GRAPHENE BASED POLYMER NANOCOMPOSITES: CHEMICAL INCORPORATION STRATEGIES AND PROPERTY ENHANCEMENT

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Abstract

Novel types of graphene-based nanocomposites where graphene or its derivatives are covalently linked to the polymer have been developed using various synthetic strategies, including esterification/amidation reactions, diazonium coupling, nitrene chemistry and 1,3-dipolar cycloaddition generally known as "click" chemistry. In all cases the thermal and mechanical properties of the developed nanocomposites were improved, and in some cases significant electrical conductivity was measured.

1. Introduction

Synergy, through the advantageous combination of different materials, is one of the most powerful approaches at the frontiers of modern materials technology. Since the pioneering work of Novoselov et al. [1] there has been a boom in the interest in incorporating graphene into polymers, mainly due to the outstanding properties of graphene and its potential for application in almost every discipline including electronics, aeronautics, biomedicine, energy storage, etc. However, two fundamental barriers remain: 1) the lack of effective methods for bulk quantity synthesis of high quality graphene, and 2) the "inertness" of graphene that limits its processability and therefore its incorporation into polymeric or biological systems [2].

Covalent methodologies to link graphene with polymers represent an interesting and versatile alternative to conventional mixing methods for the development of novel composite materials with a compendium of interfacial interactions [3]. In such nanocomposites the interface concept is displaced from the traditional view of molecular interactions between components at the polymer–filler interface, such as van der Waals, H-bonding, halogen bonding, etc., to a single compound concept where graphene becomes an integral component [4,5]. Recently, our group has developed diverse synthetic strategies for the covalent modification of graphene with polymers. These methods include esterification/amidation, coupling with diazonium salts, nitrene chemistry and 1,3-dipolar cycloaddition, generally known as "click" reactions. Whilst click reactions require previous modification of graphene with "clickable" polymers, the other methods imply the direct coupling of polymers to graphene. Despite important differences between each, it can be observed that all of these routes proceed reasonably well and some have been successful for the direct modification of graphene with polymers. These methodologies have been applied to a wide variety of families including polyolefin, vinyl, biocompatible, conjugated and conducting polymers [6-13].

The aim of this work is to present an overview of the diverse strategies that the group has developed for the covalent modification of graphene with polymers and the influence of these synthetic routes in the properties of some of the advanced graphene-based nanocomposites produced.

2. Experimental

2.1. Esterification of graphite oxide and poly(vinyl alcohol)

Graphene oxide (GO) covalently functionalized with poly(vinyl alcohol) (PVA) was synthesized by a simple esterification reaction of the carboxylic groups in graphite oxide using two different synthetic strategies [6]. The first approach involved the direct esterification of GO, whilst the second approach employed its acyl chloride derivative (GOCl). The products obtained, denominated GO-es-PVA and GOCl-es-PVA, were soluble in DMSO and water with the aid of heat, similar to PVA and PVA-CNT.

2.2. Preparation of reduced graphene oxide-poly(vinyl chloride)

PVC was modified with potassium 4-hydroxythiophenolate (KHT) by a nucleophillic substitution reaction (mPVC). The esterification of GO with mPVC was carried out suspended in CH at 70ºC under nitrogen for 72 h [7]. Subsequently, a solution of DCC and DMAP in CH were added, and the resulting mixture stirred at 40 ºC for another 72 h. Coagulation of the polymer nanocomposite was accomplished by adding the suspension to a large excess of methanol with vigorous stirring. The solid nanocomposite (denominated GO-e-PVC) was filtered, washed with methanol and dried at 50ºC under vacuum. Reduced graphene oxide-PVC (RGO-e-PVC) was subsequently prepared using hydrazine hydrate.

2.3. Preparation of polyethylene (PE) brushes clicked to graphene

Three approaches were addressed to “click” graphene with PE [8,9]. Approach 1 (CuAAC) involved coupling between an alkyne group and an azide moiety, provided by the graphene and the polymer, respectively. The graphene was furnished with alkyne groups by following a previously reported procedure [8] while the azide-terminated polymer was prepared by bromination of PE-OH and subsequent nucleophilic attack with sodium azide [9]; the product denominated GAA. In approach 2 (thiol-ene) pristine graphene representing a hyper-conjugated alkene and a thiol-terminated PE (PE-SH) were used; GTE. In Approach 3 (thiol-yne) the same polymer as in approach 2 and the alkyne-modified graphene of approach 1 were used; GTY.

Nanocomposites of HDPE with GAA, GTE and GTY were prepared using the same protocol [9]. Modified graphene (GAA, GTE or GTY) was mixed with PE-OH in hot xylene (90°C) under vigorous stirring. Subsequently the mixtures were precipitated in methanol, filtered, washed and thoroughly dried under vacuum. Samples were denominated GAA/PEOH, GTE/PE-OH and GTY/PE-OH, respectively. These mixtures with a graphene/polymer composition of around 50/50 were subsequently used as fillers for nanocomposites with HDPE. For this purpose all fillers were mixed with HDPE in xylene in order to obtain nanocomposites with final filler loading of ca. 1%. The mixtures were then precipitated with methanol, and dried under vacuum. Samples were denominated GAA-HDPE, GTE-HDPE and GTY-HDPE.

3. Results and discussion

3.1. Poly(vinyl alcohol)-graphene oxide nanocomposites

Special interest was paid to the isolation and characterization of PVA-functionalized GO. Firstly, elimination of the non-reacted GO was achieved by centrifugation leaving the PVA-functionalized GO. A comprehensive spectroscopic analysis was carried out to ensure that the esterification reactions were successfully completed. A simple inspection of the evolution of the ^{1}H spectrum shows an increase in the rr signal in detriment to the mm signal for both GO-es-PVA and GOCl-es-PVA, which suggested that the esterification reaction occurs at the isotactic configurations. Surprisingly, as shown in Figure 1, a new signal 4.2 ppm upfield, very close to the rr triads of unmodified PVA, was clearly observed in spite of the low degree of esterification. This signal is related to hydroxyl protons next to acetate groups, as was reported for esterification of PVA. By integration of this ^{1}H NMR signal we could evaluate, within the experimental uncertainties, the degree of functionalization, obtaining a modification of around 1.8%. Interestingly, this value was reasonably low due to the huge volume of graphitic laminates (GLs) and is in agreement with the decrease of mm triad content, as consequence of being less sterically hindered internally than those at syndiotactic positions, specifically in the incorporation of the GLs. The FTIR spectra of PVA, GO-es-PVA and GOCl-es-PVA retained most of the bands of PVA, although some varied in intensity or even disappeared through modification, and new bands appeared (Figure 1). The development of the band at 1715 cm^{-1} was attributed to C=O stretching of ester groups. In addition, some interesting changes in the relative intensities of the characteristics bands of PVA in the 1200-1000 cm^{-1} region could be observed. These bands were attributed to the C-O of doubly H-bonded OH in crystalline regions (1144 cm^{-1}) and unbonded C-O in amorphous regions (1096 cm^{-1}). The intensity ratio of these bands (I1144/I1096) diminishes markedly for the esterified products suggesting a large decrease in the degree of crystallinity of the modified polymer.

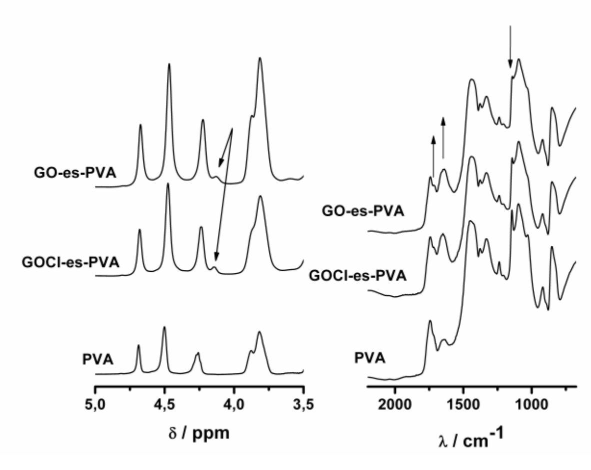

Figure 1. Spectroscopic characterization of PVA, GO-es-PVA and GOCl-es-PVA: enlarged view of the hydroxyl signals in 1H NMR, at room temperature in DMSO-d6 (left) and FTIR spectra (right). Reprinted from ref. [6], copyright 2009, with permission from ACS.

Since the dispersion of graphene achieved through covalent chemistry is much better than that achieved by other methodologies, large changes in the final properties of PVA-GO were expected. In fact, important changes in the solid state properties of the polymer due to the presence of the huge graphene laminates were observed [6]. For instance, the originally semicrystalline PVA became completely amorphous, and the glass transition temperature (T_g) experienced an increment of 35 ºC after linking to GO. While some change in T_g was predictable, the extent observed exceeded expectations. The lack of crystallinity originates in the intercalation of PVA chains between the graphene laminates as well as in the formation of “secondary” bonds, e.g. hydrogen bonding, that breaks down intra- and interchain bonding. With regard to the molecular dynamics, the rigidity was ascribed to the effective covalent GO/polymer attachment that prevents polymer chain segmental motion, and clearly the presence of enormous rigid graphene flakes amongst the polymer chains restricts mobility. Additionally, the effect of the GLs on the thermal stability of the polymer matrix was investigated by thermogravimetric analysis. TGA curves showed that just very small amounts of GLs improved remarkably the thermal stability of the nanocomposites. Furthermore, the reduction with hydrazine of PVA-functionalized GO to produce PVA-functionalized graphene was also carried out [6].

3.2. Poly(vinyl chloride)-reduced graphene oxide nanocomposites

A similar strategy to that used for PVA was extended to a commercially more important vinyl polymer, poly(vinyl chloride) (PVC) [7]. Due to the absence of susceptible groups for esterification in PVC, a previous synthetic step involving the nucleophilic substitution of labile chlorine atoms with 4-hydroxythiophenolate was undertaken. As the pre-modification reaction was stereospecific, GO was also located at specific sites in the polymer, once again the preferred being the isotactic configurations and a similar degree of modification was achieved for PVC esterified GO compared with PVA-e-GO.

With regard to the thermal behaviour, in the RGO-e-PVC samples the value of T_g was shifted by around 30 ºC with respect to PVC. Although variations in T_g were also observed after the modification of PVC by nucleophillic substitution, it is evident that graphene influence the mobility of the polymer chains conferring rigidity to the system. Also, more pronounced changes were observed for the storage modulus (E´) measured by DMA as a function of temperature (Figure 2). The samples were referred to the starting modified PVC for comparison. The modulus at 1Hz and room temperature were 1100 MPa for mPVC, and 2326 MPa in the case of RGO-e-PVC. Therefore RGO showed improved reinforcement compared to PVC. Furthermore, the shift of T_g with respect to the parent PVC obtained by DMA experiments was similar to that observed by DSC. Comparing the DMA results of PVC esterified with GO before and after reduction, the reduced material showed poorer properties since it has a 20-25% lower storage modulus. This observation suggested that the interfacial contact was more intimate in the case of the unreduced filler. Since the degree of covalently bonded graphitic material in both cases was the same, the only differences lie in the oxygenated groups in the GO that can form some secondary intra or interchain bonding with the mPVC.

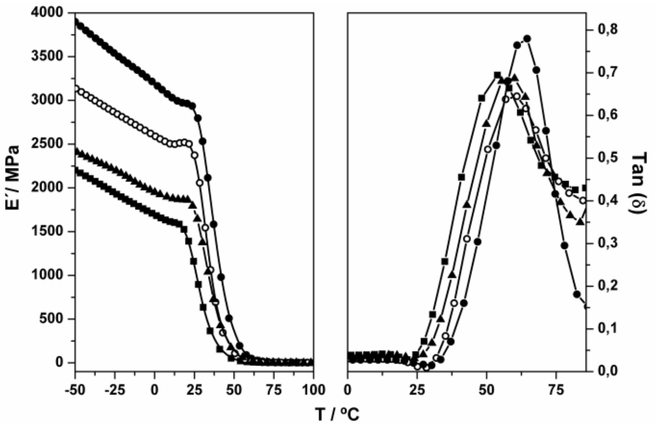

Figure 2. Comparison of (a) storage modulus and (b) Tan δ curves for mPVC (square), CNTs-e-PVC (triangle), GO-e-PVC (solid circle) and RGO-e-PVC (open circle). Reprinted from ref. [7], copyright 2011, with permission from ACS.

3.3. Polyethylene/graphene nanocomposites using click chemistry

Research on the use of thiol-ene and thiol-yne reactions in graphene is in its early stages, and only few examples are available. In our group we have succeeded in the modification of graphene with brushes of short-chain polyethylene tailored towards the preparation of nanocomposites of graphene and high density polyethylene (HDPE) [8,9]. We have studied the coupling of a thiol-terminated polyethylene to pristine and alkyne-modified graphene. While the latter permits the incorporation of two thiol groups per triple bond, leading to higher degree of functionalization, the former is conducted directly on the graphene lattice where steric hindrance is more important. However, this is of significance since no previous modification of graphene is required and the lower the degree of modification, the lower the extent of disruption of the sp^2 structure, whilst moderately improving solubility. For instance, the incorporation of polymer brushes to graphene by the thiol-ene approach produces a graphene derivative (GTE) with slight solubility in o-dichlorobenzene and conductivity in the same order of magnitude as the starting graphene.

Graphene modified with short-chain polyethylene brushes improved the incorporation of graphene into HDPE matrix due to an enhancement of the interfacial interaction between graphene and the polymer. Thus, using a two-step mixing strategy based on what we define as a “gradient interface” (Figure 3), we succeeded in the preparation of graphene-based HDPE nanocomposites with improved mechanical properties as well as thermal and electrical conductivity. The rubbery grey material (Figure 3B, left) obtained after the two-step mixing can be transformed into flexible films by hot-pressing (Figure 3B, right) and was cryo-fractured to analyse the dispersion of the filler into the matrix. Figure 3C shows a SEM image of a nanocomposite with 0.75 wt. % of graphene, where the filler laminates appear to be perfectly dispersed in the polymer matrix throughout the sampled area. This good filler/polymer compatibilization led to nanocomposites with low percolation threshold and reasonably good conductivity values (Figure 3D), which are the main challenges when nanocomposites of insulating polymers with highly conductive fillers are required.

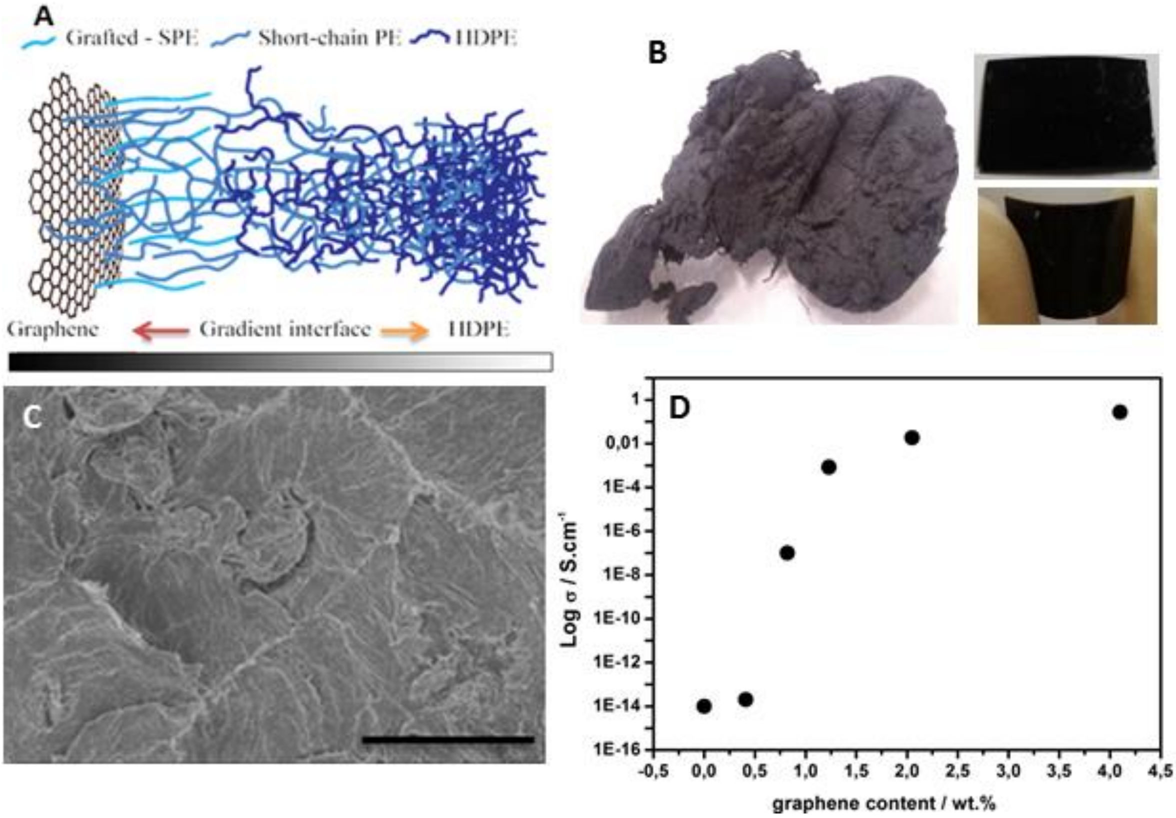

Figure 3. (A) Scheme describing the gradient interface effect of HDPE/Graphene nanocomposites. (B) Images of the raw nanocomposite (left) and as films prepared from it by hot-pressing (right). (C) SEM images of the nanocomposite with 0.75 wt. % of graphene. The scale bar corresponds to 20 µm. (D) Variation in the electrical conductivity of the nanocomposites as a function of graphene content. Reprinted from ref. [5], copyright 2014, with permission from Royal Society of Chemistry.

4. Conclusions

Graphene derivative (GO) covalently functionalized with poly (vinyl alcohol) (PVA) shows significant changes in the crystalline parameters and the thermal stability compared with PVA. The functionalization is stereospecific, with a higher reactivity in the isotactic configurations.

The covalent attachment of reduced graphene oxide to appropriately modified PVC is an effective method to produce nanocomposites with improved thermal and mechanical properties.

The electrical and thermal conductivity and the mechanical properties of polyethylene/graphene nanocomposites strongly depend on the click reaction used to modify graphene, the thiol-ene reaction giving the best results.

The election of the chemical strategy to provide graphene with functionalities common to the polymer matrix and the engineering of the interface are crucial to obtain nanocomposites with improved properties.

Acknowledgements

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References

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov. Electric field effect in atomically thin carbon films. *Science,* 306 (5696): 666-669, 2004.

[2] K. S. Novoselov, V. I. Falko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim. A roadmap for graphene. *Nature*, 490: 192-200, 2012.

[3] H. J. Salavagione, G. Martínez, G. Ellis. Recent advances in the covalent modification of graphene with polymers. *Macromol. Rapid Commun.,* 32: 1771-1789, 2011.

[4] H. J. Salavagione. "Innovative Strategies to Incorporate Graphene in Polymer Matrices: Advantages and Drawbacks from an Applications Viewpoint" in "Innovative Graphene Technologies: Developments & Characterisation" Volume 1. Ed. A. Tiwari. Rapra-Smithers, UK, 2013.

[5] H. J. Salavagione. Promising alternative routes for graphene production and functionalization. *J. Mater. Chem. A* 2014, DOI: 10.1039/c3ta15455f.

[6] H. J. Salavagione, G. Martínez, M. A. Gómez. Polymeric modification of graphene through esterification of graphite oxide and poly(vinyl alcohol). *Macromolecules,* 42: 6331-4, 2009.

[7] H. J. Salavagione, G. Martínez. Importance of covalent linkages in the preparation of effective reduced graphene oxide- poly(vinyl chloride) nanocomposites. *Macromolecules*, 44: 2685-2692, 2011.

[8] M. Castelaín, G. Martínez, G. Ellis, H. J. Salavagione. A versatile chemical tool for the preparation of conductive graphene-based polymer nanocomposites. *Chem. Comm*., 49: 8967-69, 2013.

[9] M. Castelaín, G. Martínez, C. Marco, G. Ellis, H. J. Salavagione. Effect of click-chemistry approaches for graphene modification on the electrical, thermal and mechanical properties of polyethylene/graphene nanocomposites. *Macromolecules*, 46: 8980-8987, 2013.

[10] M. Castelaín, G. Martínez, P. Merino, J. A. Martín-Gago, J. L. Segura, G. Ellis, H. J. Salavagione. Graphene functionalisation with conjugated poly(fluorene) by click coupling: striking electronic properties in solution. *Chem. Eur. J.*, 18; 4965-4973, 2012.

[11] E. Coçkun, E. A. Zaragoza-Contreras, H. J. Salavagione. Synthesis of sulfonated graphene/polyaniline composites with improved electroactivity. *Carbon*, 50: 2235-2243, 2012.

[12] M. Castelaín, H. J. Salavagione, J. L. Segura . Graphene functionalisation with conjugated poly(fluorene) by click coupling: striking electronic properties in solution. *Organic Letters*, 14: 2798-2801, 2012.

[13] M. Castelaín, P.S. Shuttleworth, C. Marco, G. Ellis, H. J. Salavagione. Comparative study of the covalent diazotization of graphene and carbon naotubes using thermogravimetric and spectroscopic techniques. *Physical Chemistry Chemical Physics*, 15(39): 1686-16811, 2013.