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Customizing thermally-reduced graphene oxides for electrically conductive or mechanical reinforced epoxy nanocomposites

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ABSTRACT

Graphene oxide (GO) can be produced through diverse synthetic routes in large quantities that lead to clear differences in the resulting graphene morphology and properties. Here, we analysed the effect of several thermally reduced graphene oxides (TRGOs), at two different concentrations, on the electrical and mechanical properties of epoxy resin nanocomposites. Natural graphite was oxidised using two methods, Brodie (GO-B) and Hummers (GO-H), and, then, thermally reduced at different temperatures, 700, 1000, and 2000 °C. Intrinsic graphene properties, such as remaining oxygen groups, specific surface area, and aspect ratio, among others, have a profound effect on the final properties of the nanocomposite. The dispersion state was heavily influenced by the specific surface area and the remaining oxygen groups on the graphene. Meanwhile, the electrical and mechanical properties showed a strong and opposite dependency with the reduction temperature, with low temperatures resulting in flakes with high reinforcing characteristics and high temperatures in flakes with high electrical conductivity performance. Finally, TRGOs synthesised via Hummers and reduced at low temperatures appeared to be more suited as reinforcing particles, while TRGOs synthesised via Brodie were more effective as electrically conductive nanofillers.

1. Introduction

Over the recent years, graphene and its derivatives have emerged as a promising material on a number of applications, such as energy technologies, biomedical, liquid separation, electronic [1,2]. Among these materials, graphene oxide (GO) and reduced graphene oxide are being heavily studied as reinforcing and functional nanofillers in polymer materials [3–7] due to their excellent physical and chemical properties and their potential to be produced on the ton scale. Common synthesis routes are the Hummers, Staudenmaier and Brodie methods, which have been suggested to result in differences in the levels of oxidation and final structure of the GO [1,2]. Such differences could significantly affect the final properties of the resulting polymer nanocomposite and could pave the way for the production of tailor-made graphene materials. Here, we investigate such hypothesis by analysing the effect of distinct thermally reduced graphene oxide (TRGO) on the performance of an epoxy resin with special attention to its mechanical and electrical properties.

In a previous work [8], we demonstrate that both the oxidation process of the graphite and the exfoliation temperature of the oxide play a crucial role on the characteristics of the resultant graphene. We thoroughly analysed the resulting material of two

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oxidising protocols, Brodie and Hummers, and established crucial differences among them. Brodie method introduces a smaller amount of oxygen than Hummers, but favours the formation of conjugated epoxy groups and hydroxyl, that at moderate temperatures generates groups that are more thermally stable. Thus, the Csp^2 structure of the carbon lattice is not recovered at all, and some of the residual oxygen cannot be removed. However, GO obtained through Hummers oxidation method exhibits less conjugated oxygen groups resulting in a better restoration of the sp^2 structure. In addition, the functional groups content is clearly decreased as increasing the exfoliation temperature of the graphite oxide. So, GO obtained by the Hummers process contains 47.8% of oxygen, whereas that reduced at 700 °C exhibits an 11.1% and at 2000 °C, the oxygen content is practically negligible.

Epoxy resins are an important class of polymers due to their strong adhesion and excellent overall mechanical properties, high chemical, thermal, and dimensional stability and solvent resistance. The intrinsic properties of epoxy resins make them suitable for a wide spectrum of applications in diverse areas due to the fact that epoxies can be chemically and physically tailored to fulfil specific requirements. Several interesting studies have already been reported illustrating the potential of graphene nanocomposites based on epoxy resin [9–18]. These studies have shown large improvements on the mechanical and electrical properties of the epoxy nanocomposites. Graphene/epoxy nanocomposites have thoroughly been reviewed by Wei et al. [19].

The aim of this paper is to analyse the effect of the structure and morphology of the graphene on the physical and mechanical properties of the resin composite, which to the authors' best knowledge has not previously been studied.

2. Experimental section

2.1. Materials

Hexflow RTM 6 monocomponent epoxy system used in this study was gently provided by Hexcel. Thermal reduced graphite oxide (TRGO) was obtained by the rapid thermal expansion of graphite oxide (GO) at several temperatures: 700, 1000 and 2000 °C. GO was previously synthesised from natural graphite powder, purchased from Sigma-Aldrich (universal grade, purum powder 60.1 mm, 200 mesh, 99.9995%), following two oxidation protocols, Brodie and modified Hummers methods. The main characteristics of the studied materials are detailed in Table 1. The samples are labelled as TRGH-700, TRGH-1000, TRGH-2000, TRGB-700, TRGB-1000 and TRGB-2000, where H and B refer to the oxidation method (H: Hummers and B: Brodie).

2.2. Preparation of TRGOs/epoxy nanocomposites

The dispersion of the TRGOs in the epoxy resin was carried out by means of a three-roll calender (EXAKT 80E), where contra-rotating rollers exert large shear forces in the knead-vortex generated between them. The materials were prepared at two TRGO contents: 1.5 and 2 wt.%. The optimal processing conditions were previously evaluated and the procedure used to achieve a fine dispersion of the flakes in the epoxy resin consists of three cycles. Details of the processing parameters, time, roller gap and velocity are presented in Table 2.

Once the mixing process has been completed, the blends were degassed for 1 h at room temperature in a vacuum chamber. Subsequently, the material was poured into preheated silicone moulds for its mechanical and electrical characterisation. The samples were cured in an oven at 160 °C for 2 h and then, post-cured at 180 °C for 1 h.

2.3. Characterisation

Optical microscopy images were taken with a NIKON DS–Fi2 microscope in order to evaluate the dispersion degree of TRGOs in the liquid formulations. The curing process was examined in a Mettler Toledo DSC822 differential scanning calorimetry. The samples were held at an isothermal scan of 160 °C. The morphology of the cured samples was observed using a Philips XL30 environmental scanning electron microscopy (ESEM) at 15 kV. The fractured cross-sections from tensile tests were sputter coated with gold/palladium (Au/Pd 80/20) in order to prevent electrical discharge during observation.

Tensile tests were measured according to ASTM D 3379-75 specifications in an Instron dynamometer (model 3366) at 23 °C, and

Table 1
Main characteristics of GOs and TRGOs.

	Elemental analysis (wt.%)			XPS					S_{BET} m^2/g
	C	O	H	C/O	O (%)	C (%)	sp^2 (%)	sp^3 (%)	
GO-H	48.0	47.8	2.2	1.8	35.2	64.8	32.2	12.8	–
TRGH-700	87.8	11.1	0.8	9.2	9.8	90.2	74.6	15.1	390
TRGH-1000	97.9	1.1	0.1	57.8	1.7	98.3	82.4	13.9	300
TRGH-2000	99.5	0.5	0.0	332.3	0.3	99.7	88.9	9.6	140
GO-B	70.1	28.2	0.9	2.9	25.7	74.3	39.2	14.5	–
TRGB-700	90.1	9.7	0.2	13.1	7.1	92.9	75.0	13.1	660
TRGB-1000	98.0	1.6	0.3	25.3	3.8	96.2	77.3	14.1	570
TRGB-2000	99.3	0.7	0.0	37.5	2.6	97.4	81.8	13.0	140