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Functionalizing graphene decorated with phosphorus-nitrogen containing dendrimer for high-performance polymer nanocomposites

Yanxian Jin [a], Guobo Huang [a,*], Deman Han [a], Pingan Song [b,*], Wenyuan Tang [a], Jianshe Bao [a], Rongrong Li [a], Yilin Liu [c]

[a] School of Pharmaceutical and Chemical Engineering, Taizhou University, Taizhou 318001, China
[b] Department of Materials, College of Engineering, Zhejiang A & F University, Hangzhou 311300, China
[c] Zhejiang Baina Rubber Equipment Co. Ltd., Taizhou 317300, China

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ABSTRACT

In this paper, we demonstrate a novel strategy for fabricating advanced polymer composites based on functionalized graphene oxide decorated with phosphorus-nitrogen-containing dendrimers (PND-GO). Both X-ray diffraction and transmission electron microscopy results show that reduced PND-GO uniformly disperses within polymer matrix and is exfoliated in polyurethane (PU) via in situ polymerization. Cone calorimetry results show that incorporating 2 wt% reduced PND-GO into PU decreases the peak heat release rate by 53% and prolongs the time to ignition by 28 s as compared with the PU bulk. Besides, the tensile strength and Young's modulus are remarkably enhanced by about 2 times and 5 times, respectively.

1. Introduction

The flame-retarding polymer nanocomposite, as an important branch of polymer nanocomposites, has shown dramatic improvements in the mechanical, thermal, flame retardant and barrier properties with very low loading (usually less than 5%) of nanofillers, compared with those filled with traditional flame retardants. The carbon-based nanofillers graphene (oxide) is emerging as a rising star in the field of flame retardancy for its prominent intrinsic properties [1–6]. Song [2] and Huang et al. [3] have found that graphene can more effectively decrease the heat release rate of polymer, prolong the time to ignition of materials, and enhance the char structure during combustion relative to layered silicates and carbon nanotubes. Unfortunately, most of polymer/graphene nanocomposites usually do not extinguish and burn slowly until most of the fuel has been burnt. To further improve fire performance of polymer/graphene nanocomposites, intumescent flame retardants (IFRs) have been used for their high flame retarding efficiency [4–6]. During combustion, the IFRs produce swollen multicellular char layers, which acts as a physical barrier against heat transmission and oxygen diffusion and protects the underlying material from the action of the fire [7].

As is well-known, the dispersion quality of nanofillers in the polymer matrix directly determines its effectiveness in improving performances of a material. However, the insolubility of nanofillers renders them difficult to be well-dispersed in the polymer matrix. Although chemical modifications with surfactants for nanofillers has been believed as a feasible method to improve the dispersion within the most hydrophobic polymers [8], there are still many obstacles that remain a huge challenge. For example, the majority of current as-used surfactants with long alkyl chains reduce the thermal stability and flame retardancy of polymer nanocomposites for the inherent flammability. Moreover, due to its low stability (normally degrade at 200 °C), it is not suitable to process these polymers under a high temperature condition.

So far, much effort has been dedicated to the functionalization of nanofillers to improve the dispersion of nanofillers in the polymer matrix and flame retardancy of the polymer nanocomposites. Recently, nanofillers modified with IFRs have been considered as a promising candidate because of their halogen-free flame retardancy and high efficiency. For instance, Fang and Song et al. has prepared the functionalized carbon nanotubes (CNTs) or fullerene (C_{60}) by grafting IFRs, and the functionalized CNTs or C_{60} is found to be better dispersed in polymer matrix, and thus greatly improve the flame retarded properties of nanocomposites [9–11]. Besides, much work about layered silicates [12,13] modified with IFRs has been done in our group to study the flame retardancy effect on polymers. It is found that the composition, chain length and polar-

* Corresponding authors.
    E-mail addresses: huangguobo@tzc.edu.cn (G. Huang), pingansong@gmail.com (P. Song).

ity of IFRs modification reagents are closely related to the formation of nanocomposites, which directly affects the performance of materials. Therefore, the functionalization with IFRs is able to improve the dispersion of nanofillers in polymer matrix, and enhance the synergistic effect between nanofillers and IFRs, which leads to the greater improvement in the performance of nanocomposites. However, there are still some challenges for creating high-performance polymer nanocomposites, especially in controlling the grafting degree of IFRs-functionalized nanofillers. In fact, the grafting degree of IFRs on the surface of nanofillers has been very low until now, thus leading to limited flame retardancy efficiency and the performance improvements of materials. This paper aims to develop a novel class of graphene-based nano-flame retardants containing high loading of IFRs, which are then used to prepare high-performance polymer composites.

2. Experimental details

2.1. Materials

Graphene oxide (GO) was prepared by the modified Hummer's method from graphite colloidal and vacuum-dried under phosphorus pentoxide at room temperature for above a week [14]. 1,6-Hexamethylene diisocyanate (HDI) was provided by Bayer Co. Amine terminated poly (amidoamine) (PAMAM, G1) dendrimer, where G represents generation, was purchased from Chenyuan Silicon Materials Co. Ltd (Weihai, China). 2,2-Dimethyl-1,3-propanediol phosphoryl chloride (DPPC) was synthesized by reacting phosphoryl trichloride with neopentyl glycol according to previous literatures [12,13]. Ester-based polyol (molecular weight M_n = 2000 g/mol), 4,4′-methylene diphenyl diisocyanate (MDI) and 1,4-butanediol (BDO) were supplied by Shanghai Hersbit Chemical Co. Ltd (Shanghai, China).

2.2. Fabrication of PND-GO

To load as much as phosphorus-nitrogen containing dendrimer on the graphene oxide surface and consider the synergistic effects of P—N system, the mole ratio of HDI, PAMAM and DCCP grafted onto the surface of GO was pre-controlled at about 1:1:7. The typical synthetic route to graphene oxide modified with phosphorus-nitrogen containing dendrimer (PND-GO) is shown in Scheme 1 mainly consisting of three steps. The first step is the synthesis of HDI-GO, 2.0 g GO was dispersed into 200 mL of anhydrous N,N-Dimethylformamide (DMF) to form a brownish black slurry with the aid of sonication for 2 h at room temperature. Then, about 20 mL of anhydrous DMF solution containing 0.336 g HDI was added dropwise into the GO slurry and the mixture was then sonicated at 60 °C for 8 h. After reaction, the slurry was filtered and the precipitate was washed with anhydrous DMF for three times. The products were termed HDI-GO.

The second step involves the grafting reaction of dendrimer PAMAM (G1) onto GO surface. Briefly, 1.429 g of PAMAM (G1) was added into a 100 mL of anhydrous DMF suspension containing 1.168 g HDI-GO. Then, the mixture was sonicated at 30 °C for 10 h. After the reaction was over, the slurry was filtered and the precipitate was washed with anhydrous methanol for three times and then dried under vacuum at 60 °C for 12 h. The products were termed D-GO.

The final step is the reaction of phosphorus oxychloride with the terminal group (amidine) of D-GO. Typically, 1.30 g of D-GO powders were dispersed in 100 mL of anhydrous DMF with the assistance of sonication for 2 h at room temperature, 1.414 g of triethylamine and 20 mL of anhydrous DMF containing 0.644 g DCCP was subsequently added dropwise into the above suspension and

the mixture was allowed to stir at 30 °C for 6 h. The product was filtered and washed with methanol and then deionized water three times to remove by-product. The resultant product was termed PND-GO.

2.3. Fabrication of PU nanocomposites

PU composites filled with reduced PND-GO were prepared via situ polymerization in DMF as follows. 1.0 g of PND-GO was dispersed into 100 mL of anhydrous DMF with the aid of sonication for 2 h. Subsequently, 74.25 g of dry polyol and 20.66 g of MDI were added to the above mixture, and a prepolymer formed by heating the mixture at 80 °C under N₂ for 3 h. The chain extender, BDO (4.09 g) and catalyzer, stannous octanoate was added to the mixture and the mixture was allowed to continue stirring for another 5 h. Then, 0.8 mL of hydrazine solution and 3.5 mL of ammonia solution (28%) were added into the above homogeneous dispersion and the mixture was stirred at 95 °C for 1 h. Finally, the solvent was removed in the vacuum oven at 110 °C for 24 h and the solid compound was pressed on a curing machine at 180 °C for 8 min to be shaped into 4.0 ± 0.1 mm thick sheets for further measurements. PU composites filled with 1 wt% and 2 wt% reduced PND-GO were designated as PU/PND-G1 and PU/PND-G2. The parallel samples of PU filled with 1 wt% and 2 wt% reduced GO were designated as PU/G1 and PU/G2, which were prepared as the above steps (reduction temperature: 95 °C, reduction time: 1 h).

2.4. Characterization

Fourier transform infrared spectroscopy (FT-IR) was carried out on a Nicolet -5700 FT-IR spectrometer using KBr pellets. X-ray photoelectron spectroscopy (XPS) measurements were conducted on Kratos AXIS Ultra DLD electron spectroscopy. Scanning transmission electron microscopy (STEM) and elemental mapping were carried out under a high-angle annular dark field (HAADF) mode on a Tecnai G2F30S-Twin transmission electron microscope. X-ray diffraction patterns were obtained in Bruker AXS D8 Advance diffractometer using a Cu-Kα radiation generator. The diffraction patterns were collected within the 2θ range 2–40° using scanning rate of 0.6°/min. Transmission electron microscopy (TEM) samples were cut using a diamond knife and RMC MTXL ultramicrotome. The ultrathin sections were then placed on 400 mesh copper grids and photographed using a JEM-1230 transmission electron microscope. Thermogravimetic analysis (TGA) was carried out on a Q600SDT thermogravimetric analyzer. The sample weight is in the range of 12.0–14.0 mg. TGA tests were done from 30 °C to 600 °C at a heating rate of 10 °C/min under nitrogen (N₂) condition. The flame retardant properties of PU composites were tested using cone calorimeter (ISQ 5660-1) with a heat flux of 35 kW/m². All samples have dimensions of $100 \times 100 \times 4$ mm³ were wrapped in aluminum foil and then put in a box with the same dimension in the horizontal direction. The cone data reported here were the average values of three replicated measurements. Char residue was examined by scanning electron microscopy (SEM) using Hitachi S-4800(II) scanning electron microscope.

3. Results and discussion

3.1. Characterization of PND-GO

Fig. 1a shows the FT-IR spectra of GO, HDI-GO, D-GO and PND-GO. Compared with GO, two new absorption peaks respectively located at 2930 cm⁻¹ and 1489 cm⁻¹ appear in the FT-IR spectrum of HDI-GO. These two peaks belong to the stretching and bending vibrations of —CH₂ group from HDI, indicating the successful graft-