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Graphene nanoplatelets thickness and lateral size influence on the morphology and behavior of epoxy composites

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ABSTRACT

Graphene nanoplatelets/epoxy nanocomposites were prepared using a high shear toroidal mixer as dispersion technique. Suitable dispersions were obtained. Several graphene nanoplatelets, with different thickness and lateral dimensions, were added in order to analyze the influence of these parameters in the final properties. An important nanofiller concentration gradient was found from the top to the bottom in nanocomposites reinforced with large nanoplatelets due to a natural deposition by gravity. This phenomenon is not appreciable when the nanoplatelets size decreased. However, the small nanoplatelets have a greater tendency to agglomerate in packages of several parallel particles. In general, graphene nanoplatelets addition caused an increment in glass transition temperature, stiffness and thermal stability compared to the epoxy resin. However, it was also found that graphene nanoplatelets dimensions significantly affect to these enhancements. Nanocomposites reinforced with larger and thicker nanoplatelets presented lower glass transition temperature, higher modulus and higher decomposition temperature.

1. Introduction

Graphene is a two-dimensional material consisting of sp^2-hybridized carbon atoms arranged in a honeycomb structure. When this material is constituted by a unique hexagonal atoms plane, it is named graphene sheet, while graphene nanoplatelets refer to particles with a nanometric thickness, in the range of 3–100 nm (GNPs) [1]. The carbon atoms are strongly bonded in a hexagonal plane but weakly bonded normal to the plane. Nowadays, the use of these materials as polymer fillers is being widely studied [2–4]. It is expected that graphene reinforced polymer composites show important improvements in their mechanical properties, electrical and thermal conductivity and other thermophysical properties [5,6]. Another advantage is that the 2-dimensional nanoplatelet can increase the gas permeation resistance of polymer composites [7]. These improvements can be maximized when graphene is exfoliated in an isolated layer and the morphology of the composites is tailored as dispersed and stretched particles in order to obtain the highest aspect ratio.

Great efforts have been made in processing of graphene/polymer composites. The van der Waals forces are the main problem of graphene dispersion and, consequently, the π–π inter-planar stacking. Most of the processing techniques are based on graphene solutions or dispersions, either in water or organic solvent [8]. However, one of the main challenges to achieve the large-scale potential for technological and engineering applications is to homogeneously disperse thin graphene nanoplatelets within the polymer matrix. Micro-mechanical dispersion and exfoliation can help to motivate research towards a scalable procedure without using intercalants. Following the developed methodology for manufacturing carbon nanotube reinforced polymers, calandering technique

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using the three-roll mill has been used in graphene/polymer composites processing [9]. Suitable dispersions have been reported for composites with epoxy matrices [10–12]. Another technique, less studied than the previous one but also based on shear micromechanical forces, is the high shear-speed mixing. No research has been found about the use of this technique in the manufacturing of graphene/epoxy composites. Its main advantage is its capability of being industrially scaled up. Also, it is probed that it allows obtaining nanofillers homogeneous dispersions, as in the case of carbon nanotubes [14,15]. Both of the techniques are based on applying high shear forces and therefore, it is necessary to carry out a deep study of the composites morphology, determining the final thickness and exfoliation degree of graphene nanofillers, their spatial arrangement (wrinkling or stretched) and the morphology of the composite, elucidating that way the dispersion and distribution of nanoplatelets (stacked or agglomerated).

Similar to previous researches about carbon nanotubes reinforced composites, the effect of numerous experimental conditions on the morphology and behavior when using graphene as nanofiller is not clear. Different results, even conflicting, have been published [2–4]. These differences may be associated to differences in the source and production of graphene nanofillers, e.g. mechanical milling of graphite, thermal or chemical reduction of graphene oxide, and differences in the nanocomposite manufacturing technique used. In this work, in addition to the effectiveness of the manufacturing technique, the effect of GNPs size and thickness is studied, by using nanofillers from the same source. This research is complementary to other previous published works [13,16,17].

2. Experimental

2.1. Materials

Three different types of GNPs (manufactured by Chemical Reduction) were purchased in Graphene Supermarket [18] and their main featured are shown in Table 1. The epoxy matrix is based on a monomer called Araldite LY556, which is cured with an aromatic amine Araldite XB3473 in a 100:23 M ratio. The epoxy monomer is based on diglycidyl ether of bisphenol A (DGEBA) and the amine hardener is based on aromatic amines. Both components were provided by Huntsman.

2.2. Fabrication of composites

The composites were manufactured by applying high shear mixing (Dispermat AE). The experimental procedure consisted of mixing GNPs into the neat epoxy monomer by a high-speed mixer at 6000 rpm for 15 min, reaching the optimum Doughnut effect. By reaching this Doughnut effect, the mixture flows moving downwards and upwards to the disc in a circular path. This movement provokes the appearance of areas with high and low stress what is advantageous in the way mixture is subjected to different efforts and the agglomerates are dispersed. Another advantage of the employed method is its scalability to industrial applications. Afterwards, the dispersed mixture was degassed in vacuum at 80 °C for 15 min and a stoichiometric ratio of the amine curing agent was then added at 80 °C. The applied curing treatment was carried out at 140 °C for 8 h. The cured samples were allowed to cool slowly to room temperature inside the oven. Composites with a 0.5 wt% GNPs content were produced.

2.3. Characterization

The commercial GNPs were characterized by X-ray diffraction (XRD), Scanning and Transmission Electron Microscopy (SEM and TEM) and Raman spectroscopy. XRD patterns were captured with a X'Pert PRO difractomer from Panalytical, using Cu Kα (λ = 1.5406 Å) radiation source operating at a voltage of 45 kV and 300 mA of electric current. The scanning was taken from 10° to 80° (2θ). SEM micrographs were obtained in a Hitachi S-3400-N microscope. A Phillips TEM Tecnai 20 microscope of 200 kV was used for TEM characterization. Raman spectra were recorded with Horiba Jobin–Yvon HR 800 UV and the excitation wavenumber was 632.8 nm from a He–Ne laser.

Morphology of composites was studied at different magnification levels using several microscopes: Optical (MO), Field Emission Gun Electron Scanning (FEG-SEM, Nova NanoSEM FEI 230) and Transmission Electron Microscopy (TEM, Phillips Tecnai 20). Optical microscopic analysis was carried out in a Leica DMR Optical Microscopy. Images were treated with a RGB mask "*white on black*" in order to enhance contrast between filler and matrix, using Image-Pro Plus software. For electron microscopy, samples were cut by cryomicrotomy. In addition, the obtained film was coated with a thin layer (5–10 nm) of Au (Pd) for FEG–SEM observation. The experimental conditions of the sputtering were 30 mA for 120 s (Baltec, SCD-005 sputter).

Thermal and thermomechanical behavior of composites was studied by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and Thermogravimetry analysis (TGA). DSC measurements were carried out in a Mettler Toledo mod. 821 apparatus, calibrated with indium and zinc. DSC test

Table 1
Main features of graphene nanoplatelets.

Graphenic nanoplatelets type	Purity (%)	Specific surface area (m/g^2)	Average flake thickness (nm)	Number of layers	Average particle lateral dimension (nm)	ID/IG Raman
A02	99.9	100	8	20–30	550 (150–3000)	0.3319
A03	99.2	80	12	30–50	4500 (1500–10000)	0.0334
A04	98.5	<15	60	150–250	3000–7000	0.1421