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# Advantages and disadvantages of the addition of graphene nanoplatelets to epoxy resins



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#### ABSTRACT

Graphene nanoplatelets (GNPs), in different contents, are added to epoxy resin. This work mainly consists of a deep characterization of the composites in order to evaluate their behavior regarding neat epoxy resin. In fact, their main properties, such as their morphological features, their thermo-mechanical and mechanical properties, their electrical conductivity and thermal diffusivity, their hydrophobic behavior and their barrier properties have been studied. It is confirmed that the GNP addition induces an important stiffing of thermosetting resin. However, the rest of mechanical properties, strength and elongation, are diminished due to a weak interface formed between the epoxy matrix and non-functionalized GNPs. The electrical conductivity and thermal diffusivity show an important increase. Electrical conductivity increases several orders of magnitude from a minimum value of percolation while the thermal diffusivity increases proportionally to GNP content. Other advantage of the GNP addition is the increase of the hydrophobic behavior of the composites, determined by measurements of contact angle of water drops. Finally, GNP/epoxy composites present higher barrier properties in humid environments. The addition of GNP decreases the maximum water content absorbed and the diffusion coefficient. However, this enhancement is not too large due to the weak interface and therefore the presence of hollows in the GNP/epoxy composites. © 2014 Elsevier Ltd. All rights reserved.

# 1. Introduction

Polymer composites reinforced with carbon nanofillers have been widely studied during the last decade [1–3]. The addition of carbon nanotubes or nanofibers into thermosetting resins can improve the mechanical and thermal properties, together with an increase of the electrical conductivity. The industrial application of these materials is mainly limited by two factors: the poor dispersion of nanofillers, which implies the need of complex procedures of dispersion, and the high cost of carbon nanotubes. Both aspects cause an excessive price increase, which does not compensate the enhancement of properties on numerous occasions. Recently, the use of graphene nanoplatelets

http://dx.doi.org/10.1016/j.eurpolymj.2014.09.022 0014-3057/© 2014 Elsevier Ltd. All rights reserved. (GNP) as nanofiller is being studied. The main advantage is their low cost regarding to that one of carbon nanotubes. This is due to a lower manufacturing cost.

Their stiffness, two-dimensional geometry and low thermal interface resistance make graphene a successful filler to manufacture composite materials with improved thermal conductivity [4–6]. In addition, their planar geometry should induce a substantial improvement of the barrier properties and hydrothermal resistance of the composites. Their effect on the mechanical and electrical properties is not clear yet. For this reason, this work constitutes a deep study of the properties and behavior of epoxy composites reinforced with GNPs in order to clarify their main advantages and disadvantages.

Graphene nanoplatelets can present very different geometric features as a function of the size and number of atomic layers. These characteristics significantly modify

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their aspect ratio and specific surface area [7]. As it is known, a higher specific surface area should induce a higher properties enhancement with a lower amount of nanofiller if a good dispersion is achieved. Large surfaces result in large van der Waals forces and strong  $\pi$ - $\pi$  interactions, which usually induces problems in the dispersion stage [8]. Very thin nanoplatelets with low amount of graphitic sheets usually are more expensive and tend to selfroll. In this work, the authors have selected GNP with an intermediate geometry. Their thickness is 6 nm, corresponding to 18 graphitic sheets, and its lateral size is 25 µm, generating a relative low specific surface, 120- $150 \text{ m}^2/\text{g}$ . This reduces possible dispersion problems and avoids large increases of the viscosity of non-cured nanoreinforced resins. Thinner and larger GNPs could cause higher enhancement of some properties of composites but also they would induce more problems during manufacturing process.

In this work, we investigate the influence of the amount of graphene nanoplatelets on numerous aspects of the materials behavior, such as their mechanical properties, maximum service temperature and electrical and thermal conductivities. The hydrophobicity is also determined and chemical resistance in aggressive humid environmental. The main objectives are to confirm which are the main advantages of adding graphene into epoxy resins, and additionally, to determine which are the optimum GNPs contents as a function of the expected enhancement. It is worthy to note that the conclusions obtained in this work will be useful for similar systems while a significant modification of the geometry of the nanoplatelets could affect to the final properties of the composite.

## 2. Experimental

### 2.1. Materials

Graphene nanoplatelets (GNPs) were supplied by XGScience, with the commercial name of M25. Their purity was higher than 99.5% w/w. The average flake thickness was 6 nm and the average lateral particle size was 25  $\mu$ m. The epoxy resin is based on Diglycidyl Ether of Bisphenol A cured with an aromatic amine. It was manufactured by Araldite with the commercial name of Araldite LY556 (epoxy monomer) and XB3473 (amine hardener).

## 2.2. Sample preparation

GNP dispersion on non-cured resin was carried out through a combination of different dispersion techniques [9]. First, an ultrasonication process was applied for 45 min with a sonicator probe UP400S from Hielscher company. The cycle was 0.5 s, the sonication power was 400 W and the amplitude was 50%. Then, the mixture was treated in a three-roll miller (Exakt 80E GmbH) [4,5,10]. The rolling speed was 250 rpm and the gap size between each pair of rolls was 5  $\mu$ m. The calendering process was applied four consecutive times. The time of each mill-rolling cycle was approximately 5 min. Afterwards, the dispersed GNP/epoxy mixture was degassed in vacuum

at 80 °C for 15 min. Then, the hardener was added in a 100:23 (LY556:XB3473) stoichiometric ratio at 80 °C. The curing treatment consisted of heating at 140 °C for 8 h. The cured samples were cooled slowly to room temperature inside the oven. The studied contents of GNPs added were 1.5; 2.0; 3.0; 5.0 and 8.0 wt%.

## 2.3. Measurements

The characterization of composites consisted of the analysis of their main morphological features, the determination of their thermal and mechanical properties, the measurement of the electrical and thermal conductivities, the study of their hydrophobicity and also the determination of their behavior during hydrothermal ageing.

The morphology of isolated GNPs was observed by High Resolution Transmission Electron Microscopy (TEM, Philips CM200) while the morphology of composites was determined by Scanning Electron Microscopy (Hitachi 2400-N). The samples of composite were cut by cryo-ultramicrotomy (Leica) and coated with a thin Pt layer ( $\sim 2$  nm).

Thermomechanical behavior was studied by Dynamic Mechanical Thermal Analysis (DMTA, Q800 V7.1 from TA Instruments) in a single cantilever bending mode. The experiments were carried at 1 Hz frequency, scanning from 20 to 250 °C using a heating rate of 2 °C/min. The dimensions of samples were  $35 \times 12 \times 1.5$  mm<sup>3</sup>. The maximum of tan  $\delta$  vs. temperature plots was used to identify the  $\alpha$ -relaxation associated to the glass transition.

The mechanical properties were determined by flexural test in a universal machine (Instron 4465), following the ASTM D-790 at a crosshead speed of 0.8 mm/min. The fracture surfaces were also covered with Au (Pd) and observed by SEM in order to study the fracture mechanisms. In order to confirm the mechanical properties of composites, some materials were also tested by tensile test. The tensile tests were carried out, following the ASTM D638 standard, to measure the tensile strength, the Young's modulus, and the deformation at break in the epoxy resin and several composites reinforced with different GNPs contents. Type I specimens with  $13 \times 3 \times 57 \text{ mm}^3$  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).

The electrical conductivity was measured following the standard ASTM D257. A Source-Meter Unit instrument (KEITHLEY 2410, Keithley Instruments) connected through an interface GPIB to a PC was used. The electrical resistance was determined by calculating the slope of the current–voltage characteristic curve, from which can be determined the electrical conductivity taking into account the geometry of specimens  $(10 \times 10 \times 1 \text{ mm}^3)$ .

The thermal diffusivity was measured with Laserflash LFA 457 MicroFlash equipment, applying a temperature scan from 20 to 200  $^{\circ}$ C.

The hydrophobicity of composites was determined by measurements of the contact angle of water. The contact angle was measured with a goniometer equipped with a Download English Version:

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