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High mobility of carbon nanotubes into thermosetting matrix

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ABSTRACT

A new manufacturing process based on applying weak magnetic field during the curing treatment is reported in order to induce a selective mobility and alignment of the carbon nanotubes on epoxy resins. Depending on experimental conditions, this procedure allows manufacturing different materials: (a) anisotropic composites with aligned carbon nanotubes and (b) composites with selected nanoreinforced areas and neat epoxy areas. Different composites have been manufactured, such as dielectric materials with insulating inside and electrically doped surfaces, or doped composites with insulating ring.

The procedure basically consists on the anchorage of magnetite nanoparticles in the surface of carbon nanotubes and the application of magnetic field during the curing treatment. The mobility of nanofillers can be directly observed through the appearance of black and transparent areas on the composites, while the alignment of carbon nanotubes is analyzed by scanning electron microscopy of high resolution. The anisotropy and different behavior of selected areas for the manufactured composites have been determined by electrical measurements.

1. Introduction

The introduction of carbon nanotubes (CNTs) into thermosetting resins is being widely studied [1,2]. The main expected advantages are new combinations of enhanced thermal, electrical and mechanical properties [3]. There are numerous published works about the dispersion and alignment of these nanofillers into a polymer matrix [4–6]. It is largely known that the final properties of CNT/polymer composites are strongly affected by the dispersion degree of CNTs, particularly, the presence of aggregations. Due to their very high length-to-diameter ratio, the orientation and alignments of CNTs into the matrix is necessary in order to reach the best properties. The composites with aligned CNTs exhibit strongly anisotropic behavior [7]. The nanotubes can be aligned by the application of shear flows, electrical fields and magnetic fields [5]. In a previous work [8], the authors studied the CNT alignment by applying a weak magnetic field (0.3 T), which can be easily obtained by permanent magnets. In order to enhance the magnetic effect, superparamagnetic magnetite nanoparticles are anchored over the carbon nanotubes [8–10]. The published procedure is a one-stage-process and environmentally acceptable because of it is an acid free-treatment [8].

In the present work, a new and unknown phenomenon is shown: the controlled mobility of carbon nanotubes in order to manufacture devices with selected regions of different electrical behavior. A modified treatment based on applying on relative weak magnetic field, in the range of 0.3–0.5 T, is reported in order to induce the mobility of the carbon nanotubes. The

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mobility of CNTs into thermosetting resin has not been reported, yet. The main objective is the selective location of CNTs on the composites. Particularly, the ability of positioning CNTs on composites' surfaces, while remaining the inner resin region unmodified, is very interesting. The control of the CNT mobility allows locating the nanotubes in the desired location, generating selected areas of the doped and neat resin. Among other aspects, the electrical behavior of these selected regions is different. Neat thermosetting resin is an insulating material, while CNT doped areas are electrically conductors. This can be especially interesting to create some particular electrical devices.

On the other hand, one of the most important applications of doped resins is their use as matrices for composites reinforced with continuous fiber reinforced composites. These materials are commonly known as multiscale materials, because they have two fillers of different size: nano- and micro-scale ones. The processing of these materials is still being studied because it presents numerous limitations. When the manufacturing technique is based on resin infusion, their main limitation is the appearance of filtration effect [11,12]. This effect consists of the accumulation of carbon nanotubes near to resin inlet. Because of this effect, the possibility of mobilizing them to the desired place would be an important advance for the manufacture of these materials.

In the present work, the procedure of alignment and mobility of carbon nanotubes into epoxy resin is described. Different experimental conditions have been analyzed in order to reach the selected target: alignment and/or mobility of CNTs. The morphology and electrical behavior of manufactured composites have been analyzed.

2. Experimental

2.1. Materials and sample preparation

The thermosetting resin was based on 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 nanofiller was multi-walled carbon nanotubes functionalized with amino-groups (<0.5% w/w), which were supplied by Nanocyl with the commercial name of NC3152. The main characteristics were their high purity (>99% C), an average length close to 1 μm and a diameter in the range of 30–50 nm, which corresponds to 8–12 walls. The magnetite nanoparticles (Fe_3O_4) were supplied by nanogap, in aqueous solution (100 g/l). Their average diameter was 10.5 ± 0.4 nm and they were coated with oleic acid. They show superparamagnetic behavior at room temperature, with a saturation magnetization of 50 emu/g.

The anchorage of magnetite nanoparticles over carbon nanotubes was based in the chemical reaction between the acid groups of oleic acid with the amine groups of CNTs at 80 °C for 1 h [8]. Then, the modified nanotubes were repeatedly washed in water and dried in a rotary evaporator. They were stored at 115 °C in a stove under vacuum conditions to ensure that the modified nanotubes were dry. In order to increase the magnetic susceptibility, a thermal treatment was applied to remove the coating at 400 °C for 1 h. This treatment allows removing the oleic acid (boiling point = 360 °C) without changes on the structure of magnetite nanoparticles or carbon nanotubes. From now, the hybrid nanofillers formed by magnetite nanoparticles anchored into carbon nanotubes will be named FCNT, while the same nanofillers thermally treated will be named tt-FCNT.

The composites were manufactured by applying high shear mixing (Dispermat AE) [13]. The dispersion of nanofillers into neat epoxy monomer consisted of stirring at 6000 rpm for 15 min, reaching the optimum Doughnut effect. Afterwards, the mixture was degassed at 80 °C in vacuum and then, a stoichiometric amount of hardener was added. The curing treatment applied was 150 °C for 3 h, followed by a postcuring stage at 180 °C for 1 h. In order to induce the alignment and mobility of FCNT or tt-FCNT into the polymer matrix, the curing treatment was carried out into a specific device for applying magnetic field. Fig. 1 shows the device specially designed by the research group for this application. The samples were cured in a polyfluoroethylene mold which is placed between permanent magnets of neodymium (N35, from Aiman company). These magnets ensured a constant magnetic field of 0.3 T at 50 mm up to 200 °C. The position of four magnets allowed obtaining a field of 0.5 T.

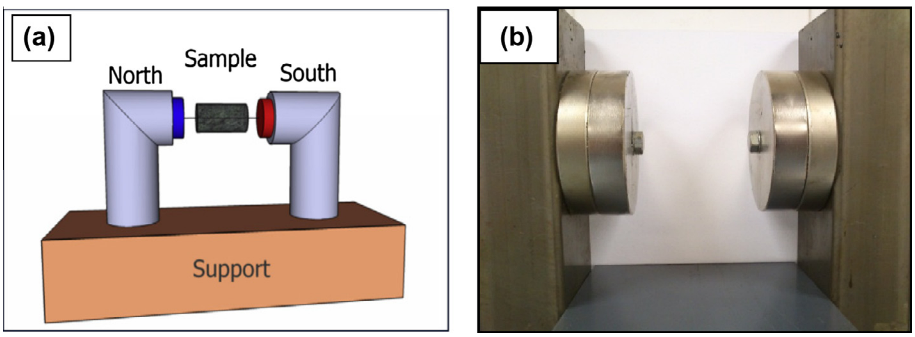

Fig. 1. Scheme and photograph of the device used for applying magnetic field.