Chemical Engineering Journal 236 (2014) 233–241

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

One-pot surface functionalization and reduction of graphene oxide with long-chain molecules: Preparation and its enhancement on the thermal and mechanical properties of polyurea

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HIGHLIGHTS

- Simultaneously reduction and functionalization of GO with long-chain molecules.
- Covalent incorporation of FGO into polyurea via in situ polymerization.
- Significant reinforcement on the thermal stability, storage modulus and tensile strength of the polyurea/FGO nanocomposites.

ARTICLE INFO

Article history:
Received 17 April 2013
Received in revised form 15 July 2013
Accepted 15 September 2013
Available online 25 September 2013

Keywords:
Functionalization
Reduction
Graphene oxide
Polyurea
Nanocomposites

ABSTRACT

Graphene oxide (GO) was simultaneously reduced and functionalized with amine-terminated polyether. The results from FTIR, XPS and XRD showed that amine-terminated polyether was successfully attached onto the surface of FGO and most of FGO was reduced. Subsequently the amine-terminated polyether functionalized GO sheets were covalently incorporated into the polyurea matrix via in situ polymerization. The XRD, TEM, SEM and immersion phenomenon showed that FGO sheets were uniformly dispersed in the polyurea matrix and formed the strong interfacial adhesion with polyurea matrix. The properties reinforcements of the nanocomposites were investigated by thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and tensile testing machine. The TGA results indicated that the T50 wt.% of the nanocomposites was increased by about 10 °C compared to pure polyurea at loading of 1.0 wt.% FGO. Meanwhile, the storage modulus of the nanocomposites was enhanced due to incorporation of FGO. Furthermore, the tensile test indicated that the FGO could also improve tensile properties of polyurea. It is believed that the reduction and covalent functionalization of graphene can improve both the dispersion of FGO in the polymer matrix and the interfacial interactions between FGO and polyurea matrix.

1. Introduction

In the past few years, polymer-based nanocomposites have attracted considerable research interest with the objective of obtaining high-performance materials. The polymer nanocomposites reinforced by nano-fillers such as carbon nanotubes (CNTs), montmorillonite (MMT), layered double hydroxides (LDH) and graphene have often been reported [1–4]. Among them, CNTs, LDH and clays have been considered potential candidates for the properties reinforcements of polymer materials due to their high aspect ratio, thermal and mechanical properties. Although CNTs, LDH and clays start to appear in large quantities in consumer products, graphene provides an exciting opportunity as the new nano-fillers, because it offers properties that are equal to or better than those of CNTs but with the scale and practicality of montmorillonite. Therefore, graphene is considered as a good choice of the nano-fillers for fabricating advanced polymer nanocomposites.

Graphene, as single layered two-dimensional carbon materials, has been applied in high-performance polymer nanocomposites due to its high thermal conductivity, superior mechanical strength and excellent electronic conductivity [5–8]. As for the graphene/polymer nanocomposites, homogeneous dispersion of the nano-fillers and utilization of their high available surface area for interaction with the polymer matrix are critical point for the

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http://dx.doi.org/10.1016/j.cej.2013.09.061

preparation of the nanocomposites with improved mechanical, thermal, electrical, and barrier properties [9,10]. In view of the oxygen functional groups (e.g., hydroxyl, epoxy and carbonyl groups) on the basal planes and edges [11], it is convenient to chemically modify the GO with organic groups, imparting improved compatibility and good dispersion of GO in polymer matrixes. As a result, the organic modification of the GO is the focus of recent works. For example, Stankovich and his co-workers functionalized GO with isocyanate derivatives and the resulting modified GO were well dispersed in organic solvents [12]. Lu reported the preparation of PS-functionalized graphene nanosheets through grafting of ATRP initiator to the reduced graphene surface. The nanocomposites exhibited 70% increase in tensile strength and 57% increase in Young's modulus [13]. In addition, Salavagione had successfully modified graphene laminates by the esterification between the carboxylic groups in GO and the hydroxyl groups in PVA [14]. The chemical modification of GO not only weakens the interactions between the graphene sheets, but also strengthens the interface interactions between polymer matrix and GO. Therefore, the better dispersions of GO in the polymer matrix result in the enhanced properties of the nanocomposites.

Generally, the graphene sheets can be prepared by three techniques: (i) micromechanical cleavage, which can only produce graphene sheets in very limited quantities, (ii) epitaxial growth of graphene films in strict conditions, and (iii) chemical approach, which includes the production of graphite oxidation, the exfoliation and the reduction of graphite oxidation [15,16]. Among them, the most promising method for the large scale production of graphene, which is beneficial for the practical application of graphene/polymer nanocomposites, is based on the chemical approach. The Hummers method is the most widely used method to prepare GO [17] and many different kinds of reducing agents, including hydrazine, sodium borohydride, and hydrohalic acids, have been used to prepare reduced GO [18–20]. However, the reduced GO usually aggregates during the reduction process which significantly influences the further fabrication of the graphene based nanocomposites. As a result, modification of GO during the chemical reduction process is necessary to prevent the aggregation of rGO nano-sheets and also improves the dispersion of rGO in the polymer matrix. Recent works demonstrate that the molecules containing amino-groups, hydroquinone or hydroxyl can reduce the GO through simple processes. In addition, the amine groups could react with the epoxy groups on the surface or edge of GO through the nucleophilic substitution reaction, resulting in the functionalization of GO [21–23]. Thus, a new idea, simultaneous reduction and functionalization of GO with amine-terminated polymer, appears.

Polyurea (PUA) is an attractive industrial material for industrial primers or as protective coatings. Applications for polyurea include concrete coatings, repair of roofs and parking decks, and linings for storage tanks, freight ships and truck beds. Thus, the strict mechanical and thermal properties are required due to its special purpose. The polyurea is usually prepared at room temperature and the amine-terminated polyether is the basic ingredient of polyurea. Thus, in this work, the amine-terminated polyether is used as the modification substance and polyurea is chosen as the polymer matrix.

Herein, GO was simultaneously reduced and functionalized with amine-terminated polyether by a simple process. Subsequently the amine-terminated polyether functionalized graphene sheets (FGO) were covalently incorporated into the polyurea matrix via in situ polymerization. The reinforced effects of FGO on the thermal and mechanical properties of polyurea were investigated. The simultaneous reduction and functionalization of GO are considered as a large-scale method for the production of the modified graphene for the use in polymer nanocomposites.

2. Experiments

2.1. Raw materials

Graphite powder (Spectrum Pure) was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). 3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI), JEFFAMINE D-2000 D-400 polyetheramine which are a difunctional, primary amine with average molecular weight of 2000 and 400 respectively, were supplied by Shanghai Hengyi Co. Ltd. (Shanghai, China) and dried at 90 °C under vacuum for 3 h. Diethyltoluenediamine was supplied by Shamu Co. Ltd. (Qingdao, China). Concentrated sulfuric acid (98%), sodium nitrate, potassium permanganate, 30% H_2O_2 solution, hydrochloric acid and N,N-dimethylformamide (DMF) were all reagent grade and provided by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

2.2. Reduction and functionalization of GO with D400

GO was prepared by a modified Hummers' method [17]. The procedure for fabricating FGO is presented in Scheme 1a. In a typical procedure for preparing FGO, GO (1 g) was well dispersed in 200 mL of N,N-dimethylformamide (DMF) via ultrasonication. Subsequently, D400 (6 g) were added. The mixtures were refluxed with mechanical stirring at 120 °C for 24 h and filtrated with a polytetrafluoroethylene (PTFE) with an average pore size of 0.2 μm. The filtrate cake was rinsed in DMF with the aid of ultrasonication and then filtrated. The rinsing-filtration process was repeated for several times to remove the physical adsorbed amine-terminated polyether. Finally, the filtrate products were dried in an oven at 80 °C for 24 h and then the black powders (FGO) were obtained.

2.3. Preparation of the polyurea, GO/polyurea and FGO/polyurea nanocomposites

The procedure for fabricating FGO/polyurea nanocomposites is presented in Scheme 1b. The nanocomposites were prepared by a solvent casting technique. Briefly, the preparation of PUA-1 was as follows: 0.28 g of FGO was dispersed in 75 mL of DMF with the assistance of sonication at room temperature. Then, IPDI (5.55 g) was introduced into the above mixture at room temperature for 2 h in a three-necked flask protected by N_2. Afterwards, D2000 (20.00 g) was added into the flask and the mixtures were stirred at room temperature for another 2 h. Then diethyltoluenediamine (2.67 g) as the chain extender was added to the mixtures and kept stirring for 3 h. Afterwards, the products were dried at 80 °C for 24 h. Other samples containing 0.2 wt.% FGO(PUA-0.2), 0.5 wt.% FGO (PUA-0.5) and 1 wt.% GO (PUA-GO-1.0) were synthesized by the same procedures (Table 1).

2.4. Characterization

The FTIR spectroscopy was recorded with Nicolet 6700 FTIR spectrophotometer. The transition mode was used and the wavelength range was set from 4000 to 500 cm^{-1}. The morphology and structure of GO, graphene and polyurea nanocomposites were studied by transmission electron microscopy (TEM) (JEOL JEM-2100 instrument with an acceleration voltage of 100 kV). The nanocomposites were cryomicrotomed with a diamond knife into a thickness of 50–70 nm. The ultrathin films were placed on copper grids before observation. Moreover, GO and graphene were dispersed in DMF with ultrasonication and then dripped onto copper grids. The thermogravimetic analysis (TGA) was carried out on a TGA Q5000 IR thermalgravimetric analyzer (TA instruments).