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Morphological changes on graphene nanoplatelets induced during dispersion into an epoxy resin by different methods

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ABSTRACT

A structural analysis demonstrating how the manufacturing method of graphene nanoplatelets (GNPs) into a polymer matrix can strongly modify the GNPs morphology and, consequently, their properties, was carried out. Three different methods based on sonication and high shear forces were used to elucidate defects induction and possible size diminution. Manufacturing methods including high shear forces caused the extension of the GNPs while sonication induces wrinkling of the sheets. Residual stresses are induced in the nanoplatelets structure showing an increase in the Raman intensities ratios I_D/I_G and $I_{D'}/I_G$ when a major cycles number of calendering are applied.

1. Introduction

Graphene is an atomic layer of sp^2-hybridized C that forms a honeycomb arrangement. This 2D material has attracted the interest in many different industries and research fields due to the particular properties that presents [1–5]. The reason of becoming interesting is that graphene shows high electrical conductivity in the order of $\sim 10^4$ S/m [6] and high thermal conductivity, around 5000 W/m K [7], which makes it a candidate for being used in different fields. When a limit number of graphene layers are stacked bonded by van der Waals forces through the (002) plane [8] with a nanometer size, less than 100 nm, they are denoted graphene nanoplatelets (GNPs).

GNPs have been widely used as nanofiller in polymer matrices to make them electrically and thermally conductive, enhance mechanical properties and achieve good barrier properties [9,10]. The high thermal conductivity of graphene makes it especially interesting for thermal interface materials (TIMs) applications [11]. On the other hand, the morphology and the structure of graphene, the presence of defects and residual stresses in the final nanocomposite are going to be influent in the material performance. Some published papers confirm that the GNPs waviness can strongly affect thermal properties [12] and electrical conductivity [13] of the nanocomposites. For that reason, the effect of the dispersion method on GNPs structure needs to be elucidated to achieve enhanced properties in the resulting nanocomposite.

In the present work, structural analysis and morphology study of GNPs are discussed. In order to clarify how the manufacturing process can strongly affects the quality of the GNPs, different dispersion methods were applied and resulting materials were characterized. Three different methods, that are industrially scalable, are used in this study. Those methods are based on ultrasonication, by using a sonication probe that is located inside the GNP/epoxy mixture, and shear forces, by applying different calendering cycles. Structural and morphology studies were carried out by different analytical and microscopic techniques to characterize induced changes on the GNPs structure.

2. Materials and methods

2.1. Materials

Epoxy resin was obtained from a basic DGBEA monomer (*Araldite LY556*) cured with an aromatic amine (*Araldite XB3473*), both purchased from *Huntsman*. GNPs powder grade M25, with an average thickness in the range of 6–8 nm and an average lateral size of 25 μm, were provided by *XGScience*.

2.2. Preparation of GNP/epoxy nanocomposites

Nanocomposites with a GNPs content of 3 wt% were manufactured by three different methods. Dispersion of GNPs through the

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monomer was carried out by different methods including sonication and calendering processes, as it is detailed in Table 1, to optimize the manufacturing process. Once the mixing process has been completed the mixture is degassed under vacuum at 80 °C for 15 min to remove dissolved gas. After degassing, the hardener is added in a weight ratio 100:23 (monomer:hardener) and the mixture is cured at 140 °C for 8 h into an open mold.

Three different processes were used to disperse GNPs into the epoxy matrix (Table 1). The first method is based on probe sonication for 45 min under a 50% of amplitude and a cycle of 0.5 s. The second one is constituted by 7 cycles of calendering in a 3 roll mill with the parameters that are detailed in the same table. Finally, the last method combines both of sonication and calendering. Conditions of sonication are the same as in the first one, but in this case only 3 cycles of calendering are applied maintaining at 5 μm the rollers spacing and modifying rolls speeds at 250, 300 and 350 rpm during each cycle.

2.3. Characterization

The X-ray diffraction (XRD) was carried in a *Panalytical X'Pert PRO* diffractometer, with a Cu Kα ($\lambda = 1.5406$ Å) radiation source that operates at 45 kV of voltage and an electrical current of 300 mA. The scanning of 2θ was recorded from 10° to 90° with a step of 0.02 and an acquisition time of 20 s. Resulting peaks were analyzed by using *X'Pert HighScore Plus* software where fitting for calculation of the crystal domain size was performed.

Raman spectroscopy was performed using a *Horiba Jobin–Yvon HR800UV* spectrometer with a 632.8 nm excitation wavenumber He–Ne laser, in a back scattering geometry. Scan was carried out with an acquisition time of 40 s and 5 accumulations with a hole of 500 μm. Spectra were recorded in two ranges that were 1200–1700 cm^{-1} and 2300–2700 cm^{-1} that correspond with the ranges of the active bands of graphene.

Optical microscopy images were taken with a *Leica/DMR* microscope in order to evaluate the dispersion of particles. Scanning electron microscopy (SEM) images were obtained on a *Hitachi S-2400N* microscope and transmission electron microscopy (TEM and HRTEM) images were taken on a *200 kV Philips CM200* microscope equipped with a supertwin objective lens and a LaB_6 filament and a *300 kV TECNAI G2 F30* microscope.

3. Results and discussion

The characterization of how dispersion processes affects the structure of graphene nanoplatelets (GNPs) is important as final nanocomposite properties are strongly dependent on different factors like the aspect ratio, induced residual stresses or defects. For

Table 1
Dispersion methods.

Method	Step	Sonication			Calendering		
		Amplitude (%)	Cycle (s)	Time (min)	Repetitions	Roller gap (μm)	Velocity[*] (rpm)
Sonication	1	50	0.5	45	–	–	–
Calendering	1	–	–	–	1	120–40	250
	2	–	–	–	1	75–25	250
	3	–	–	–	1	45–15	250
	4	–	–	–	4	15–5	250
Two-step method: sonication and calendering	1	50	0.5	45	–	–	–
	2	–	–	–	1	5–5	250
	3	–	–	–	1	5–5	300
	4	–	–	–	1	5–5	350

[*] Velocity refers to the gap between the first roller (ω_1) and the velocity in the others is calculated as: $\omega_1 = 3$, $\omega_2 = 9\omega_3$; ω_2: second roller, ω_3: third roller.

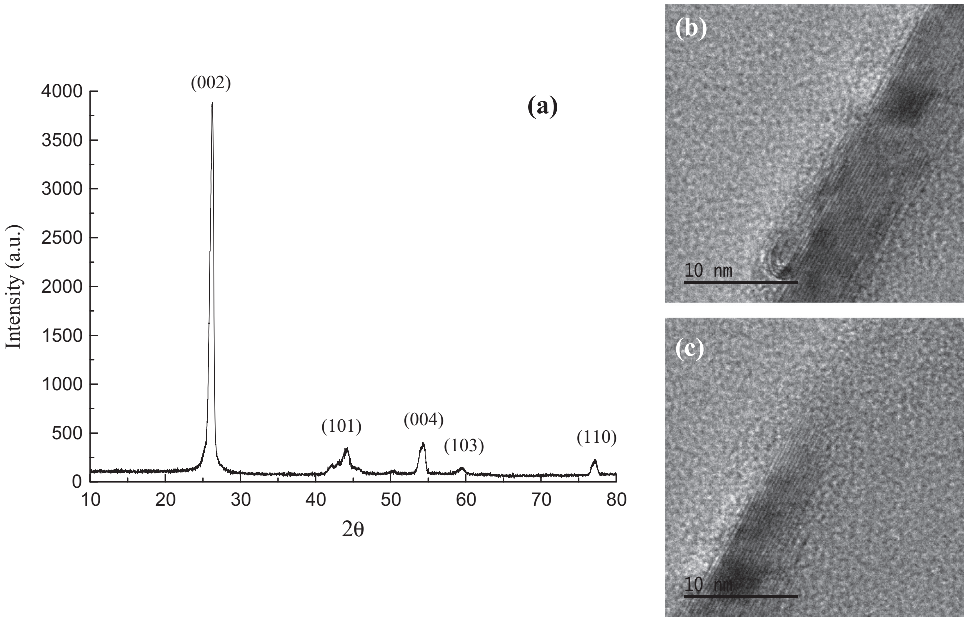

Fig. 1. (a) XRD and (b) TEM micrograph showing the thickness of as-received GNPs.