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Magnetic studies of polystyrene/iron-filled multi-wall carbon nanotube composite films

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ABSTRACT

Polystyrene/iron-filled multi-wall carbon nanotube composite films were prepared by solution processing, forge-rolling and stretching methods. Elongated iron carbide nanoparticles formed because of catalytic growth are situated inside the hollow cavity of the nanotubes. Magnetic susceptibility measurements as well as records of isothermal hysteresis loops performed in three perpendicular directions of magnetic field confirmed that the nanotubes have a preferential alignment in the matrix. Strong diamagnetic anisotropy in the composites emerges not only from the MWCNTs but also from the polystyrene matrix. The polymer sticks to the honeycomb lattice through the interaction of the π-orbitals of the phenyl ring and those of the carbon nanotube, contributing to anisotropic diamagnetic response. The contribution of iron nanoparticles to overall magnetic response strongly depends on nanotube concentration in the composite as well as on matrix-filler non-covalent stacking, which influences magnetic interparticle interactions.

1. Introduction

Carbon nanotubes (CNTs) are ideal fillers for composites used in many practical areas as light-weight structures with multifunctional properties for engineering applications. Composites with aligned nanotubes are very attractive for conductive applications or for electromagnetic shielding, used in military and biomedical applications to prevent the interaction of electromagnetic fields and biological tissues. CNT composites are highly attractive in shielding due to their low cost, high strength, and simple processing. It was shown that the better the orientation, the higher the polymer composites' mechanical strength and shielding effectiveness. Electromagnetic properties of polymer composites can be improved by controlling the orientation of MWCNTs, which results in an anisotropic response of polymer composite relative to low frequency [1] and terahertz radiation [2].

The magnetic catalytic particles embedded into the carbon nanotubes during the synthesis can lead to novel magnetic properties of the nonmagnetic polymer matrix. Recent experiments and simulations investigated the role of catalytic particles in composite properties: shielding effectiveness of composites with iron-filled nanotubes is higher than that for purified nanotubes, without contribution from the nanotube-enclosed metal catalysts. The explanation is not trivial because carbon nanotubes constitute about 1% in the composites, and iron nanoparticles, in turn, constitute several per cent of nanotube weight. Therefore, the effect was thought of being due to the contributions of 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. Here we show that the properties of iron-based nanoparticles inside the composite strongly differ from the properties of the same nanoparticles in freestanding nanotubes: we identified signs of magnetic interactions between iron and the carbon walls, as well as magnetic interparticle interactions, presumably mediated by the extended intermolecular stacking.

The alignment of CNTs is mostly evaluated by the microscopy

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techniques like atomic force microscopy (AFM) and transmission electron microscopy (TEM) which provide surface information or spectroscopic techniques including polarized Raman spectroscopy. In this work, magnetic susceptibility measurements were used to evaluate iron-filled multi-wall CNTs (MWCNTs) orientation in polystyrene matrix, as well as to evaluate interface interactions. The measurements of magnetic moment versus field and versus temperature performed in three orthogonal 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 prepared by different methods showed that the samples with strongly anisotropic diamagnetic properties provide anisotropic electromagnetic response and show high shielding efficiency in gigahertz range.

2. Materials and methods

2.1. MWCNT synthesis

Arrays of MWCNTs on silicon substrates were produced using aerosol-assisted catalytic chemical vapour deposition method, which is described in detail elsewhere [3]. Synthesis was carried out in a quartz tube inserting into a horizontal tubular reactor. 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. Concentration of iron nanoparticles in the nanotube channels determined by elemental analysis was 3 wt. %.

2.2. Composite preparation

Polystyrene plates with 1–5 wt% MWCNT loading were prepared using forge-rolling and stretching methods [4]. MWCNT array (so-called nanotube forest) was gently detached from silicon substrate; 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. The plate produced after complete solvent evaporation contains randomly distributed nanotubes. To provide predominant orientation of nanotubes in polymer matrix we used a procedure of forge-rolling or stretching.

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 [5].

3. Results and discussion

3.1. Electron microscopy and atomic force microscopy

For transmission electron microscopy (TEM) investigation, the MWCNTs were mixed with ethanol and after ultrasonication; the suspension was deposited on 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. 1a). Dark-contrast nanoparticles observed on the TEM images correspond to metallic compounds produced from ferrocene $Fe(C_5H_5)_2$. The catalytic nanoparticles are elongated with average diameter 5–10 nm and length of 10–20 nm and are captured in the interior cavity of nanotubes (Fig. 2b). 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 [6]. From the results obtained after the sample treatment with a diluted sulfuric 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 [7].

SEM images of the composites obtained from a Jeol JSM-7001F microscope confirm that the processing conditions ensure a good dispersion of the MWCNTs in the polystyrene (Fig. 1c). Atomic force microscopy (AFM) show that MWCNTs are embedded into the polystyrene matrix, and only in rare exceptions are lying on the surface (Fig. 1d).

3.2. Thermomagnetic measurements

Measurements were done using a superconducting quantum interference device (SQUID) magnetometer. Magnetic properties of samples were studied by measuring the zero filed cooled (ZFC) and field cooled (FC) magnetizations at $H = 100$ Oe as a function of temperature and isothermal magnetic hysteresis loops, M(H), at a given temperature. The magnetic field was varied in the range -5 T to 5 T, within the temperature range 2–400 K. The magnetic moment was measured with the sensitivity of 10^{-8} emu (emu).

Fig. 2 summarises the results of magnetic measurements on pristine MWCNT forest and the composite materials. Fig. 2a plots the coercive force values, extracted from isothermal magnetization loops measured parallel and perpendicular to the nanotube axis. There is distinct anisotropy in magnetostatic parameters extracted from the isothermal magnetization loops which is apparently due to the iron particles inside the nanotubes. For a rod-like shape ferromagnetic material, the demagnetizing factor is zero when the field is parallel to the axis and increases up to 2π when the field is perpendicular to the rod axis, which results in a nonsquare hysteresis loop. This anisotropy confirms that the easy axis is parallel to the nanotube axis and that the nanotubes are well aligned both in the forest and in the composites.

Fig. 2b –2f present the results of magnetic moment measurements performed in ZFC and FC protocols. Fig. 2b shows the plot for raw MWCNT forest, 2c for the composite prepared by forge-rolled method, and 2d–f are the plots for the stretched composites with different MWCNT load.

The results in Fig. 2a–f, namely, increased coercive force and the difference between the ZFC and FC protocols, in a first approximation can be described by the Stoner and Wohlfarth model which accounts for the non-interacting single-domain particles with uniaxial anisotropy resulting from shape or from the magnetocrystalline anisotropy in the assumption of coherent rotation of the magnetization. Isothermal field dependencies for the nanotube forest indicate difference between the coercive fields for in-plane field orientation compared to that for out-of-plane orientation. The obtained coercivities are larger than those for bulk