Magnetic properties of multi-walled carbon nanotube–epoxy composites

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Abstract

Epoxy matrix composites have been prepared using as filler different weight fractions (0.03–1 wt%) of CVD grown multi-walled carbon nanotubes (MWCNTs) containing trapped iron nanoparticles. Magnetic characterization performed at room temperature with magnetic field between -19 and $19\,\mathrm{kG}$ shows that the nanocomposites are weakly ferromagnetic at room temperature. An abrupt variation in the dependence of both the coercivity field, B_C, and remanent magnetization, M_R, with the weight fraction of MWCNTs, ϕ, was found for $\phi = 0.4\%$. Results suggest the formation of MWCNTs agglomerates for increasing weight concentrations, in accordance with SEM micrographs.
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1. Introduction

In the last years magnetic nanoparticles have been employed in several applications such as recording media, ferrofluids, high-density information storage and in many biomedical applications [1–4]. Most of the current studies deal with oxide nanoparticles because it is difficult to prevent metallic magnetic (Fe, Ni, Co) nanoparticles from oxidation at conventional experimental conditions. Recently, scientific interest in ferromagnetic nanoparticles encapsulated into carbon nanotubes has increased because the carbon shell provides an effective barrier against oxidation ensuring a long-term stability of the metallic magnetic filler [5,6]. Particularly, synthesis of MWCNTs by chemical vapor deposition (CVD) of iron(II)

phthalocyanine has demonstrated that Fe nanoparticles are trapped at the tips of the grown nanotubes [7,8].

Use of magnetic nanoparticles as fillers in polymer matrix composites has diverse interests from technological applications to basic theoretical research. Novakova et al. [9] have studied the magnetic behavior of polymer nanocomposites containing nanoparticles of oxidized magnetite in a polyvinyl alcohol matrix. Their results show that the concentration of iron oxide nanoparticles within the polymer matrix volume greatly influences the magnetic properties of nanocomposites, but magnetic anisotropy is observed in the sample as result of heterogeneous distribution of oxidized magnetite agglomerates. The magnetic behavior of iron and iron-oxide nanoparticles uniformly dispersed into polymethylmethacrylate films with varying concentrations was studied by Baker et al. [10]. They observed that interparticle effects such as dipolar interaction are reduced as the particles are separated apart from each other, leading to an increase in coercivity.

It is well known that the behavior of a nanocomposite depends on nanoparticles properties, matrix properties and procedure of fabrication. The use of carbon nanotubes as

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fillers in epoxy matrix composites is nowadays attracting a great deal of attention [11,12]. These new nanocomposite systems could have broader application potentials due to their unique mechanical, optical and electrical properties. Several works about the electric properties of multi-walled carbon nanotube–epoxy composites have been carried out [13–16]. All these works have shown that the composite conductivity increases with increasing nanotubes content and that an experimental percolation threshold exists at MWCNTs weight fractions between 0.0025 and 0.5 wt% depending on the method used for making the composites.

Particularly, the use of carbon nanotubes with ferromagnetic properties as filler in epoxy matrix could lead to nanocomposites with novel magnetic properties. To our knowledge, the magnetic properties of this type of composites have not been yet investigated.

The goal of this work is to evaluate the magnetic behavior of MWCNTs–epoxy composites. With this aim, the epoxy matrix was filled with different amounts of MWCNTs containing trapped iron nanoparticles. The magnetic behavior of the composites was explained in terms of the dispersion degree of the MWCNTs in the epoxy matrix.

2. Experimental

The nanocomposites investigated in this study consist of catalytically grown carbon nanotubes employed as filler in an epoxy system.

Carbon nanotubes were synthesized by CVD of analytical grade iron(II) phthalocyanine, under Ar/H_2 atmosphere in a flow reactor consisting of a quartz glass tube. It was heated by a dual furnace fitted with independent temperature controllers, following the procedure reported elsewhere [17]. Growing conditions involved temperatures of around 880 °C, a total gas flow rate of 30 mL/min and Ar/H_2 ratio of 1:1.

The epoxy pre-polymer and the curing agent used were diglycidyl ether of bisphenol A (DGEBA LY 556) and isophorone-diamine (IPDA HY 2962), both from Ciba Geigy.

The appropriate amount of carbon nanotubes was incorporated into the diamine and the mixture was sonicated in an ultrasonic bath for 30 min. The pre-polymer DGEBA was then added to the compound, mixed at 700 rpm during 15 min, and sonicated again for other 15 min. Then the intimate mixture was placed in a vacuum chamber for 120 min to eliminate air bubbles introduced during the mixing and sonication processes. The stoichiometric ratio (aminohydrogen/epoxy) used was equal to 1.

The degassed composite was poured in a Pyrex tubular mold of 3.6 mm diameter and 1 cm length and in a Pyrex prismatic mold of $11 \times 27 \times 2$ mm^3 thickness.

The cure schedule was 60 min at 60 °C, 60 min at 140 °C,

and 360 min a 190 °C. The carbon nanotubes weight fractions (ϕ) were 0, 0.03, 0.1, 0.2, 0.4, 0.5 and 1 wt%.

The structure of the carbon nanotubes was studied using scanning electron microscopy (SEM-Phillips 500) and transmission electron microscopy (TEM-Phillips CM200) equipped with energy dispersive spectroscopy (EDS). Fracture surface of the prismatic composite samples was studied under SEM.

Magnetization hysteresis loops were measured on all specimens at room temperature in the magnetic field range between −19 and 19 kG using a commercial vibrating sample magnetometer (VSM) LakeShore 7407. The step field variation was not constant for the whole magnetic field range. In the vicinity of the coercive field (± 300 G) magnetic field was increased/decreased in steps of ± 30 G, while at higher field, the step was ± 200 Oe. Cylindrical samples of 3.6 mm in diameter and 1 mm thick were employed for these tests.

3. Results and discussion

Fig. 1(a) shows a typical SEM image of the carbon nanotubes grown on quartz substrates. The edges were peeled off using a razor blade in order to visualize the configuration. As can be seen, carbon nanotubes grow well aligned vertically to the substrate. The tubular structure of the nanotubes was verified by TEM microscopy, as shown in Fig. 1(b). In this figure it can be observed that the carbon nanotubes are multi-walled (MWCNTs) and have a bamboo-like structure with iron nanoparticles encapsulated at the tips (dark spots in Fig. 1(b)). The synthesized MWCNTs are (18 ± 2) μm in length, and have average inner and outer diameters of (21 ± 3) and (48 ± 5) nm, respectively. The diameter of the iron particles is of (21 ± 3) nm. According to the literature, the size of catalytic particles usually determines the inner diameter of MWCNTs in CVD growth [18–20].

For BCC α-Fe, the accepted critical size for single domain particles is about 20 nm [8]. We have, therefore, assumed that for our samples the Fe-particles are single domain, and the observed magnetic behavior may be described considering only particle–particle interactions. The main magnetic interactions that dominate in fine particle assemblies are dipole–dipole interactions (which are always present) and exchange interactions through the surface of particles that are in close contact [21].

In Fig. 2 the hysteresis curves for the composites containing different weight fractions of MWCNTs, ϕ, are displayed. The non-filled sample ($\phi = 0$) shows diamagnetic behavior, while the nanocomposites exhibit increasing ferromagnetic character. The remanent magnetization (M_R) and coercive field (B_C) were obtained from the magnetic hysteresis loops, as exemplified in Fig. 3.

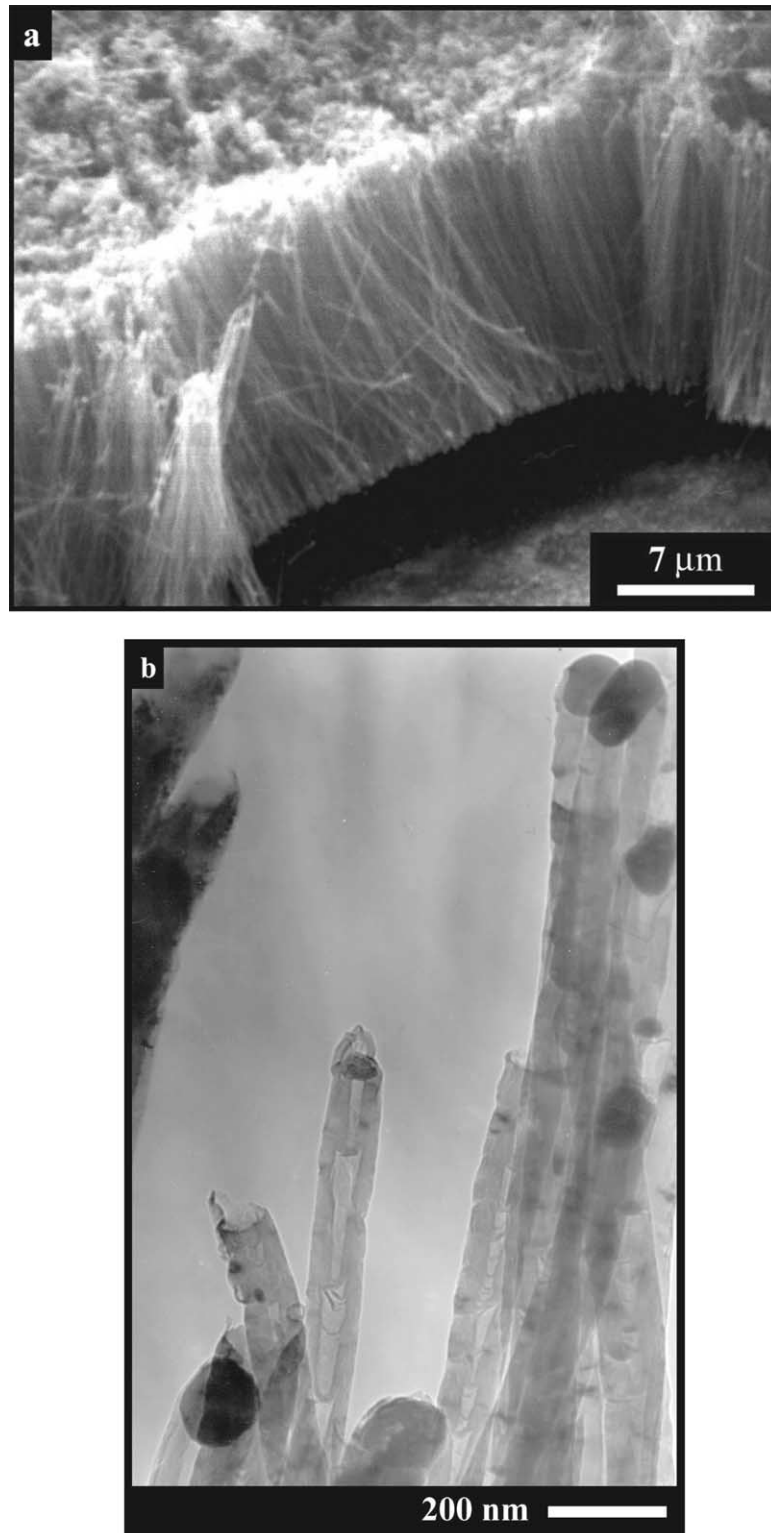The dependence of M_R and B_C on the MWCNTs weight fraction is shown in Fig. 4. It is interesting to

Fig. 1. (a) SEM and (b) TEM micrographs of multi-walled carbon nanotubes.

notice that both M_R and B_C show a change in behavior at about carbon nanotubes filler percentage of 0.4 wt%. As observed, M_R increases with ϕ. This behavior is expected because an increase in ϕ implies an increase in the amount of Fe nanoparticles in the sample. It is

notable, however, that for about 0.4 wt% the increase rate grows abruptly.

On the other hand, the coercive field of the diluted samples decreases with the weight fraction of MWCNTs for values below 0.4 wt%. The decrease in B_C results from the
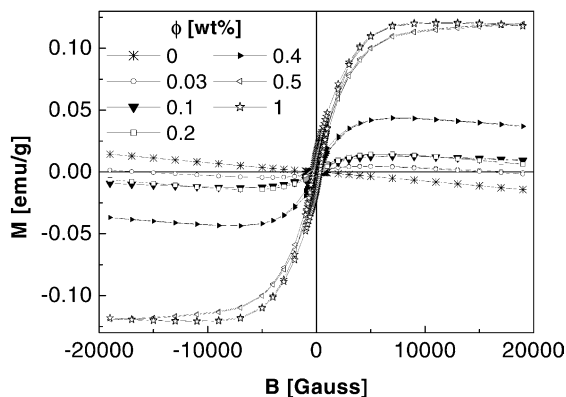
Fig. 2. Hysteresis curves for the multi-walled carbon nanotubes–epoxy composites at different MWCNTs weight fractions.

Fig. 4. Dependence of the magnetic properties with MWCNTs weight fraction, ϕ. Left axis shows coercivity field B_C as a function of ϕ. Right axis shows remanent magnetization M_R as a function of ϕ.

low nanotubes concentration, where magnetic behavior is controlled by dipole–dipole interactions that favor the demagnetized state [22]. Computer simulations performed for interacting magnetic particles of fixed size, where dipole–dipole interactions dominate show the same qualitative behavior [22,23].

However, as ϕ is increased, strong magnetic correlations among particles are settled through the matrix. At $\phi =$ 0.4 wt%, B_C reaches a minimum and then increases with ϕ. According to Kechrakos and Trohidou [22], simulations, where growing particle volume occurs show that B_C increases with weight fraction of magnetic particles in qualitative agreement with our present results. Data shown in Fig. 4 suggest that for weight fractions higher than 0.4 wt%, agglomerates of MWCNTs occur.

For comparative purposes, it should be mentioned that the electrical conductivity of carbon nanotubes–epoxy composites as a function of the filler weight fraction has been studied in several works in the literature. An electrical conduction threshold at a weight percentage of the same order of magnitude as the one reported in the present work for the magnetic properties has been found [13,15,16,24]. Celzard et al. [24] have made a theoretical approach and

calculated the percolation threshold for a composite containing randomly oriented conductive fibers in an insulating matrix. Such calculations for an aspect ratio of 500 (as our MWCNTs) yielded a critical concentration of 0.5 wt% to form a network of touching particles.

An indirect observation of the MWCNTs clustering process was obtained from the vein pattern in the fracture surface of the composites. Through a flexion test of three points, the flat samples of the composites were broken, at room temperature, using a Vickers indentation as initiator of the fracture. Fig. 5(a), (c) and (e) show SEM images of the specimen surface near the fracture section of MWCNTs–epoxy composites for various ϕ around the threshold value. For all the composites, a well-developed vein pattern can be observed, suggesting that the residual amorphous matrix controls the deformation behavior. The space between veins and the size of them increase with ϕ. This result is in clear opposition to that observed in bulk metallic glasses containing nanocrystals [25,26], where the vein pattern becomes thinner and denser with increasing volume fraction of nanocrystals without clustering of nanocrystals, as shown by TEM images. Then, it is reasonable to infer that the clustering of MWCNTs occurs around the threshold value of ϕ leading to the inversion of the normal evolution in the vein pattern. Looking at the surface of the fracture with a higher magnification (Fig. 5(b), (d) and (f)), it is possible to observe details of the veins and bundles of MWCNTs clustering together as the weight fraction increases.
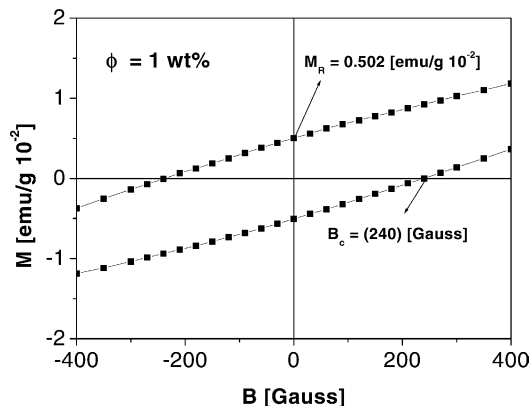

Fig. 3. Hysteresis curves in the vicinity of the coercive field for MWCNTs weight fraction of 1 wt%, showing the remanent magnetization and coercivity fields.
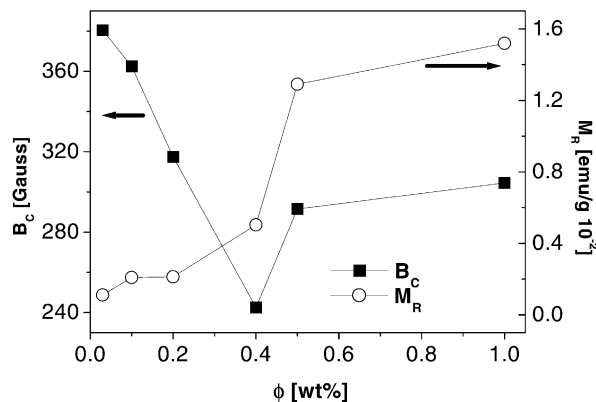
4. Conclusions

A study on the magnetic properties of epoxy matrix composites using as filler different weight fractions of multi-walled carbon nanotubes with trapped iron has been carried out.

It was shown that magnetic properties are a function of the MWCNTs weight fraction, ϕ. In particular, we have found an increase in the remanent magnetization, M_R, and a
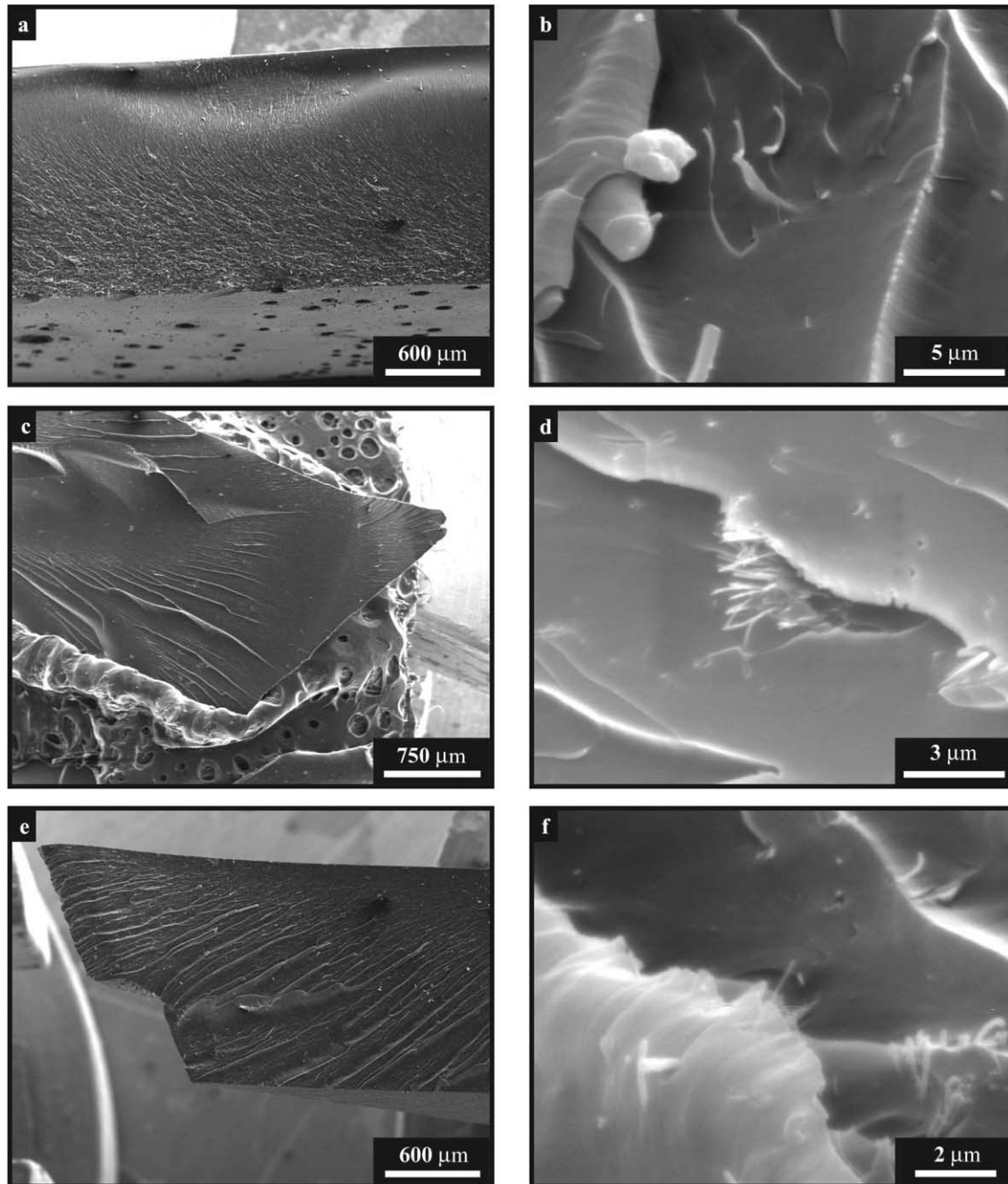
Fig. 5. SEM micrographs of the specimen surface near the fracture section of multi-walled carbon nanotubes–epoxy composites, (a) and (b) 0.1 wt%; (c) and (d) 0.5 wt%; and (e) and (f) 1.0 wt%.

decrease in the coercive field B_C with ϕ for low weight fractions ($\phi < 0.4$ wt%) that are well understood in the framework of isolated magnetic particles. However, an important change in the magnetic behavior is observed above a threshold weight fraction, where the rate of growth of M_R with ϕ abruptly increases, and B_C stops decreasing, showing a non-monotonic dependence. Both behaviors point to the agglomeration of magnetic particles for weight fractions above 0.4 wt%. The explanation of the experimental magnetic behavior is in good agreement with that observed in the SEM micrographs of the fracture surfaces of the composites, indicating the formation of agglomerates on MWCNTs for concentrations above the threshold.

Acknowledgements

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