



Macromolecular Nanotechnology

Benzoxazine-functionalized graphene oxide for synthesis of new nanocomposites



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ABSTRACT

The new approach was to grow benzoxazine rings on graphene oxide chemically modified. This paper describes the preparation of benzoxazine-functionalized graphene oxide using the activation of the carboxylic groups from graphene oxide (GO) surface by 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide/N-Hydroxysuccinimide system (EDC/NHS) and the chlorination method employing SOCl_2 respectively. The carboxylic groups from GO surface were treated with tyramine for synthesizing the hydroxyl groups that will further react with benzylamine and formaldehyde in order to form the benzoxazine rings. Finally a nano structure with strong covalent bonds between the graphene sheets and the polybenzoxazine chains was achieved. The formation of multi-benzoxazine functionalized graphene oxide was checked by FT-IR, ^1H NMR, TGA, Raman spectrometry, XRD, HR-TEM and XPS analysis.

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1. Introduction

Due to their great potential, the interest in carbon materials has noticeably increased in the last years thus leading to a significant development for scientific and industrial research. As a two-dimensional monolayer of sp^2 -bonded carbon atoms arranged in a hexagonal lattice [1], graphene has attracted important attention due to its unique combination of superior properties. With high specific surface area, intrinsic mobility, Young's modulus and good thermal and electrical properties [2] graphene and its derivatives have determined the scientists to use them as nanofiller incorporated in polymer matrix leading to a new class of polymer nanocomposites with enhanced properties [3].

By chemical oxidation of graphite using strong oxidizing agents and ultrasonic cleavage [4] graphene oxide (GO) is obtained, as monolayer carbon nanomaterial. In order to improve the compatibility and performance of GO and enlarge its application, especially in the area of polymer nanocomposites, a better interaction between graphene sheets and polymer matrix by functionalization of GO surface is required. Since a lot of oxygen functional groups such as hydroxyl, epoxy, carbonyl and carboxyl attached to the basal planes and sheet edges of graphene oxide are given by oxidative treatment [5], functionalization of graphene sheets is much easier to perform and allows the transfer of the excellent properties of graphene oxide to polymer-based nanocomposites. There are many functional groups that can be chemically anchored onto graphene oxide surface like amines [6] or alkyl amines of varying chain length [7], trimethoxy silanes [8], benzazoles [9], polyhedral oligomeric silsesquioxane (POSS) [10,11], and others. A lot of papers are related to formation of new covalent bonds between GO and various amines. Hu and coworkers have successfully functionalized graphene sheets with different

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amine groups that showed good dispersion in the used solvents and increased thermal properties of composites [12]. Jian-lin et al. have also functionalized graphene oxide with ethylenediamine (EA) and 1,6-hexanediamine (HA) showing that one carbon atom in nine to ten of the carbon atoms in GO was functionalized by an amine group and that the thermal stability of the GO functionalized by HA was much higher than the one functionalized by EA [13]. In particular, carboxylic groups of the graphene oxide surface have proven to be good candidates for chemical modification. Therefore, in order to realize a covalent bond between carboxylic acid functionalized graphene oxide (GO-COOH) and amines, some coupling reactions are required for the activation of these groups. Most activation reactions are done using thionyl chloride (SOCl_2) [14–16], 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) [17] or N,N'-dicyclohexylcarbodiimide (DCC) [18].

The benzoxazine resins have lately generated much interest due to their many advantages against the conventional phenolic thermosets [19]. As a novel type of phenolic resins, polybenzoxazines have many unique characteristics including low water absorption, near-zero volumetric shrinkage upon polymerization and molecular design flexibility to tailor the properties [20]. Another attractive advantage of these monomers is that benzoxazines may be thermally polymerized without using any catalyst [19]. However, pure benzoxazine-based polymers exhibit also some drawbacks, such as high curing temperature and poor mechanical properties like brittleness of the material in the polymerized and crosslinked form [21]. To improve these shortcomings, the addition of nanofillers to polybenzoxazine matrix is an important method to produce nanomaterials with increased stiffness, toughness and higher dimensional stability compared with the neat polymer.

Although several types of polybenzoxazine – based composites have been obtained [22–26], no study referring to the growth of the benzoxazine monomers on the graphene oxide surface was reported. A study about the introduction of benzoxazine rings onto graphene oxide surface was reported by Meng and coworkers [27] using the click chemistry route involving the benzoxazine monomer already prepared, not synthesizing it. Our study aims to develop a new route to produce benzoxazine-modified graphene oxide by synthesizing the benzoxazine rings directly onto the graphene oxide surface through adequate chemical modification of the surface. Furthermore a new concept is proposed for the exfoliation of graphene sheets which considers as a key factor the balance between polymerization -in and -out of the graphene layers. Therefore we proposed for the first time a simpler alternative to produce polybenzoxazine – graphene oxide nanocomposites with exfoliated structure which are formed by polymerization of benzoxazine rings attached to the same graphene layer. Thus true covalent bonds between polybenzoxazine matrix and graphene oxide as nanofiller are to be established. The final nanocomposite structure will be an exfoliated one with very high stiffness and also less brittle than usually produced polybenzoxazines.

2. Materials and methods

2.1. Materials

Graphene oxide with carboxylic groups (GO-COOH) was received from NanoInnova Technologies (Spain). The amount of COOH groups in GO-COOH was 0.7 mmol of COOH/g. Tyramine, paraformaldehyde, tetrahydrofuran (THF), 1,4-dioxane, 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC), sodium phosphate dibasic (Na_2HPO_4) were purchased from Sigma Aldrich (Germany). Thionyl chloride (SOCl_2) and potassium phosphate monobasic (KH_2PO_4) were received from Riedel - de Haen. Benzylamine and N-Hydroxysuccinimide (NHS) were supplied by Fluka (Germany). All reagents and solvents were used as received without further treatment.

2.2. Instruments

Fourier Transform Infrared Spectroscopy (FTIR) spectra were registered on a BRUKER VERTEX 70 spectrometer in 400–4000 cm^{-1} region. The samples were mixed with KBr powder and pressed in a pellet. The resolution was 4 cm^{-1} and 32 scans were performed.

Proton nuclear magnetic resonance (^1H NMR) spectra were used to check the formation of benzoxazine rings. The spectra were registered on a BRUKER equipment operating at 400 MHz. Deuterated chloroform was used as a solvent and tetramethylsilane as an internal standard.

Thermogravimetric analyses (TGA) were done on a Q500 TA instrument from 30 to 800 °C using nitrogen with a heating rate of 10 °C/min and a nitrogen flow rate of 90 ml/min.

The Raman spectra were recorded on a DXR Raman microscope, from Thermo Fisher Scientific (Wisconsin, USA). The excitation laser wavelength was 532 nm using a laser power of 14 mW. The Raman spectra were collected in the range of 3200–200 cm^{-1} .

The X-ray Diffraction Analysis (XRD) was done on a XRD 6000 SHIMADZU diffractometer. A test was carried out using the $\text{Cu K}\alpha$ radiation source filtered with Ni. The patterns were automatically recorded with scan step of 0.02° and counting time of 0.6 s/step for diffraction angles 2 theta ranged between 3 and 12°, at room temperature.

The HR-TEM analysis was performed on Tecnai G2 F30 S-TWIN equipment provided with 200 kV emission gun.

XPS analysis was done on a K-Alpha instrument from Thermo Scientific, using a monochromated $\text{Al K}\alpha$ source (1486.6 eV), at a pressure of 2×10^{-9} mbar. Charging effects were compensated by a flood gun and binding energy was calibrated by placing the C 1s peak at 284.8 eV as internal standard. Deconvolution of C 1s peaks was done after subtraction of Shirley background.

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