Morphology and electrical properties of graphene–epoxy nanocomposites obtained by different solvent assisted processing methods

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ABSTRACT

We report a comparative study of graphene nanoplatelets (GNPs)–epoxy nanocomposites with enhanced electrical conductive properties obtained with two different processing techniques. In the first one (TEC1), the epoxy monomer was added to a previously produced GNP–chloroform suspension and after the evaporation of the solvent, the hardener was added. In the second technique (TEC2), the hardener was added to a GNP–tetrahydrofuran suspension and after the evaporation of the solvent, the epoxy monomer was added. Although there was good dispersion of GNPs in the epoxy matrix with both techniques, the nanocomposite based on TEC1 showed a slightly better dispersion than the one based on TEC2. Electric and dielectric characterization showed that it is possible to reach the electrical percolation threshold at reasonably low GNP contents.

1. Introduction

In recent years, graphene has become greatly interesting in polymer science thanks to its possibility of improving the performance of the polymer in which it is embedded. This is due to the combination of high specific surface areas, peculiar in these single layers of graphite and strong filler–matrix adhesion [1–9]. Graphene is a single layer of sp²-bonded carbon atoms that can be imagined as an individual atomic plane extracted from graphite [1]. Several methods are commonly used to produce graphene. Through chemical vapor deposition [2] and epitaxial growth of graphene films on electrically insulating substrates [3], well exfoliated graphene layers are attained due to the thermal decomposition of gaseous precursors. The use of scotch tape to induce the mechanical exfoliation of bulk graphite was considered a real breakthrough [4]; whereas a reduction in graphene derivatives such as graphene oxide [5,6] is the most commonly used technique. Finally it is worth citing the possibility of obtaining graphene from solution extraction in ultrasonic baths [7,8]. Nonetheless, scaling up single-layer graphene sheets production as a filler for polymer composites to an industrial level is still quite far from happening.

In order to prove the effectiveness of the processes to obtain graphene, several analysis techniques were utilized. In particular,

Ferrari et al. [8] have demonstrated that Raman spectroscopy can accurately calculate the number of graphene layers in the measuring point through the position and shape of the 2D peak ($\sim$2700 cm^{-1}). Moreover, high resolution transmission electron microscopy can show the graphene particles dispersed in the polymeric matrix and the stacked-up layers can be counted [11]. Finally, X-ray diffraction is useful in verifying the presence of reduced or oxidized forms of graphene, since the interlayer distance is different in the two cases [12].

Recent studies have demonstrated that few stacked graphene layers, which basically correspond to partially exfoliated graphite, can be used successfully as a filler for polymers [10–21]. This filler is commonly referred to as graphene nanoplatelets (GNPs). Nowadays, this filler is available on the market at a significantly lower price in comparison to single-layer graphene and can play an important role in the industrial scale up of polymer nanocomposites.

As an example, Rafiee et al. [11] demonstrated that GNPs in epoxy matrix outperform the mechanical performance of carbon nanotubes in terms of Young modulus and tensile strength and also in terms of the buckling resistance. Liang et al. [16] studied the electromagnetic interference (EMI) shielding of graphene/epoxy composites, showing that these systems have a low electrical percolation threshold and good shielding efficiency, indicating that they may be used as lightweight effective EMI shielding materials. Enhanced electrical conductivity for exfoliated graphite based composites was also found by Biswas et al. [17].

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Martin-Gallego and coworkers [19] studied a graphene nanocomposite based on a UV-cured epoxy resin, showing that the addition of the graphene platelets induced an increase in the stiffness of the matrix, achieving advanced UV-cured epoxy films with outstanding mechanical behavior while Koo et al. [20] investigated the possibility of using graphene nanoplatelets to improve the thermal stability of polymers.

In this research, we used commercial GNPs to enhance the electric conductivity of the epoxy resin in which they were embedded. The possibility of dispersing graphene in different solvents is already widely reported in literature [22–25] and the exfoliation level obtained is quite easy to measure with common techniques, such as, Raman spectroscopy, transmission electron microscopy and atomic force microscopy. The dispersion of carbon nanoparticles in chloroform as a route to obtain epoxy matrix composites was also reported in literature [26–28]. So, in this paper we propose to compare two different processing techniques: one based on the dispersion of GNPs in chloroform and epoxy monomer and the other based on the dispersion of GNPs in THF and aromatic amine. The use of solvents in these processing methods was necessary to work with low viscosity suspensions which can allow better exfoliation of the graphene layers. Moreover, both chloroform and tetrahydrofuran are generally considered good dispersing media for carbon fillers [26] and they have been investigated further in this study. An in-depth morphological analysis was performed and the electrical properties of the produced nanocomposite were studied.

2. Experimental

Graphene nanoplatelets used in this study were supplied by Cheap Tube Inc (Grade 2). As claimed by the manufacturer, they have a surface area of about $100\ m^2/g$, an average thickness of a bit less than 10 nm and an average diameter of 25 μm. They were used as supplied by the manufacturer without any functionalization process. GNPs were studied by XRD and TEM (Philips EM 208 TEM) in order to have a morphological characterization of the starting material. Wide angle X-ray diffraction patterns were collected on a PW 1729 Philips, using Cu Ka radiation in reflection mode ($\lambda = 0.154$ nm).

The epoxy matrix was a diglycidyl ether of bisphenol F Epikote 862 (169 g/eq epoxy equivalent), kindly supplied by Hexion. Diethyltoluenediamine (DETDA, 26.4 phr), kindly supplied by Lonza, was used as a curing agent. The curing cycle was 130 °C for 5 h. The GNP–epoxy nanocomposite mixtures were realized with the two following techniques.

2.1. First technique (TEC1)

GNPs were added to chloroform (Sigma–Aldrich), 2 mg/ml, and the colloidal dispersion was sonicated for 1 h (Vibracell 75043 tip sonicator). Then, the epoxy monomer was added to the suspension and the new mixture was further sonicated for 1 h. Afterwards, this mixture was heated while magnetically stirred on a hot plate to fully remove the solvent. Finally, the curing agent was added, the reactive system was poured into disposable aluminium dishes (70 mm diameter) and allowed to cure.

2.2. Second technique (TEC2)

GNPs were added to THF (Sigma–Aldrich), 2 mg/ml, and the suspension was sonicated for 1 h. Then, DETDA was added to the colloidal dispersion and the new mixture was further sonicated for 1 h. Afterwards, this mixture was heated while magnetically stirred on a hot plate to fully remove the THF solvent. Finally,

the epoxy monomer was added and the reactive system was poured into disposable aluminium dishes (70 mm diameter) and allowed to cure.

In both methods, after the evaporation step, FTIR measurements (Jasco FTIR 615) were performed on the cast material to verify the complete evaporation of the solvent (not reported in this paper).

Several GNP contents were taken into account, namely 0.5, 1, 2 and 3 wt.%. These concentrations were calculated on the total weight of the reactive system (epoxy monomer + hardener). For the purposes of clarity, Table 1 reports the materials codes used in this paper.

The dispersion of GNPs in the solvents was evaluated using both transmission (Philips EM 208 TEM) and scanning electron microscopy (FESEM Zeiss Supra 25) and Raman spectroscopy. Raman spectra were recorded using a Reflex Raman System (Renishaw plc, Wotton-under-Edge, UK) employing a laser wavelength of 785 nm (laser power at sample = 10 mW; microscope objective = 100×). Spectra were recorded at room temperature after the exposure time of 10 s, necessary to decay the fluorescence. In order to perform these tests, a drop of diluted graphene solution was poured in a silicon substrate and allowed to evaporate. More than ten Raman measurements per sample were taken in order to have reliable results.

A morphological characterization was also performed on the cured samples by using a high resolution transmission electron microscope (TEM). The TEM measurements were performed on a JEOL JEM-2100 TEM instrument (JEOL Ltd., Akishima, Tokyo, Japan), with a LaB6 filament, with an operating voltage of 200 kV. Nitrogen-fractured cross-sections of the nanocomposites were examined by transmission electron microscopy operated at 300 kV after cutting them with a microtome Leica UC6. Diamond knives (Diatome) have been used for trimming (model cryotrim 45°) and wet sectioning (model cryo 35° with a boat). The slices, with a thickness of approximately 70 nm, were deposited on 400-mesh carbon coated copper grids (Agar Scientific).

DC electrical measurements were performed using a model 6517B Keithley electrometer. The dielectric tests were performed with a HP 4284A (Hewlett–Packard) impedance spectrometer, in a 20 Hz 1 MHz frequency range, with a voltage amplitude of 0.5 V.

Calorimetric tests (DSC Q200, TA Instruments) were also performed. Two consecutive heating scans (25–250 °C at 10 °C/min in a nitrogen atmosphere) were performed on the reactive formulations to study the overall cure behavior and identify the glass transition temperature of the fully cured materials.

Rheological properties were studied to investigate the influence of graphene nanoplatelets on the viscosity of the nanocomposites through dynamic tests, performed with a model ARES N2 rotational rheometer, Rheometric Scientific using the parallel plate geometry with an oscillation frequency growing from 0.1 to 100 rad/s. The temperature was set at 25 °C and the strain at 1.5%, in order to keep the measurements in the linear viscoelastic range. All the measurements were performed on the reactive

Table 1
Materials codes.

Material	Code
Neat epoxy	E
Epoxy – 0.5% GNPs via ($CHCl_3$ – monomer)	E-0.5GNP-Tec1
Epoxy – 1% GNPs via ($CHCl_3$ – monomer)	E-1GNP-Tec1
Epoxy – 2% GNPs via ($CHCl_3$ – monomer)	E-2GNP-Tec1
Epoxy – 3% GNPs via ($CHCl_3$ – monomer)	E-3GNP-Tec1
Epoxy – 0.5% GNPs via (THF – hardener)	E-0.5GNP-Tec2
Epoxy – 1% GNPs via (THF – hardener)	E-1GNP-Tec2
Epoxy – 2% GNPs via (THF – hardener)	E-2GNP-Tec2
Epoxy – 3% GNPs via (THF – hardener)	E-3GNP-Tec2