Material properties

Multifunctional nanocomposites based on tetraethylenepentamine-modified graphene oxide/epoxy

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ABSTRACT

Composites based on epoxy/graphene were investigated for thermal-mechanical performance. Initially, few-layer graphene oxide (GO) was modified with tetraethylenepentamine (GO-TEPA) in a reaction assisted by microwave radiation. GO and GO-TEPA samples were characterized for their structure and morphology. Composites containing 0.1, 0.3 and 0.5 wt.% of GO and GO-TEPA were prepared, and the effect of fillers on the morphology of cryofractured regions of epoxy matrix was observed through electron microscopy images. Dynamic mechanical thermal analysis (DMA) tests revealed increases of approximately 20 °C in glass transition. Moreover, when compared to neat polymer, composites containing 0.5 wt.% of GO-TEPA gained up to 103% in thermal conductivity (obtained by flash laser). Finally, nanoindentation analyses showed increases of 72% in Young's modulus and 143% in hardness for the same sample. The system is characterized as multifunctional nanocomposites because of the simultaneous gains in thermal and mechanical properties. The best results of the multifunctional composites were strongly associated with the chemical modification of the GO by TEPA.

1. Introduction

There is a growing need in various industrial sectors for the production of high-performance composite materials. Graphene has been widely investigated [1] in the fabrication of different types of composites, and great improvement is expected as this type of material shows exceptional physical properties [2,3]. For example, graphene thermal conductivity is ~5,000 W m^{-1}K^{-1} [4] and as a monolayer presents high superficial area (2,630 m^2 g^{-1}) [5]. Furthermore, graphene presents Young's modulus of ~1,100 GPa and tensile strength of ~125 GPa, ~200 times higher than steel [6]. Graphene will soon allow sectors such as electronics, automotive, naval and aeronautics [2] to use materials with improved thermal, electrical and mechanical properties [8,9]. It has been introduced in many polymeric systems [2], such as polyurethanes [10], poly (ethylene vinyl acetate) [11] and epoxy [12,13]. Epoxy systems are traditionally required by the industry because they belong to a class of thermosetting polymers featuring high chemical stability, excellent adhesive properties, good

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corrosion resistance and low shrinkage in the curing process [7]. Different types of nanofillers have been added to epoxy to improve their properties, for example, the incorporation of silicon and alumina reduced cost and increased the stiffness. Nevertheless, a major obstacle found is that the addition of rigid particles promotes reduction of the epoxy ductility, making it more brittle [14]. To overcome this problem, more flexible and tough carbon nanomaterials (CNMs) such as carbon nanotubes (CNTs), graphene and carbon nanofibers [9,15–17] are used. Moreover, these composites show low thermal expansion and relatively high thermal conductivity [18,19]. For example, Martin-Gallego et al. obtained significant increase of 40 °C in T_g for a UV cured epoxy composite containing 1.5 wt.% of graphene by DMA [20]. Chatterjee et al. observed increases of up to 10% of Young's modulus and hardness in nanoindentation tests by using 1.5 wt.% of GO functionalized with dodecylamine [14]. Tang et al. explored different types of dispersion of thermally reduced GO (RGO) in epoxy, which were verified by tensile and flexural tests. They obtained a 52% increase in quasi-static fracture toughness (K_{IC}) for samples containing 0.2 wt.% of RGO dispersed in the matrix [21]. Li et al. observed increases of 75% in Young's modulus and 30% in hardness by nano-indentation testing for samples containing 5 wt.% of CNTs functionalized with methyl 4-aminobenzoate in epoxy [22]. The groups that attained good final properties, in general, had improved wettability between the graphene and the polymer matrix to produce good dispersion [23,24]. The agglomeration of graphene, due to its low compatibility with polymer matrices, has been one of the main barriers limiting its potential use as a mechanical reinforcing agent. In order to increase the dispersibility of CNMs in different chemical environments, a large number of routes to chemical modification of its surface have been proposed [15,19,24,25]. Many strategies adopted were based in initial oxidation processes [26–28] and, usually, the oxidised surface of the CNMs had different functional groups such as epoxy, alcohols, ketones, carboxylic, ethers and/or presence of debris [29]. Depending on the nature of the functional groups found in the walls of CNMs as carboxylic acid or hydroxyl groups, they can be derivatized to ester, amide and/or carbamates, opening new possibilities of reaction routes [24]. Several studies have demonstrated that the presence of the amine group on CNMs can increase the adhesion of the nanofiller to epoxy, since these functional groups have great compatibility with this polymer system [14,19,22]. For example, Niyogi and co-workers described an effective way to obtain GO covalently linked with octadecylamine: after the oxidation of graphite in sulfuric acid, there followed treatment with thionyl chloride ($SOCl_2$) and octadecylamine, which forms GO-ODA [30]. Hu et al. functionalized different types of CNMs with 4,4′-diaminodiphenyl sulphone (DDS) in the presence of $SOCl_2$ at 130 °C under an inert atmosphere and refluxed for 6 days [19]. Different processes of amino functionalization of CNMs have been reported in the literature and most of them use, in one of the chemical steps, $SOCl_2$ as intermediate reagent [19,24,31]. In general, the use of $SOCl_2$ limits the functionalization process of CNMs because of its dangerous nature and high level of toxicity. Another

drawback found in this kind of synthesis is the time spent on extended reflux lasting days, making it a very costly process.

In this work, we investigated the influence of GO and GO-TEPA on the thermal and mechanical properties of epoxy based composites. The GO-TEPA were synthesized rapidly by microwave in comparison to methods commonly used and without the use of $SOCl_2$. Through a three roll mill, these nanofillers were mixed into resin, obtaining homogeneous dispersion.

2. Experimental

2.1. Materials

Expanded graphite (EG) and GO, were both supplied by Cheaptubes USA, and TEPA from Sigma Aldrich. Commercial epoxy resin DER-331 liquid (based on diglycidyl ether of bisphenol A (DGEBA)) and the curing agent DEH-24 liquid based on triethylenetetramine (TETA), were supplied by Dow Chemical Brazil.

2.2. GO functionalization

100 mg of GO were added to 150 ml of tetraethylenepentamine (TEPA) in a round bottom flask. This flask was coupled to a microwave reactor programmed to work at 120 °C, increasing from 0 to 200 W for 30 min. Throughout the reaction period, the system remained under magnetic stirring. After the microwave reaction, the mixture was cooled to room temperature and transferred to a beaker containing 300 ml of anhydrous ethanol. The final mixture was dispersed in ultrasound bath for 30 minutes, filtered under vacuum and washed exhaustively with anhydrous ethanol to remove excess TEPA. The filtrate was dried in an oven at 100° C for 12 hours to yield of GO-TEPA, as shown in the schematic model in Fig. 1.

2.3. Preparation of GO and GO-TEPA/epoxy composite

Composites were prepared containing 0.1, 0.3 and 0.5 wt.% of GO and GO-TEPA. The nanofillers were mixed manually with the epoxy resin at room temperature and dispersed at 80 °C employing a three-roll mill (Exakt80E) with zirconium oxide rollers. The distance between the rolls was fixed at 5 μm, with a speed of 250 rpm. After this step, the material was degassed and mixed slowly with TETA (Phr 15) to avoid the formation of bubbles. The mixture was transferred to silicone molds and cured for 12 hours at room temperature and, subsequently, at 120 °C for 4 hours.

2.4. Characterization

To evaluate the degree of exfoliation of GO and GO-TEPA, samples were dispersed in isopropyl alcohol for 1 hour in an ultrasonic bath. The resulting suspensions were dropped onto a silicon substrate and dried for atomic force microscopy (AFM) studies. The same suspensions were dropped onto a grid of carbon and copper (Holey Carbon Copper Grids) for TEM studies. The TEM micrographs were obtained on a FEI Tecnai G2 equipment operating in