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High performance of reduced sulfonated graphite oxide nanoplatelets/polyurethane composites

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ABSTRACT

In the study reported in this paper, sulfonated graphite oxide (SGO) was chemically reduced and then incorporated into a polyurethane matrix to produce reduced sulfonated graphite oxide/polyurethane (RSGO/PU) composites. Following reduction, the oxygen-containing functional groups attached to SGO had been effectively removed. The thermally conductive and electrical properties of RSGO/PU composites were thereby enhanced. Percolation thresholds of PU composites filled with RSGO were obtained at loadings below 1 wt%. The RSGO/PU composites exhibited improved gas barrier properties as the loading of RSGO was increased. Based on the fracture morphology investigation, the RSGO was evenly distributed throughout the PU composites and strong filler–matrix interactions were observed.

1. Introduction

In recent years, graphite oxide (GO) has been found to be one of the most important derivatives of graphene. To extend the potential properties of electrical and thermal conductivity in GO, its fabrication has always been followed with a reduction process to eliminate the oxygen-containing groups [1]. Recently, sulfonated graphite oxide (SGO) has been found to be more effective in facilitating the oxygen reduction reaction of GO. Thus, reduced SGO has great potential to enhance the electrical and thermal conductivity of polymer composites [2]. Number of processes have been reported to chemically reduce GO including hydrazine hydrate [3], sodium borohydride [4], sodium hydroxide solution [5] among others. Hydroiodic acid (HI) is a strong reducing agent that is also an environmentally-friendly inorganic acid. HI has been found to be capable of improving both the strength and conductivity of GO-filled polymers by reacting with the epoxy groups in GO [6,7]. However, due to a structural transformation, HI reduction of SGO is not fully understood and requires further investigation.

In this reported study, HI was employed to reduce sulfonated graphite oxide (SGO) to eliminate the oxygen containing groups of graphene sheets. The reduction effects of SGO was characterized using Fourier transform infrared spectroscopy (FT-IR), UV–visible spectroscopy (UV–vis) and thermal gravimetric analysis (TGA). Polyurethane (PU) was chosen as the polymer matrix in this study to evaluate the properties of the composites that were formed by addition of the reduced sulfonated graphite oxide (RSGO). The electrical, thermal conductivity and gas barrier properties of RSGO/PU were systematically studied.

2. Materials and methods

2.1. Materials

A one-component polyurethane formulation was acquired from Tianjin Dengta Coating Co., China. Sulfonated graphite oxide (SGO, GTO-804L) was supplied by Gaotong Advanced Materials Co., Ltd., China and used as received. Hydroiodic acid (HI, 47%) was purchased from Aladdin Industrial Co., Ltd, China. All other chemicals, including acetic acid (HAc), sodium bicarbonate ($NaHCO_3$) and acetone were reagent grade and obtained from Sinopharm Chemical Reagent Co., Ltd, China.

2.2. Preparation of RSGO and RSGO/PU composites

RSGO was prepared by chemically reduction of SGO. This process began with 100 mg SGO which was dispersed in 40 ml HAc using ultra-sonication for 30 min. Then 2 ml of HI was added dropwise into SGO solution while stirring for 10 min at 125 °C. The resultant RSGO product was isolated by filtration, washed with saturated $NaHCO_3$, distilled water and acetone, and then vacuum dried overnight at room temperature.

Different contents of RSGO powder (0.1 wt%, 0.5 wt%, 1 wt%, 2 wt%) were separately added into a PU matrix with constant

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stirring for 1 h. The RSGO/PU mixtures were casted in individual Teflon molds and cured at ambient temperature to obtain RSGO/PU hybrid films.

2.3. Characterization

Fourier transform infrared spectroscopy (FT-IR) spectra of the SGO and RSGO powders were recorded using a Nicolet 370 spectrometer (Thermofisher Co., USA). Ultraviolet visible (UV–vis) absorption spectra of the SGO and RSGO powders were recorded using a UV-2550 spectrophotometer (Shimadzu Co., Japan). Thermo gravimetric analysis (TGA) of the SGO and RSGO powders was conducted in nitrogen using a PT-1000 instrument at a heating rate of 20 °C/min (TA Instruments, USA). Fracture morphologies of liquid nitrogen quenched RSGO/PU samples were obtained using a S3400-N scanning electron microscope (SEM, Hitachi Co., Japan). The electrical conductivities of RSGO/PU composites higher than 10^{-8} S/cm were measured with ST2263 four-probe conductivity meter (Suzhou Jingge Instrument Co., China) and the electrical conductivities lower than 10^{-8} S/cm were measured using an Anbiao ZC36 high-resistance meter (Shanghai Anbiao Meter Co., China). The thermal conductivity coefficient of the RSGO/PU composites was measured using DRL-2B steady state heat-flow meter (Xiangtan Instrument Co., China). The oxygen permeability of RSGO/PU composite films were tested using a gas permeability tester (BTY-B2P, Labthink Instruments Co., China).

3. Results and discussion

According to the experimental data presented in Fig. 1, the structure and features of the SGO platelets were transformed after reduction. Functional groups distinctions between SGO and RSGO could be seen as shown by FT-IR spectra (Fig. 1a). As shown the oxygen-containing functional groups were significantly removed after reduction. As evidenced by the FT-IR spectrum of the SGO showed significant bands around 3423 cm^{-1} (–OH) and 1723 cm^{-1} (–C=O). Characteristics peaks corresponding to various functional groups, including –C=C (1633 cm^{-1}), –CH_2 stretching (2925 cm^{-1}, 2856 cm^{-1}) and –CH_2 bending vibration (1394 cm^{-1}), were observed in the FT-IR spectrum of the SGO. The sulfonic acid groups of the SGO can be seen at 1166 cm^{-1}, 1124 cm^{-1} and 1043 cm^{-1} (two v_{s-o} and one $v_{s-phenyl}$) [8]. After the reduction of the graphenes using HI, the intensities of the v_{s-o} peaks were considerably attenuated. The $v_{s-phenyl}$ peak at 1041 cm^{-1} was retained, which was suggested that most of the oxygen-containing sulfonic acid groups were removed from the SGO. This restored the highly conjugated structure of the graphene resulting in a red shift of the absorption bands for the C=C and –CH_2 bonds to 1623 cm^{-1}, 2920 cm^{-1}, 2949 cm^{-1} and 1384 cm^{-1} [9]. This structural variation of SGO was also confirmed by the UV–vis spectrum. The UV–vis absorption spectrum results showed that the absorption peak of the SGO corresponded to π–π transitions of aromatic C=C bonds, which red-shifted from 207 nm to 234 nm after the HI reduction treatment (Fig. 1b). This results suggest that the electronic conjugation within the SGO sheets was restored by its chemical reduction [10].

The TGA results for SGO and RSGO are shown in Fig. 1c. The TGA trace for SGO showed that it exhibited poor thermal stability. As shown, there was an initial 10% mass loss below 100 °C, which was attributed to the removal of adsorbed water and a slower, steady mass loss (~29%) over the whole temperature range between 100 °C and 400 °C. This was attributed to the decomposition of labile oxygen functional groups within the composites. The main mass loss (~38%) occurred at around 400–800 °C, which was attributed to the removal of more stable oxygen functionalities as well as the bulk pyrolysis of carbon skeleton [11]. By comparison, the RSGO exhibited a 22% mass loss through the range of 100–400 °C and a more than 21% mass loss between 400 and 800 °C. After reduction, RSGO exhibited an improved thermal stability over that of SGO which was attributed to the effective removal of the oxygen-containing functional groups.

Fig. 2 shows the morphology of cryogenically fractured surfaces of the RSGO/PU composites which was performed to investigate the dispersion of the filler and the filler–matrix interaction. As can be seen, no obvious aggregates were visible even at 2 wt% loading of RSGO, which indicated good dispersion of the RSGO. Unfilled PU exhibited a very smooth surface with some stripes in the fracture direction (Fig. 2a and b). By contrast, the incorporation of RSGO into the PU matrix led to the formation of numerous irregular bulges evenly distributing over the fracture surface (Fig. 2c–f). At 2 wt % loading (Fig. 2e and f), RSGO platelets remained embedded and adhered to the PU matrix (arrows), suggesting a strong interfacial interaction between RSGO and PU.

To facilitate feeding of functionalized graphene sheets (FGSs) into a compounder, Raghu et al. [12] dispersed FGS in acetone under ultrasonication before mixing with PU emulsion. Percolation threshold values of the resulting WPU/FGS was 2 wt%. Liao et al. [13] have described a route to prepare reduced graphite oxide/TPU composites using a co-solvent blending method, which resulted in a composite with a similar percolation threshold value (0.5–1 wt%). However, the preparation method was too cumbersome to scale-up in experiments. Fig. 3a shows the electrical conductivity of the RSGO/PU films as a function of RSGO content. As shown, the conductivity of the RSGO/PU composites was 1.6×10^{-15} S/cm when the RSGO content was 0.1 wt% and the conductivity of the composite increased to 1.35×10^{-14} S/cm when the RSGO was 0.5 wt%. The percolation threshold of the RSGO/PU composites occured when the filler concentration reached 1 wt%. At this concentration the conductivity of the composite was 9.34×10^{-5} S/cm, because the finely dispersed RSGO filler formed an effective conducting network even at very

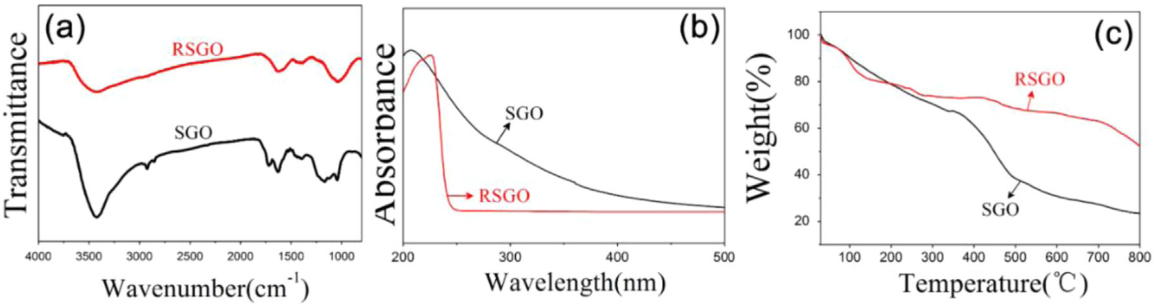

Fig. 1. (a) FTIR spectrum, (b) UV–vis spectrum and (c) TGA diagrams of SGO (Black) and RSGO (Red) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).