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Comparison of filler percolation and mechanical properties in graphene and carbon nanotubes filled epoxy nanocomposites

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ABSTRACT

This paper compares the filler percolation network of multi-walled carbon nanotubes (MWCNTs) grown by chemical vapor deposition and thermally reduced functionalized graphene sheets (FGSs) in an epoxy resin. The filler network was evaluated by the plate–plate rheological response of un-cured dispersions and the electrical properties of cured materials. We found that FGS did not raise the viscosity of the system as much as MWCNT, maintaining the Newtonian behavior even at 1.5 wt.% FGS. MWCNT readily formed a filler network compared to FGS, evidenced by lower electrical and rheological percolation thresholds, presence of yield stress and higher storage modulus of the dispersions. On the other hand, the mechanical performance of the cured FGS nanocomposites outperformed the MWCNT, with enhancements of 50% and 15% of Young's modulus and strength, respectively. This combination of good processing properties with low viscosity and enhanced mechanical properties makes FGS great candidates to develop multifunctional polymer materials.

1. Introduction

In the last decades, polymer nanocomposites with carbon based nanofillers have been widely studied in order to develop materials with multifunctional properties like high mechanical performance and heat dissipation, damage sensing [1–3], electrostatic discharge, large operating temperature range and chemical resistance among others [4]. Furthermore, in the last few years, researchers have made vast studies in performing multifunctional polymer nanocomposites based on carbon nanotubes (CNTs) and graphene sheets [5–8] due to the extraordinary intrinsic properties of these fillers.

Nanofiller morphology could greatly influence both processing and final properties of nanocomposites. Comparative studies of the final properties of sheet-like (graphene) and rod-like (CNTs) polymer nanocomposites are starting to appear, due to the recent large availability of graphene. For example, Du et al. [9] comparatively studied the electrical properties of graphene and CNT high density polyethylene nanocomposites. They observed lower percolation thresholds and higher conductivities for the CNT nanocomposites. Meanwhile, graphene sheets nanocomposites show a better mechanical performance [10,11] which is attributed to the large specific area and planar geometry of the graphene and/or to a better mechanical interlocking of the nanofiller/matrix interface. A significant number of articles regarding the rheology of CNTs in polymers, especially epoxy resins, can be found in the literature [12–19]. However, to the best of our knowledge, no experimental works have already been completed comparing the rheological behavior and, hence, processing properties of graphene and CNTs polymer nanocomposites.

It is well known that the greatest enhancements on the properties of nanocomposites are reached when a network of the filler is formed within the polymer matrix. There are two main strategies to analyze filler networks when we

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use conductive particles. The first one is by analyzing the rheological response of the dispersion in the liquid state and the second one is by evaluating the electrical properties [15–18], in both cases the material presents a clear change of the variables involved in the analysis, either rheological or electrical studies, when we pass from a non-percolated system to a percolated one. It is worth mentioning that the rheology of the dispersions plays a key role from a processing point of view due to the big increments in the viscosity of the system when we add nanoparticles, favoring the presence of voids.

In this paper we evaluate the formation of filler networks for multi-walled carbon nanotubes (MWCNTs) and thermally reduced functionalized graphene sheets (FGSs) epoxy nanocomposites by means of their rheological behavior and electrical conductivity. Finally, we also tested their mechanical performance and concluded that FGS nanocomposites present a wider range of improvement than MWCNTs due to the lower viscosity of the initial dispersions and higher mechanical enhancement at low filler contents.

2. Experimental part

2.1. Materials

Diglycidyl ether of bisphenol-A epoxy resin (product number: 405493), and diethylene triamine curing agent (D93856) used in this study were purchased from Sigma–Aldrich, while multi-walled carbon nanotubes (MWCNTs with an aspect ratio between 2500 and 3000 and a specific surface area of 50 m^2/g [20,21]) were synthesized in-house by a chemical vapor deposition technique [22]. Functionalized graphene sheets (FGSs) were also synthesized in-house by the rapid thermal expansion of graphite oxide (GO) at 1000 °C under an inert atmosphere. This results in a high surface area carbon material consisting on wrinkled graphene layers with residual hydroxyl, carbonyl and epoxy groups. The atomic amount of oxygen atoms, estimated by XPS (data not shown) is 9.2%. GO was synthesized from natural graphite flakes obtained from Sigma–Aldrich (universal grade, purum powder $\leqslant$0.1 mm, 200 mesh, 99.9995%), according to the Brödie method. Full characterization of the functionalized graphene sheets used in this work is described elsewhere [23].

2.2. Characterization

FGS and MWCNTs were directly dispersed in the epoxy resin by means of Ultraturrax and sonication batch, a mixing procedure at 30,000 rpm for 10 min and 60 min in an ultrasonic bath at 60 °C was carried out to reach a good dispersion of the carbon filler in the epoxy resin.

The rheological measurements were performed using a TA Instruments Advanced Rheometer AR1000. The geometry used was a stainless-steel parallel plate with a diameter of 25 mm. The gap was fixed to 0.25 mm and the measurements were recorded in frequency from 0.01 to 100 Hz at 21 °C and at an amplitude of 1% in order to be within the linear viscoelastic range. The results are averaged over three different samples. The standard error for each set of samples was less than 1%.

The next protocol was followed to cure the formulations: the liquid formulations containing nanoparticles and epoxy resin were mixed with diethylene triamine in a stoichiometric ratio; the blends were degassed for 15 min in a vacuum chamber and casted in Teflon molds. Thermal treatments of 60 min at 70 °C and 90 min at 130 °C were applied to complete the curing reaction (DSC measurements were carried out to prove the material was completely cured). Electrical conductivity of the cured nanocomposites was determined on an ALPHA high-resolution dielectric analyzer (Novocontrol Technologies GmbH, Hundsangen, Germany) over a frequency range window of 10^{-1}–10^7 Hz at room temperature. The cured films were held in the dielectric cell between two parallel gold-plated electrodes. The amplitude of the alternating current electric signal applied to the samples was 1 V.

The dispersion state of the nanoparticles was examined using transmission electron microscopy (TEM Leo 910 microscope at an acceleration voltage of 80 kV). Ultra-thin sections of the cured samples were prepared by cryo-ultramicrotomy at −140 °C (Leica EM UC6).

Tensile tests were performed with dog-bone specimens using an Instron model 3366 tensile tester at a crosshead speed of 1 mm/min. The results are the average of at least five measurements.

3. Results and discussion

3.1. Rheological response (un-cured state)

The formation of filler networks in nanocomposites can be determined evaluating the rheological response in the melt state of the system. In the case of epoxy resins, the rheological measurements have to be performed before the curing reaction takes place.

Fig. 1a shows the variation of the complex viscosity versus frequency for studied systems. Epoxy resin clearly has a Newtonian flow behavior with the viscosity independent of the frequency. The addition of MWCNTs significantly alters the flow behavior of the epoxy dispersions. The viscosity gradually increases as the MWCNT content increases. This effect is particularly evident in the low frequency range and decreases with increasing frequency due to shear-thinning behavior. When the viscosity is plotted versus the torque applied (Fig. 1b) we can observe the presence of a yield stress for MWCNT dispersions because the viscosity tends asymptotically to infinite at a certain value of torque. Below that stress limit the material does not flow, showing a solid-like behavior. These changes in the rheological behavior are attributed to the formation of a nanotube network randomly dispersed. As high enough shear rates are applied, this network breaks down and CNTs can then align in the direction of the flow and/or disaggregate [24] causing the decrease in the viscosity. On the other hand, FGS does not change the Newtonian regime of the pristine epoxy resin, therefore, the effect of FGS concentration on the viscosity is much smaller compared with the viscosity enhancement produced by MWCNTs.

The increase in the viscosity as a function of MWCNT loading fraction and the change from Newtonian to

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