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Self-stratifying and orientation of exfoliated few-layer graphene nanoplatelets in epoxy composites

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ABSTRACT

A deep morphological study was carried out in graphene/epoxy composites reinforced with two types of nanoparticles: chemically exfoliated graphene and non-treated graphene nanoplatelets. Different morphological features, such as exfoliation, distribution, dispersion and orientation were analyzed. Composites with exfoliated graphene nanoparticles presented stratification, where few-layer graphene particles occupy top positions while thicker nanoplatelets fell down at the bottom. In order to solve this heterogeneity, a rotating mould was designed. Rotating the reinforced probes during curing treatment, up gelation, the stratification of graphene nanoplatelets could be avoided. It was also corroborated that the graphene/epoxy composites show preferential orientation, where most of graphene particles lies parallel to the sample surface, leading anisotropy in materials. This effect was specially marked in composites with thicker graphene nanoplatelets reinforcement regard to those with exfoliated nanosheets.

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1. Introduction

Graphene is a two-dimensional layer consisting of sp^2 carbon atoms, arranged in a honeycomb structure. In the last years, their use as reinforcement for polymers has attracted a lot of interest because of its potential to improve mechanical properties, electrical and thermal conductivity and barrier properties [1–3]. This is because graphene is an electrically and thermally conducting platelet with large specific surface area. It is stronger and stiffer than diamond and can elongate a quarter of its length. Its Youngś modulus (~1 TPa), mechanical strength (~130 GPa) and electrical conductivity (up to 6000 S/cm) is as high as those of carbon nanotubes (CNT) but its thermal conductivity seems to be higher (~5000 W/mK) [4–6]. Another advantage of graphene is its 2-dimensional geometry, which can significantly reduce gas permeation and increase hydrothermal resistance of polymer matrix. Also, the manufacturing cost of graphene is expected to be much lower than those of CNT.

It is well known that properties of this kind of composites strongly depend on how nanofillers are distributed and oriented into the matrix as well as interfacial bonding with polymer. Behavior enhancement by graphene addition can be maximized when graphene is exfoliated in single layers with the highest aspect ratio. When the number of graphene layers increases, the stiffness of nanoparticle remains nearly the same but its mechanical strength is reduced. Preferential orientation of graphene platelets through the matrix induces anisotropy. An in-plane alignment of graphene must improve the stiffness and barrier properties in the preferential direction whereas gas permeation will be lowest perpendicular to the orientation. On the other side, a random orientation benefits properties that require rigidity and connectivity percolation of filler networks.

As property enhancement correlate strongly with composite micro- and nano-structure, effective characterization of morphology is essential. Transmission electron microscopy (TEM), wide-angle X-ray scattering (WAXS) and X-ray diffraction (XRD) are perhaps the most common techniques by which dispersion state is studied [7]. However, all of them present important limitations. The observed area by TEM is very small and cannot be representative enough, while the scattering and diffraction intensity in WAXS and XRD varies with the concentration of the scattering or diffracting domains, respectively. For this, some morphological information may be missed [7]. Besides, these techniques give useful information about the exfoliation of graphene nanoparticles but they are limited to the study of the stacking and dispersion of graphene. In the present work, we present a new analysis stereographic procedure based on the observation of several cuts from the sample surface by optical microscopy. Results lead additional important information of graphene/epoxy composites morphology regard to conventional techniques. This developed technique could not be applied to CNT/epoxy composites because it is necessary particles with at least two micro-scale dimensions.

Graphene/epoxy composites have been fabricated with two types of graphene nanoparticles: chemically exfoliated graphene

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and non-treated graphene platelets. A deep morphological study was carried out in order to determine different morphological features: exfoliation, distribution, dispersion and orientation. In addition, their anisotropy was also studied analyzing the coefficient of thermal expansion in different space directions.

2. Materials and methods

2.1. Materials

Graphene nanoplatelets, named AO-2, were supplied by Grapene Supermarket (US Company) with 99.2% of purity. The average flake thickness was 12 nm, corresponding to 30–50 nanolayers and the average particle size was 4500 nm (1500–10,000 nm). Henceforth, these nanoparticles will be named GNPs. The epoxy matrix was based on a monomer called Araldite LY556, cured with an aromatic amine Araldite XB3473. Both components were provided by Huntsman.

2.2. Chemical exfoliation of graphene nanoparticles (EG)

Chemical exfoliation process was carried out following the procedure published by Wang et al. [8]. GNPs were diluted in a 70 vol.% ethanol in water solution. The solution was sonicated for 90 min. After that, the resultant dispersion was centrifugated at 3000 rpm for 60 min. Finally the treated nanoparticles were dried at 120 °C in vacuum for 24 h. These will be named EG.

2.3. Preparation of GNP/epoxy and EG/epoxy composites

Composites reinforced with 1 wt% GNPs and EG were prepared using different dispersion techniques: conventional mixing, ultrasonication and high shear toroidal mixing (Dispermat AE). In all cases, desirable amount of nanoparticles were added into epoxy monomer. Then, the mixture was subjected to ultrasonication at 50–60 Hz for 45 min. After sonication hardener was added in stoichiometric ratio at 80 °C. The final composite was cured at 140 °C for 8 h in steel mould, whose walls were previously treated with an antiadherent. In order to avoid the found stratification in composites reinforced with non-exfoliated nanoplatelets, a rotating mould into the stove was designed and developed. Its main goal is to avoid the gravity effect, rotating the non-cured probes with a light and constant rotation rate, during the curing treatment. The used device was designed and developed by the authors.

2.4. Characterization

X-ray diffraction of the samples (XRD) was measured with X'Pert PRO diffractometer from Panalytical, using Cu Kα (λ = 1,5406 Å) radiation source operated at a voltage of 45 kV and 300 mA of electric current. The scanning was from 10° to 80° (2θ). Morphology of composites was studied at different levels using different microscopes: Optical Microscopy (OM), Field Emission Gun Electron Scanning Microscopy (FEG-SEM) and Transmission Electron Microscopy (TEM). A stereographic study was carried out by OM. For that purpose, each sample was cut at different distances from surface (0, 1.5 and 5 mm). Microscopic analysis was carried out with Leica DMR optical microscopy. The used image software was Image-Pro Plus. Images were initially treated with a RGB mask "*white on black*" in order to enhance the contrast between filler and matrix. Quantification of images was carried out making measurements of bright objects. Cryomicrotomy cutting was used to prepare samples to be observed in FEG-SEM and TEM. In addition, the film was coated with a thin layer (5–10 nm) of Au (Pd) for FEG-SEM observation. The experimental

conditions of sputtering were 30 mA for 120 s (Bal-tec, SCD-005 sputter). Finally, anisotropy of the samples was analyzed measuring coefficient of thermal expansion (CTE) using a TA Instruments Thermal Mechanical Analyser (TMA Q400). The test was carried out from 25 °C to 200 °C at a heating rate of 10 °C/min.

3. Results and discussion

The present work tries to clarify the different morphological levels that are necessary to analyze to obtain a complete characterization of the morphology of graphene nanoplatelets based-composites. For this reason, results are divided in several parts, from the final geometry of nanoplatelets ergo the exfoliation degree; nanofillers distribution in the three spatial directions, analyzing also their dispersion degree and even the orientation of the nanoplatelets, considering that platelets are formed by one or a few layers with two micro-scale dimensions and one nano-scale dimension (2D-nanomaterial).

3.1. Study of exfoliation degree

The most common approach to produce graphene sheets is from the reduction and exfoliation of graphene oxide [1–3,8,9]. However, the graphitic structure is partially destructed during oxidation process [10]. Recently, another liquid-phase methods have been published which are based on direct exfoliation of graphene platelets in solvent [8,11,12]. Among them, the proposed method by Wang et al. [8] is based on the mixture of ethanol and water, avoiding the use of expensive, toxic and difficult to remove solvents and the addition of any surfactants. However, the efficiency of hydroxyl groups is based on their ability to react with oxygen-containing groups in graphene powder [13]. This is why this method must be more effective with the presence of oxygen in the initial graphene platelets. In our case, we use GNPs with 2% oxygen content in mass.

As it is mentioned above, one of the most used techniques to analyze graphene exfoliation has been X-ray diffraction because graphene nanoplatelets present a characteristic diffraction pattern. Fig. 1 collects the XRD pattern of commercial graphene powder with the (h k l) index. The characteristic peak at 26.17° corresponds to a *d*-spacing of 3.40(2) Å that is associated with the graphitic plane (0 0 2). Unfortunately, this peak also appears in XRD patterns of EG nanoparticles, which means that not all GNPs have been exfoliated. It is possible to evidence the existence of few-layer graphene nanoplatelets. Also, in accordance with the results published by Clark et al. [14], the addition of methanol induces a shift of peak to 3.35(8) Å. However, the drying of powders for 48 h makes the peak returns to its initial position.
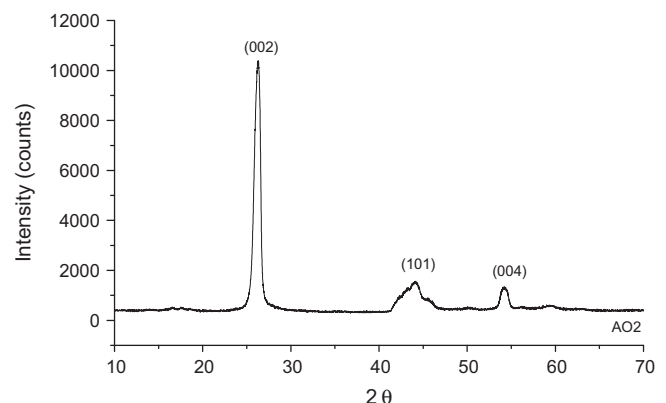

Fig. 1. XRD pattern of commercial graphene powder.