Composites: Part B 46 (2013) 166–172

Contents lists available at SciVerse ScienceDirect

Composites: Part B

journal homepage: www.elsevier.com/locate/compositesb

New alignment procedure of magnetite–CNT hybrid nanofillers on epoxy bulk resin with permanent magnets

S.G. Prolongo [a,*], B.G. Meliton [a], G. Del Rosario [b], A. Ureña [a]

[a] Dpt. Materials Science and Engineering, University Rey Juan Carlos, C/Tulipán s/n, Móstoles 28933, Madrid, Spain
[b] Technological Support Center, University Rey Juan Carlos, C/Tulipán s/n, Móstoles 28933, Madrid, Spain

ARTICLE INFO

Article history:
Received 23 July 2012
Received in revised form 11 September 2012
Accepted 2 October 2012
Available online 22 October 2012

Keywords:
A. Polymer–matrix composites
A. Nanostructures
B. Thermomechanical
B. Mechanical properties
B. Electrical properties

ABSTRACT

The main properties of epoxy composites reinforced with aligned carbon nanotubes (CNTs) have been studied. The alignment was carried out in a specific designed device applying a weak magnetic field (0.3 T) with permanent magnets. CNTs were modified with magnetite nanoparticles (Fe_3O_4) functionalized, in a one-stage-process which does not require use of strong acids or aggressive treatments which could affect the structural integrity of CNTs. The study by transmission electron microscopy confirmed that the Fe_3O_4 nanoparticles were closely bonded over CNT surfaces. The thermo-mechanical and tensile properties of composites measured were higher than neat epoxy resin and were similar for both composites: reinforced with neat CNTs and magnetite–CNT hybrid nanofillers. The electrical behaviour indicates a high anisotropy for aligned composites, showing an increase of one order of magnitude for the electrical conductivity in the direction of aligned nanotubes.

1. Introduction

Carbon nanotubes (CNTs) have excellent mechanical properties and high electrical and thermal conductivity but their properties strongly depend on spatial direction [1]. Their high aspect ratio makes them highly anisotropic. For it, several recent researches about polymer/CNT fabrication have focused on the alignment of CNTs into matrix [2–6]. It is essential to obtain a homogenous dispersion of aligned CNTs with a good chemical interaction with polymer in order to reach efficient load transfer and to provide a conductive pathway for electrons and phonons. These polymer materials would present unique mechanical, thermal and electrical behaviour.

Different approaches have been studied to align nanotubes based on mechanical stretching [6,7] or application of electrical [5,8,9] or magnetic field [10–16]. The highest aligning degrees, obtaining through application of magnetic field, required: (1) High magnetic field (several Tesla) [11–13], which requires the use of powerful electromagnet due to relative low magnetic susceptibility of CNTs or (2) The addition of magnetic nanoparticles on their surfaces [16–18]. However, it is necessary to follow researching this process, because of conflicting results have been recently published. Sharma et al. [14] confirmed the alignment of neat CNTs by applying relative low external magnetic field (0.12 T) while other authors [15] needed the functionalization of CNTs with magnetic nanoparticles onto their walls for aligning them with a weak magnetic field (0.3 T). In some cases, pulsed magnetic field (up to 40 T) [4] has been applied to induce dynamic orientation of neat CNT. The controversy can be explained by the influence of shape and size of nanotubes on the efficiency of their alignment under magnetic fields. Jang and Sakka [12] confirmed that thick straight CNTs showed a greater tendency to align that did thin curved CNTs.

The addition of magnetic maghemite nanoparticles (γ-Fe_2O_3) is usually carried out through sol–gel process using iron salt as precursor [17,18]. This chemical treatment implies several stages. Between them, the first step consists on the oxidation of CNT surfaces through the chemical reaction with strong acid mixture (concentrated H_2SO_4 and HNO_3). However, this treatment could induce surface defects on the nanotubes and their shortening. Wang et al. [16] published a less aggressive approach based on the functionalization of CNT with magnetite (Fe_3O_4). However, this also involves several complex chemical stages and the heating of nanotubes up to 500 °C. It is worth noting that the electrical conductivity of nanocomposites reinforced with multi-wall carbon nanotubes mainly occurs by outshells while that the mechanical behaviour strongly depends on the specific surface and the length of nanotubes [19]. Both may be affected by aggressive treatments.

In this work, we study the alignment of neat CNTs and ones functionalized with magnetite applying a weak magnetic field (0.3 T). The main goal is the surface addition of Fe_3O_4 on nanotubes using magnetite nanoparticles functionalized, which present

* Corresponding author.
E-mail address: silvia.gonzalez@urjc.es (S.G. Prolongo).

1359-8368/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compositesb.2012.10.002

superparamagnetic behaviour. This procedure is a one-stage-process and it does not require use of strong acids or aggressive treatments which could affect the structural integrity of CNTs. Other advantages regard to previous works published are that the designed devise allows manufacturing specimens (not only films) and the magnetic field is obtained with a weak permanent magnet, not electromagnet. Nanocomposites with epoxy matrix have been manufactured and characterized, analysing their anisotropic behaviour.

2. Experimental

2.1. Materials

The nanocomposites were manufactured from diglycidyl ether of bisphenol A (DGEBA, 178 g/epoxy equivalent) and 4,4-methylenedianiline (DDM, 49.6 g/amine hydrogen equivalent). Both were purchased from Sigma–Aldrich. The used multi-walled carbon nanotubes (MWCNT) were produced through Catalytic Carbon Vapour Deposition (>99% C) and functionalized with amino-groups (<0.5% w/w) by Nanocyl. They have an average length close to 1 μm and a diameter in the range of 30–50 nm. The magnetite nanoparticles (Fe_3O_4) coated with oleic acid, were supplied by Nanogap. They present superparamagnetic behaviour at room temperature, with a saturation magnetization of 50 emu/g.

2.2. Synthesis of magnetite–CNT nanohybrid material and their nanocomposites

An aqueous solution of magnetite was prepared with a concentration of 100 mg/ml and 0.5 g amino-functionalized CNTs was added. The mixture is stirring at 80 °C for 1 h in order to enhance the chemical reaction between acid groups of magnetite particles and amine groups of amino-functionalized CNTs. Then, the magnetite-nanotubes were dried in a rotary evaporator. Finally, they were repeatedly washed in water and dried. In order to ensure that the nanotubes were dry, they are stored in a vacuum stove at 115 °C.

The nanocomposites were manufactured using chloroform as solvent. The dispersion procedure was optimized in previous works [20,21]. A solution of epoxy monomer and carbon nanotubes in chloroform was prepared and suggested to different stages of magnetic stirring, high shear mixing and sonication. In order to remove the solvent, the mixture was placed in a vacuum oven at 90 °C for 24 h. Then a stoichiometric amount of DDM was added into the epoxy/CNT mixture. The curing treatment applied was 150 °C for 3 h, followed to a postcuring stage at 180 °C for 1 h. In the required cases, the curing treatment was applied out under weak magnetic field of 0.3 T. Fig. 1a shows a scheme of experimental devise specially designed for this application. The samples were cured in glass tubes in whose ends were positioned the permanent magnets. The permanent magnets, neodymium (N38), were purchased by Aiman (Spain company), which ensured a constant magnetic field of 0.3 T up to 200 °C. It was confirmed that the intensity of magnetic field was approximately constant with a value of 0.3 T at a magnets distance of 50 mm. The gaussmeter used for these measurements is Magnetic meter PCE-MFM 3000. The cylindrical specimens manufactured have a maximum volume of 15 mm of diameter and a height of 50 mm. A theoretical simulation of magnetic field lines (Fig. 1b) is carried out in order to confirm the directionality of magnetic field in the sample zone.

Different samples kits were prepared: (A) randomly oriented CNT/epoxy and CNT–Fe_3O_4/epoxy nanocomposites, which are nanocomposites reinforced with non-modified and magnetite–CNT nanotubes cured in a conventional heater. (B) magnetically aligned CNT/epoxy and CNT–Fe_3O_4/epoxy nanocomposites which were cured using a special device in order to apply a weak magnetic field. Table 1 collects a list with all the manufactured samples with a referential code, from which will be named the probes.

2.3. Characterisation

The morphology of magnetite–CNTs was determined by transmission electron microscopy (TEM) (TEM, 200 kV Phillips Tecnai). Small amount of Fe_3O_4 nanoparticles and modified nanotubes were dispersed in acetone and one drop was placed on a copper grid coated with a polymeric membrane. On the other hand, the dispersion and alignment degree of nanotubes on the different nanocomposites was analysed by Field Emission Gun Scanning (FEG–SEM) Electron Microscopy (Nova NanoSEM FEI 230). The surface of the samples was sputter coated by a thin layer (5–10 nm) of Au (Pd). The experimental conditions of the sputtering were 30 mA and 120 s (Bal-tec, SCD-005 sputter).

The behaviour of composites was determined by different experimental technique. The thermomechanical properties were measured by Dynamic Mechanical Thermal Analysis (DMTA). DMTA was performed in dual cantilever bending mode using a DMTA V Rheometric Scientific instrument. All the experiments were done at 1 Hz frequency, by bending deformation, scanning from 20 to 250 °C using a heating rate of 2 °C/min. The maximum of tan δ vs. temperature plots was used to identify the α-relaxation associated to the glass transition. Two scans have been performed for each sample, whose dimensions were $35 \times 12 \times 1.5$ mm^3.

DC volume conductivity was evaluated according to ASTM D257 using Source Meter Unit instrument (KEITHLEY 2410) connecting through an interface GPIB to a PC. Electrical resistance was determined by slope of current–voltage ratio, from which can be obtained electrical conductivity taking into account the probe geometry. Two probes ($10 \times 10 \times 1$ mm) were measured per each sample. For the samples subjected to align by magnetic field, the electrical conductivity was measured in the perpendicular and parallel direction of the possible CNT alignment.

The mechanical properties was determined by tensile tests, which were carried out, following the ASTM D638 standard, to

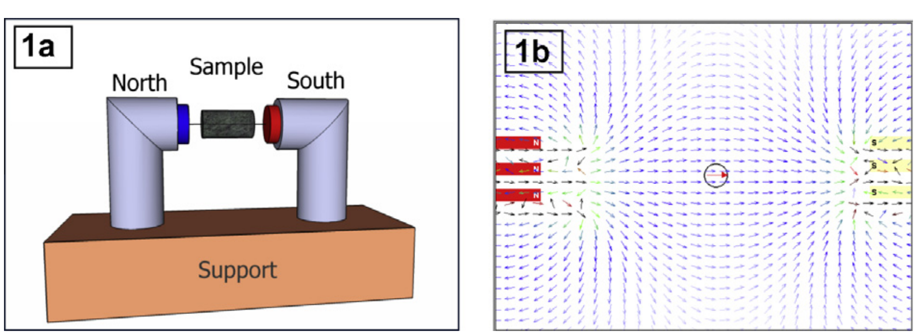

Fig. 1. Designed device to apply magnetic field during the curing treatment (a) and spatial distribution of magnetic field lines (b).

Table 1
Experimental conditions for manufacturing of studied composites.

Sample Code	CNT Load (wt%)	Modification with magnetite	Application of magnetic field
0.1-CNT	0.1	No	No
0.1-CNT–CM		No	Yes
0.1-FeO–CNT		Yes	No
0.1-FeO–CNT–CM		Yes	Yes
0.25-CNT	0.25	No	No
0.25-CNT–CM		No	Yes
0.25-FeO–CNT		Yes	No
0.25-FeO–CNT–CM		Yes	Yes

measure the tensile strength, the Young's modulus, and the deformation at break in the epoxy resin and composites. Type I specimens with $13 \times 57 \times 3\ mm^3$ in the narrow section were tested on an electromechanical testing machine (MTS Alliance RF/100), under displacement control at a crosshead speed of 1 mm/min. The strain was measured during the tests with an extensometer attached to the sample (model MTS 654-12F).

3. Results

3.1. Morphological characterization of magnetite–CNT nanohybrid materials and their epoxy composites

Fig. 2 shows TEM micrographs of magnetite nanoparticles and magnetite–CNT hybrid nanofiller. The average diameter of Fe_3O_4 particles is 10 ± 2 nm determined by image analysis (Fig. 2a). The size distribution is close; the most of particles presents diameters from 8 to 14 nm. On the other hand, the average diameter of multiwall carbon nanotubes used is 10 nm, which corresponds with 5–10 walls. CNTs with magnetite particles present a homogeneous distribution of both components (1b). The Fig. 2c and d show a magnification of magnetite–CNT nanohybrid materials. The quantification of crystalline interplanar distance through image analysis confirmed the crystalline structure of both Fe_3O_4 nanoparticles and nanotubes. The interplanar C–C distance measured for CNTs is close to 0.35 nm, according to the distance between nanotube walls. The inteplanar distance measured for magnetite particles is around 0.2 nm. The same lattice fringe was observed by Wang et al. [16] and it was associated to the separation between (400) lattice planes of magnetite. The most important observation of

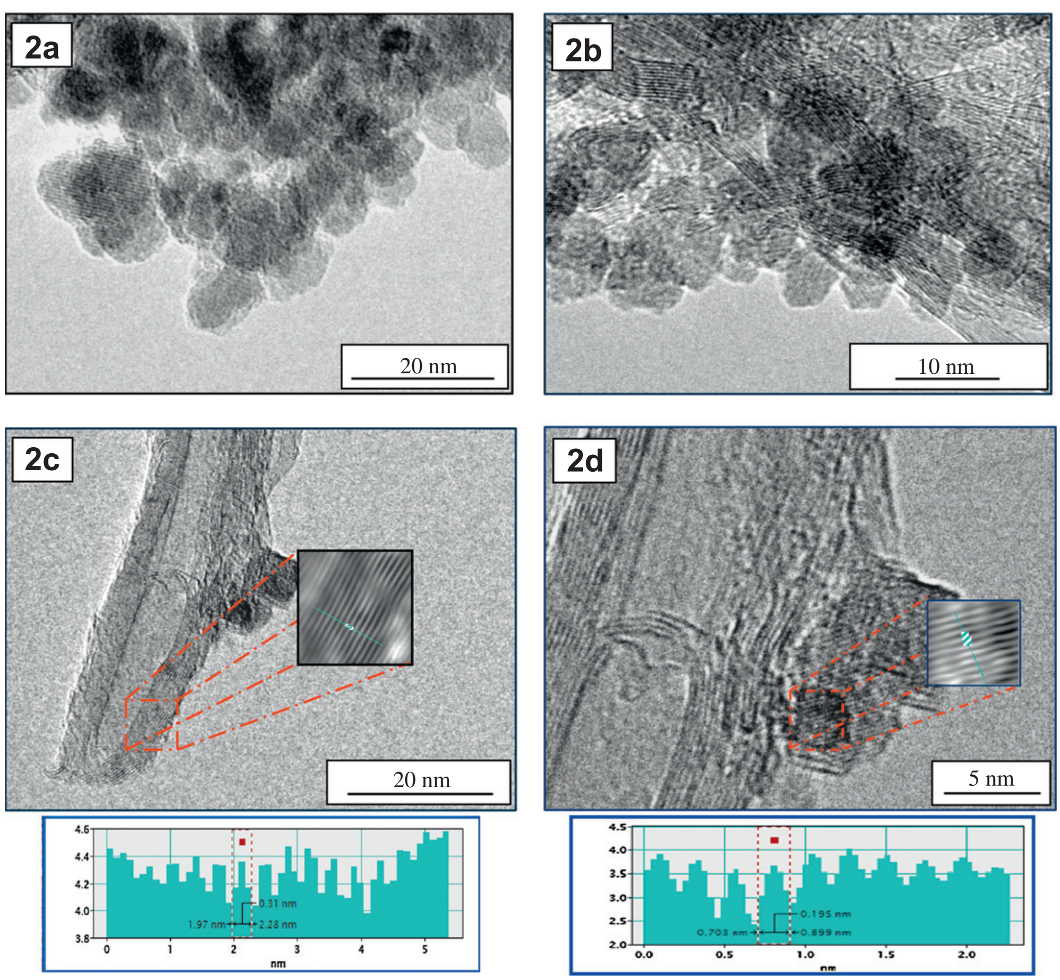

Fig. 2. TEM micrographs of magnetite nanoparticles (2a) and magnetite–CNT hybrid nanofillers (2b, 2c, 2d). Interplanar spacing measurement CNTs (2c) and Fe_3O_4 (2d).

these micrographs is the good bond observed between the nanotube and nanoparticles. The applied treatment in the magnetite/CNT mixture allows obtaining a close anchorage, indicating chemical bond the amine-fucntionalized CNTs with acid-modified magnetite particles. It is worthy to stand out that the anchorage of magnetites seem not occur in the ends of nanotubes. This implies that amine groups in the initial functionalized CNTs should be sited along the nanotube. The ferromagnetic behaviour of synthesised magnetite–CNT hybrid nanofillers was confirmed by the approximation of permanent magnet (Fig. 3).

The non-treated CNTs and magnetite–CNT hybrid nanofillers has been added to epoxy matrix in two different concentrations. Some samples were cured in conventional moulds and in the designed devise to apply magnetic field (Fig. 1a). Fig. 4 shows micrographs obtained by FEG-SEM for some representative samples. Two surfaces were analysed for each sample, in perpendicular directions. In the case of applying magnetic field, the cross-section surface is the surface perpendicular to this field while the longitudinal direction is the surface oriented in the direction of field lines. The resin reinforced with 0.1 wt% CNT present high dispersion degree of nanofillers which are randomly oriented in the matrix. The application of a weak magnetic induces a weak orientation of non-treated nanotubes because their own intrinsic magnetic susceptibility. Finally, the use of magnetite–CNT nanofillers causes a clear orientation of the same. The modified nanotubes are aligned in the direction of magnetic field. This can clearly observed in the cross-section micrograph, where the nanotubes are shown as white points because they are shown their cross-section. In the other samples, the nanotubes are curved while the application of magnetic field makes that the Fe_3O_4–CNTs is stretched. This effect has been studied for other authors [22], which explain why the nanotubes are oriented in the direction of magnetic field when they are functionalized with magnetic particles. In some published works [8], the alignment degree reached for modified CNTs is higher but the most of them manufactured films. It is worthy to sand out that the samples manufactured in this work have a 3-D volume.

3.2. Thermo-mechanical characterization of composites

DMTA measurements were made for all manufactured samples. The results are shown in Table 2. In the case of oriented magnetite-modified nanotubes, the test in bending mode was applied in the perpendicular direction of CNT alignment. The α-relaxation temperature, which can be associated to glass transition temperature of epoxy resin, lightly decreases by the addition of nanofillers. This decrease have been already observed for several authors [23,24] and it can be explained by several reasons, such as the breakage of stoichiometric balance due to the addition of functionalized nanotubes or the selective absorption of monomers into the nanotubes. The composites reinforced with Fe_3O_4–CNT nanofillers present lower values of glass transition temperature, which can associated to the presence of acid-functional groups on the magnetite particles, which can react with the epoxy monomer, causing higher stoichiometric decompensation. The aligned composites present similar value of α-relaxation temperature than randomly oriented ones. Therefore, the weak magnetic field applied in this work is not able to induce orientation and alignment of polymer epoxy chains, as it has been published by Camponeschi et al. [11].

On the other hand, the addition of nanofillers induces an important increase of the average modulus of composites, up to 25%, in the glassy region. This enhancement is similar for all composites manufactured without magnetic field, indicating that the modification of CNT with magnetite particles does not seem affect to their elastic modulus. Finally, all the samples cured in presence of magnetic field present a light reduction of their elastic modulus comparing with the same composites cured by traditional method. This could mean that the nanotubes have been aligned, showing lower modulus in the perpendicular direction to the preferential orientation direction.

3.3. Electrical behaviour of composites

The electrical behaviour of manufactured composites was studied through measurements of electrical as function of applied voltage in dc. These measurements were made in two perpendicular directions for each sample. In all cases, the *I*–*V* ratio is linear, confirming that the manufactured composites present ohmic behaviour. The electrical conductivity, calculated by slope, is collected in Table 2 and Fig. 5. As it is well known the addition of CNT induces an important increase of the electrical conductivity of composites, which increases with CNT content. For the studied systems, the percolation threshold is lower than 0.1 wt%. The conductivity of composites modified with magnetite–CNT hybrid nanofillers is lower than the ones for corresponding composites reinforced with non-modified CNTs without applying magnetic field. This could be associated to the CNT modification with insolating Fe_3O_4 nanoparticles induces a decrease of their intrinsic electrical conductivity. The application of magnetic field on the epoxy composites with non-modified CNTs induces an important increase of their electrical conductivity in their longitudinal direction. A light decrease of this property is measured in transversal direction. This confirms the alignment of nanotubes due to their magnetic susceptibility, obtaining anisotropic materials. The most important increase is registered for 0.25-FeO–CNT–CM in the direction of nanotube alignment in spite of the possible decrease of their electrical conductivity. This implies that the alignment of magnetite–CNT hybrid nanofillers is higher than the one of non-treated CNTs, as confirming by microscopic analysis. It is worthy to note that for the same nanofiller content, the electrical conductivity increases one order to magnitude by alignment with magnetic field.

3.4. Mechanical behaviour of composites

In order to complete the characterization of manufactured composites, it was necessary to determine their mechanical behaviour. In the previous section, it was probed that the application of weak magnetic field during the curing treatment of composites in the developed devise is an easy and economic procedure to get increasing the conductivity in at least one order of magnitude. However, the addition of magnetite particles over CNTs could affect to their mechanical properties and therefore to the composites. Fig. 6 shows the obtained results confirming that the mechanical properties of composites are lightly enhanced by the addition of carbon nanofillers. The modification of CNTs by

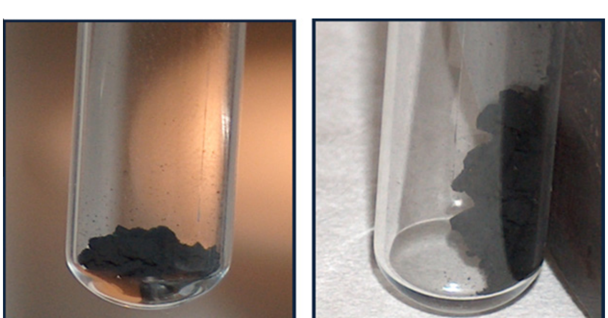

Fig. 3. Ferromagnetic behaviour of hybrid magnetite–CNT nanofillers.

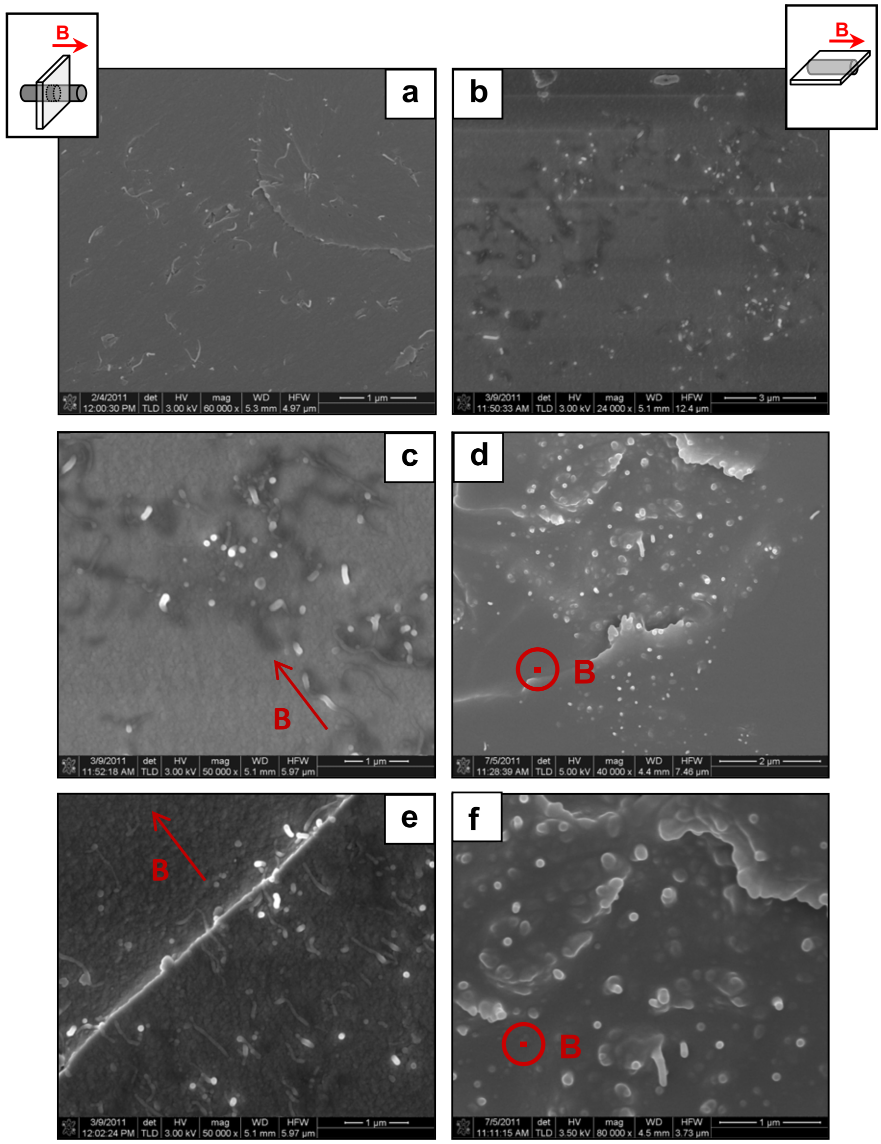

Fig. 4. FEG-SEM micrographs of cross-section (left) and longitudinal section (right) of 0.1-CNT (a, b), 0.1-CNT–CM (c, d) and 0.1-FeO–CNT–CM (e, ef). Red symbols indicate the direction of magnetic field lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
DMTA results, electrical conductivity: Average modulus at room temperature (E'_G), α-relaxation temperature (T_α) and electrical conductivity (σ) in longitudinal and transversal direction to CNT alignment.

Sample code	E'_G (GPa)	T_α (°C)	σ (S/m)	
			Transversal	Longitudinal
Neat epoxy resin	2.10	181.4	$\sim 10^{-12}$	
0.1-CNT	2.49	174.3	6.34×10^{-2}	6.07×10^{-2}
0.1-CNT–CM	2.38	167.2	2.00×10^{-2}	8.64×10^{-2}
0.1-FeO–CNT	2.63	164.8	3.81×10^{-3}	3.32×10^{-3}
0.1-FeO–CNT–CM	2.39	165.2	8.95×10^{-2}	5.21×10^{-1}
0.25-CNT	2.55	170.7	1.00×10^{-1}	9.36×10^{-2}
0.25-CNT–CM	2.48	168.2	9.36×10^{-2}	4.09×10^{-1}
0.25-FeO–CNT	2.40	170.0	4.77×10^{-2}	3.32×10^{-2}
0.25-FeO–CNT–CM	2.30	168.8	2.05×10^{-1}	9.45×10^{-1}

the addition of magnetite nanoparticles does not seem affecting to their mechanical properties because the corresponding composites present similar mechanical behaviour. It would have been interesting to study the anisotropic behaviour of composites manufactured applying magnetic field. However this has not been possible due to the impossibility to manufacture large specimens

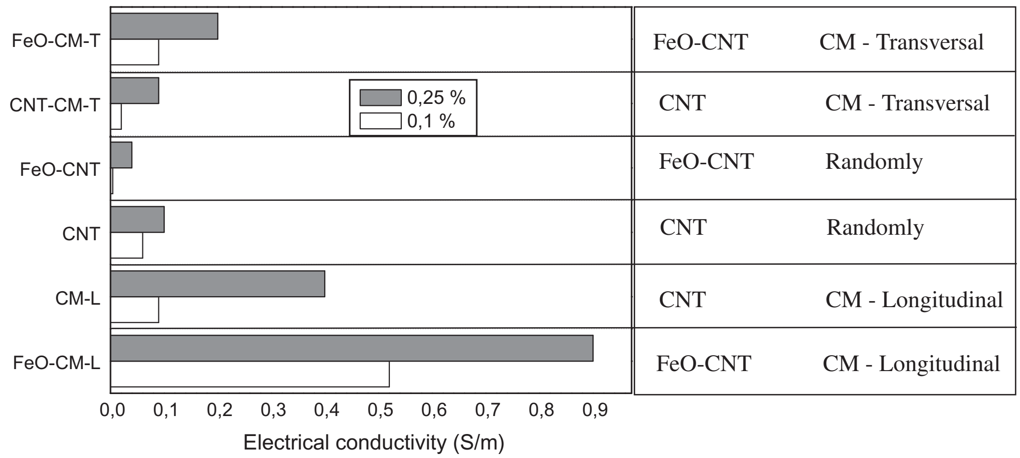

Fig. 5. Electrical conductivity of some manufactured composites.

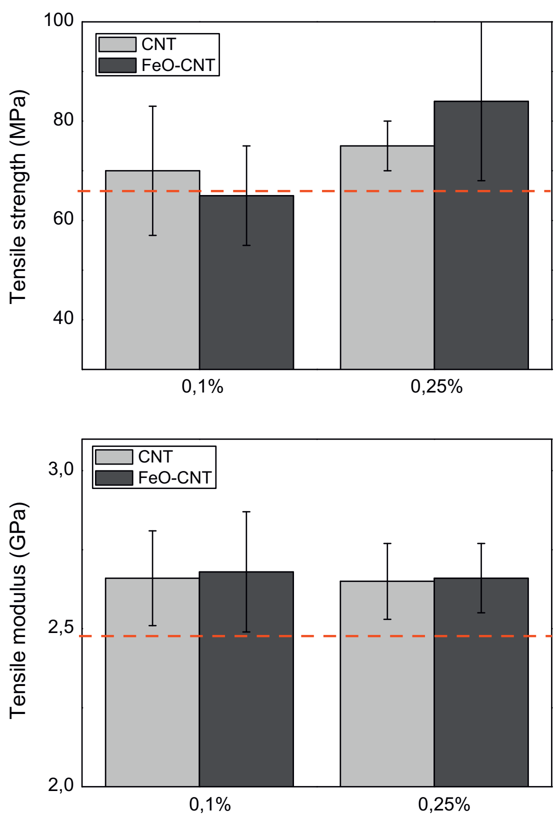

Fig. 6. Tensile mechanical properties of some manufactured composites. The properties of neat epoxy resin are marked with dotted red lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in the designed device. This is being actually developed for a future work.

4. Conclusions

In this work, a new procedure of synthesis of magnetite–CNT hybrid nanofillers has been proposed together with their dispersion and alignment into epoxy matrix applying a weak magnetic field obtained through permanent magnets. The synthesis is based on functionalized Fe_3O_4 nanoparticles and nanotubes, avoiding the use of strong acids. The intimate chemical bond between both is confirmed by TEM. The addition of CNT and magnetite–CNT hybrid nanofillers induces an enhancement of mechanical properties of neat epoxy resin. An anisotropic electrical behaviour has been found for the composites cured in presence of magnetic field. The electrical conductivity of composites reinforced with 0.1 and 0.25 wt% Fe_3O_4–CNT is 0.09 and 0.5 S/m, respectively for perpendicular direction while this parameter changes to 0.2–0.9 S/m for parallel direction to aligned nanotubes. This means that it is possible to obtain higher conductivity for samples with half CNT load when the magnetic devise is used. For the same nanofiller content, the electrical conductivity increases one order to magnitude by alignment with magnetic field.

Acknowledgements

Authors wish thank the support of *Ministerio de Ciencia e Innovación* of Spain Government (Project MAT2010-207024-C02-01) and *Direction General de Universidad* of Madrid Community (Project S2009/MAT-1585).

References

[1] Ajayan PM, Schadler LS, Baun PV. Nanocomposite science and technology. Weinheim, Germany: Wiley-VCH; 2003.
[2] Xie XL, Mai YW, Zhou XP. Dispersion and alignment of carbon nanotubes in polymer matrix: a review. Mater Sci Eng 2005;49:89–112.
[3] Joshi UA, Sharma SC, Harsha SP. Effect of carbon nanotube orientation on the mechanical properties of nanocomposites. Compos B: Eng 2012;43:2063–71.
[4] Takeyama S, Nakamura S, Uchida K. Dynamical orientation of carbon nanotubes by pulsed magnetic fields. J Phys 2006;51:446–9.
[5] Martin CA, Sandler JKW, Windle AH, Schwarz MK, Bauhofer W, Schulte K, et al. Electric field-induced aligned multi-wall carbon nanotube networks in epoxy composites. Polymer 2005;46:877–86.
[6] Wang Q, Dai J, Li W, Wei Z, Jiang J. The effects of CNT alignment on electrical conductivity and mechanical properties of SWCNT/epoxy composites. Compos Sci Technol 2008;68:1644–8.
[7] Bradford PD, Wang X, Zhao H, Maria JP, Jia Q, Zhu YT. A novel approach to fabricate high volume fraction nanocomposites with long aligned carbon nanotubes. Compos Sci Technol 2010;70:1980–5.
[8] Ma C, Zhang W, Zhu Y, Ji L, Zhang R, Koratkar N, et al. Alignment and dispersion of functionalized carbon nanotubes in polymer composites induced by an electric field. Carbon 2008;46:706–20.
[9] Oliva-Aviles AI, Aviles F, Sosa V. Electrical and piezoresistive properties of multi-walled carbon nanotube/polymer composite films aligned by an electric field. Carbon 2011;49:2989–97.
[10] Shi D, He P, Zhao P, Guo FF, Wang F, Huth C, et al. Magnetic alignment of Ni/Co-coated carbon nanotubes in polystyrene composites. Compos B: Eng 2011;42:1532–8.
[11] Camponeschi E, Vance R, Al-Haik M, Garmestani H, Tannenbaum R. Properties of carbon nanotube–polymer composites aligned in a magnetic field. Carbon 2007;45:2037–46.

[12] Jang BK, Sakka Y. Influence of shape and size on the alignment of multi-wall carbon nanotubes under magnetic field. Mat Lett 2009;63:2545–7.
[13] Abdalla M, Dean D, Theodore M, Fielding J, Nyairo E, Price G. Polymer 2010;51:1614–20.
[14] Sharma A, Tripathi B, Vijay YK. Dramatic improvement in properties of magnetically aligned CNT/polymer nanocomposites. J Membr Sci 2010;361:89–95.
[15] Kim IT, Tannenbaum A, Tannenbaum R. Anisotropic conductivity of magnetic carbon nanotubes embedded in epoxy matrix. Carbon 2011;49:54–61.
[16] Wang X, Zhao Z, Qu J, Wang Z, Qiu J. Fabrication and characterization of magnetic Fe_3O_4–CNT composites. J Phys Chem Solid 2010;71:673–6.
[17] Qu S, Huang F, Yu S, Chen G, Kong J. Magnetic removal of dyes from aqueous solution using multi-walled carbon nanotubes filled with Fe_3O_4 particles. J Hazardous Mater 2008;160:643–7.
[18] Huiqun C, Maifang Z, Yaogang L. Decoration of carbon nanotubes with iron oxide. J Solid State Chem 2006;179:1208–13.
[19] Collins PG, Hersam M, Arnold M, Martel R, Avrouris Ph. Current Saturation and electrical breakdown in multiwalled carbon nanotubes. Phys Rev Lett 2001;86:3128–31.
[20] Prolongo SG, Gude MR, Ureña A. Improving the flexural and thermomechanical properties of amino-functionalized carbon nanotube/epoxy composites by using a pre-curing treatment. Compos Sci Technol 2011;71:765–71.
[21] Prolongo SG, Gude MR, Ureña A. Synthesis and characterisation of epoxy resins reinforced with carbon nanotubes and nanofibers. Nanosci Nanotechnol 2009;9:1–7.
[22] Wang Z, Zhao H, Fan L, Zhuang P, Yuan WZ, Hu Q, et al. Carbohydr Polym 2011;84:1126–32.
[23] Xiao KQ, Zhang LC. Effective separation and alignment of long entangled carbon nanotubes in epoxy. J Mater Sci 2005;40:6513–6.
[24] Shen J, Huang W, Wu L, Hu Y, Ye M. Thermo-physical properties of epoxy nanocomposites reinforced with amino-functionalized multi-walled carbon nanotubes. Composites: Part A 2007;38:1331–6.