM topography revealed that MWCNTs are embedded into the polystyrene matrix, and only in rare exceptions are lying on the surface. However, Phase channel can be used to distinguish separate materials by their summarised mechanical properties. Although topography data has shown mostly flat areas not containing any MWCNTs (Fig. 1e), they were clearly distinguished in phase data channel (Fig. 1f). The nanotubes are obviously oriented in same left-right direction, while only one of them, represented by a dark loop-like feature in right part of the image in Fig. 1f, is actually lying upon the surface.

3.2. Polarized Raman spectroscopy

Raman spectra in the backscattering geometry were excited with a HeNe laser (632.8 nm) at low power density (~10^4 W/cm^2) and recorded using a micro-Raman setup (Horiba Jobin Yvon LabRAM 300). A 50× microscope objective was used for focussing of the laser beam and collection of the scattered light. Polarization direction of the incident and scattered light was analysed with the polaroid quinine iodosulphate.

The Raman spectra of MWCNTs are dominated by three main peaks: a graphitic non-dispersive G-band around 1580 cm^{-1} related to in-plane tangential stretching of the C–C bonds, a defect/disorder D band around 1331 cm^{-1}, using laser excitation of 633 nm, and second-order overtone G′ at 2652 cm^{-1}. The intensity of the D band is defect dependent, and the ratio of D and G intensity I_D/I_G is used to evaluate the structural purity of graphitic materials. For carbon nanotubes, both SWNT [8] and MWNT [9], the Raman intensities are maximum when the polarization direction of the probing light is parallel to the nanotube axis ($E_{||}$), whereas in perpendicular direction ($E_{\perp}$) the Raman scattering is forbidden. Raman intensities exhibit approximately $cos^2\alpha$-dependence in which α is the angle between the CNT axis and the polarization direction of the incident light. Remarkable difference in the intensity of Raman peaks for $E_{||}$ and $E_{\perp}$ was reported in several studies of polymers with aligned nanotubes [10–16].

Fig. 2 shows the orientation-dependent Raman spectra of the stretched (Fig. 2 a) and forge-rolled (Fig. 2 b) PS-MWNT composites