



Nylon-6/Graphene composites modified through polymeric modification of graphene



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ARTICLE INFO

Article history:

Received 5 May 2014

Received in revised form 25 October 2014

Accepted 5 December 2014

Available online 13 December 2014

Keywords:

A. Polymer–matrix composites (PMCs)

B. Microstructures

E. Thermal analysis

D. Chemical analysis

Graphite oxide

ABSTRACT

The covalent functionalization of graphene oxide (GO) with poly(vinyl alcohol) (PVA) via ester linkages (GO-es-PVA) as well as the characterization of modified graphene based Nylon-6 (PA6) composite prepared by solution mixing techniques was examined. The anchoring of PVA chains on GO sheets was confirmed by XPS and FTIR measurements. The resulting functionalized sample became soluble in formic acid, allowing solution-phase processing for preparation of PA6/GO composites. Answering to the efficient polymer-chain grafting, a homogeneously dispersion of GO sheets in PA6 matrix and a dramatic improvement of interface adhesion between nanosheets and matrix were observed in PA6/GO-es-PVA composites by SEM and TEM. The depressed crystallization of PA6 chains in PA6/GO-es-PVA composites was investigated by their DSC and XRD results.

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1. Introduction

Carbon is a common and marvelous element. Besides the wellknown allotropes of graphite and diamond, other new forms of carbon have been discovered in the last few decades in succession, mainly including fullerene [1,2], carbon nanotubes (CNTs) [3], and graphene [4]. Graphene is an atomically thin, 2-dimensional network of sp²-hybridized carbons. It has been found that electrons move ballistically in the graphene structure with a mobility exceeding 15,000 m² V⁻¹ s⁻¹ [5]. Theoretical and experimental results show that single-layered graphene sheets are the strongest materials developed thus far [6]. Graphene nanosheets also have high thermal conductivity and high specific surface area [7].

Graphene can be derived from naturally abundant, low cost graphite via a two step approach. First graphite is converted to graphite oxide (GO) via strong acids and oxidizing agents [8]. After oxidation, abundant functional groups (e.g., hydroxyl, carboxyl, epoxy, ketone, etc.) were introduced onto the graphitic layers, and simultaneously part of sp²-carbons were converted into sp³ ones [9–11]. Because of the strong repulsion between negative charged layers and the enlarging of interlayer distance, the oxidized bulk graphite could be easily exfoliated into individually dispersed single layers by sonication in water. Then GO is reduced to graphene by numerous methods. One of these is to

exfoliate GO sheets by rapidly heating to ~1050 °C [12]. The decomposition product, CO₂, mechanically splits apart GO layers bound by van der Waals forces [6], yielding substantial volume expansion (100–300 times), very high surface area (~1700 m²/g) and high electrical conductivity (10–20 S/cm) of the produced sheets [12,13]. Residual oxygen groups on this thermally reduced graphene oxide (TRG) improve interaction with polar polymers, which leads to polymer composites with significant increase in stiffness [14]. Chemical reduction of graphene oxide (CRG) is another addressed route to prepare graphene on large-scale using hydrazine [15–17], dimethylhydrazine [18], sodiumborohydride followed by hydrazine [19], hydroquinone [20], and UV-irradiated TiO₂ [1]. Although chemical reduction of graphene oxide provides an efficient route for production of CRG, the hazardous nature and cost of the chemicals used in reduction may limit its application. An alternative chemical reduction is dehydration of the hydroxyl groups on graphene oxide in water [21,22] at high pressure and temperature, 120–200 °C. Aluminum powder appears to catalyze this process in an acidic condition [23].

One of the potential applications of graphene is reinforcement for polymers. Significantly improved electrical, mechanical and gas barrier properties of graphene/polymer nanocomposites have been attracting tremendous interest [14,18,24–30]. Till now, in situ polymerization [18,29], melt compounding and solvent blending are the three most commonly used blending techniques for polymer composites with nano-particles including graphene [31]. Successful polymerizations of PVA [32], MMA [33], epoxy

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[34,35], and poly(arylene disulfide) [36] with graphene oxide or silicone foams [37,38] and PU [39,40] with TRG have been reported. Especially for poly(arylene disulfide), grapheme oxide was used as an oxidation agent which converts thiol salts to disulfide. The most economically attractive and scalable method for dispersing nanoparticles into polymers is melt blending. However, because of thermal instability [31] and the low bulk density [41] of most chemically modified graphene, the use of melt blending for graphene has so far been limited to a few studies with the thermally stable TRG [39]. Compared to melt blending, solvent blending produces better dispersion.

However, further development is hindered due to poor dispersion and incompatible of these reinforcing nanostructures in the polymer matrix. Restacking of the flat sheets, especially after chemical reduction, can significantly reduce their effectiveness. Restacking can be prevented by either use of surfactants that can stabilize the reduced particle suspensions [42] or blending with polymers prior to the chemical reduction [18]. Using GO after chemical modification with isocyanate or amine, composites have also been produced in aprotic solvents with hydrophobic polymers such as polystyrene (PS) [18,43], polyurethane (PU) [44], or poly(methyl methacrylate) (PMMA) [45].

As a charming matrix for the polymer/grapheme composites, Nylon-6 (PA6) has already obtained great attention, because it is one of the most widely used engineering polymers. The inhomogeneous dispersion is still a problem for melt blending [46]. Though in situ polymerization can make some compensation [29], so far monomers have only been polymerized in solvents that are unhealthy and environment unfriendly. The high viscosity of even dilute dispersion of graphene makes bulk-phase polymerization difficult to be controlled [31]. Herein, we firstly report an effective and environment friendly protocol to prepare Nylon-6 (PA6)/graphene oxide (GO) composites via formic acid solvent blending on the basis of covalent functionalization of GO with PVA through the esterification reaction between the carboxylic acid moieties on the graphene and hydroxyl groups on PVA. Successful polymeric modification of graphene through esterification of graphite oxide and poly(vinyl alcohol) [47,48] is the basis. Moreover, the excellent compatibility of PA6/PVA blend because of the function of hydrogen bond [49,50] provides the possibility for the improvement of GO sheets exfoliation in the PA6 matrix through the intrinsic interaction between the chains of PVA and PA6.

2. Experimental section

2.1. Materials

Graphite powder with an average particle size of 45 mm and a purity of 99.9% was obtained from Changsha Shenghua Chemical Co., Ltd. PVA (88% hydrolyzed, Mw ~ 72,600–81,400) were bought from Chengdu Kelong Chemical Co., Ltd. sulfuric acid (H₂SO₄), hydrochloric acid (HCl), hydrogen peroxide (H₂O₂), potassium permanganate (KMnO₄), sodium nitrate (NaNO₃), dimethyl sulfoxide (DMSO), methanoic acid, N,N'-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)-pyridine (DMAP), and N-hydroxybenzotriazole (HOBT) were purchased from Chengdu Haihong Chemical Co., Ltd. and used as received. Commercial PA6 resins, EG-8200 was obtained from the DMS Chemical Co. Its weight (Mw) and number (Mn) averaged molecular weight are 201 and 67 kg/mol, respectively.

2.2. Fabrication of GO-es-PVA

The GO was prepared from graphite by the modified Hummers methods [51]. The covalent functionalization of GO with PVA was

through the carbodiimide-activated esterification reaction between the carboxylic acid moieties on the graphene and hydroxyl groups on PVA (Fig. 1), similar to what was reported previously for the PVA functionalization of carbon nanotubes or nanosheets [52,53]. In the reaction, a dispersion of oxide graphene in DMSO was prepared via sonication, and it was added to a solution of DCC, DMAP, and HOBT in DMSO. Upon sonication for 1 h, a separately prepared solution of PVA in DMSO was added, followed by sonication for 24 h. The reaction mixture was precipitated into acetone to recover the functionalized sample. For purification, the sample was dissolved in hot water, and then precipitated into acetone. The procedure was repeated three times, and the resulting sample was washed with acetone in Soxhlet extractor for 12 h to obtain the final oxide graphene esterification with PVA (GO-es-PVA).

2.3. Fabrication of PA6 composites

A typical procedure to prepare PA6 (Nylon 6)/GO-es-PVA composites with 0.2 wt% containing was depicted as follows: 10 mg of GO-es-PVA was first dispersed in a 250 ml flask with 100 ml formic acid, and exfoliated by sonication for 30 min, then the solution was added to a solution of 5 g PA6 in 100 ml formic acid, followed by sonicated and equipped a mechanical stirring at 50 °C for 2 h. The mixture was precipitated into deionized water to recover the composites. The final products of PA6/GO-es-PVA composites were dried at 80 °C in vacuum for 24 h. In the end, we obtained NGP composites noted as NGP-0.2, NGP-0.5, NGP-1, and NGP-2 according to the feed weight percentage of GO-es-PVA, while the PA6/GO composites as comparison prepared by the aforesaid procedure were noted as NG-0.2, NG-0.5, NG-1, and NG-2 according to the feed weight percentage of GO.

2.4. Characterization

Typical tapping-mode atomic force microscopy (AFM) measurements were carried out using Multimode SPM from Digital Instruments with a Nanoscope IV controller made by Veeco Instruments Inc. The sample for AFM tests was fabricated by depositing an aqueous solution of graphite oxide (1.0 mg/ml) onto a fresh mica surface and allowing them to dry in air at room temperature.

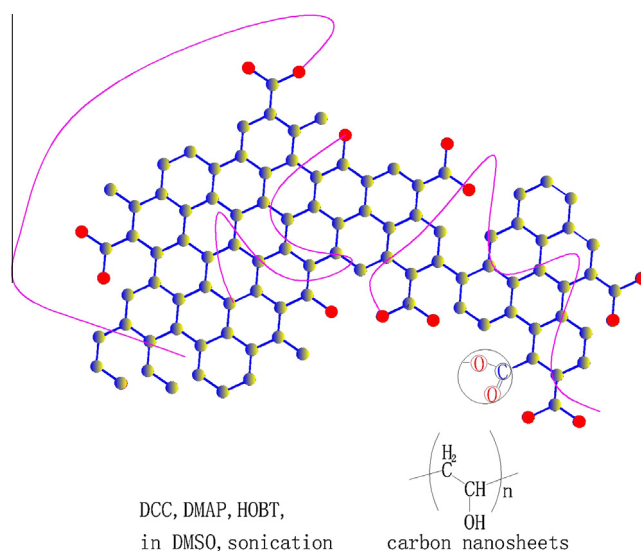


Fig. 1. The functionalization via esterification of the carboxylic acid moieties in oxidized carbon nanosheets by hydroxyl groups in PVA.

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