



# Enhanced stress transfer and thermal properties of polyimide composites with covalent functionalized reduced graphene oxide



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## ABSTRACT

This work prepares (3-aminopropyl) trimethoxysilane (APTMS)-functionalized reduced graphene oxide (APTMS-rGO)/polyimide (PI) composite (APTMS-rGO/PI) through in-situ polymerization. NH<sub>2</sub>-functionalized rGO coupled by APTMS demonstrates the good reinforced efficiency in mechanical and thermal properties, which is ascribed to the covalent-functionalized PI matrix by APTMS-rGO sheets. The uniform dispersion of APTMS-rGO increases the glass transition temperature (T<sub>g</sub>) and the thermal decomposition temperature (T<sub>d</sub>), exhibiting 21.7 °C and 44 °C improvements, respectively. The tensile strength of the composites with 0.3 wt% APTMS-rGO is 31% higher than that of neat PI, and Young's modulus is 35% higher than that of neat PI. Raman spectroscopy show the obvious G band shift, and also clearly demonstrates the enhanced interfacial interaction between rGO nanofillers and PI matrix. The high mechanical property of the APTMS-rGO/PI composites is attributed to the covalent functionalized GO by NH<sub>2</sub> groups and its good dispersion in comparison with GO.

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## 1. Introduction

Polyimide (PI)/graphene composite has been widely explored due to its excellent thermal stability and mechanical properties [1–10]. At present, two methods, the solution-mixing and in-situ polymerization, are used to prepare graphene/PI composite by incorporating the covalent or non-covalent functionalized graphene (FG). Typically, non-covalent FG offers the weak interfacial adhesion and the poor interfacial strength. Therefore, using covalent FG to improve the dispersion [11] and the interfacial strength has paid lots of attention for preparing high performance materials [12,13].

Previously, graphene/PI composite mainly is fabricated via solution-mixing process, and it shows the poor mechanical property and interfacial slippage due to the formed weak van der Waals interactions [2,14–18]. Liu et al. obtained the maximum mechanical property in GO/PI composite with 2 wt% GO, and the tensile strength and the Young's modulus increased 34% and 31%, respectively [2]. However, Tseng and co-workers [18] found the mechanical property of FG/PI composite with 10 wt% FG enhanced slightly. In comparison to the direct blending process of FG, the covalent FG sheets are widely used in PI composites [19]. Huang et al. prepared

the NH<sub>2</sub>-rGO/PI composite, and 2 wt% NH<sub>2</sub>-rGO afforded a 40% and 42% increment for the tensile strength and the modulus, respectively [6]. Park et al. reported the increased mechanical property of FG/PI composites when 3 wt% FG was covalently bonded with PI matrix [20,21], and further prepared the iodo functionalized GO/PI nanocomposites, showing a significant improvement for electrical conductivity and mechanical properties [22]. Recently, Liao et al. presented a 240% increase in the tensile strength at 0.3 wt% NH<sub>2</sub>-functionalized GO [23]. These results show that the interfacial state of GO with PI matrix plays a crucial role for improving the mechanical property. Lots of studies have focused on the mechanical behavior of PI composites at a high FG loading, however, few studies report the interfacial behavior and the mechanical property of graphene/PI composite at ultralow content. And, direct evidence that the covalent bonding enhances the interfacial interaction and the stress transfer behavior between PI matrix and FG needs to be further clarified.

Herein, we report the preparation, thermal and mechanical properties of graphene/polyimide composite using an ultralow (3-aminopropyl) trimethoxysilane (APTMS) functionalized reduced-graphene oxide (APTMS-rGO) loading by in-situ polymerization. The APTMS-GO containing amino groups further react with polyamic acid (PAA, the precursor of PI), and then the APTMS-rGO/PI composites are prepared through in-situ thermal imidization process. This study aims to systematically evaluate the surface

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energy, dynamic mechanical properties, morphological characteristics and interfacial stress transfer of APTMS-rGO/PI composites at ultralow APTMS-rGO loading. The exerted study to the interfacial stress transfer by dynamic in-situ Raman spectroscopy is crucial to understand the dynamic mechanical behavior and dispersion of graphene in the PI matrix.

## 2. Methods

### 2.1. Materials

Pyromellitic dianhydride (PMDA) and 4,4'-oxidianiline (ODA) were purchased from Sinopharm Chemical Reagent Co., Ltd. and used after purification. (3-Aminopropyl) trimethoxysilane (APTMS) was supplied from Sigma–Aldrich reagent Co. Natural graphite powders (NGP) (325 mesh) were kindly provided by Qingdao Laixi Graphite Co., Ltd. Concentrated  $\text{H}_2\text{SO}_4$  (98%),  $\text{KMnO}_4$ ,  $\text{NaNO}_3$ ,  $\text{H}_2\text{O}_2$  (30%),  $\text{HCl}$  (37%),  $\text{N,N}$ -dimethylformamide (DMF), ethanol were provided by Tianjin Guangfu fine Chemical Research Institute and used as received.

### 2.2. Preparation of APTMS-functionalized GO

Graphite oxide (GO) powder was prepared from natural graphite powders using a modified Hummers method [24]. Exfoliation of GO powder (100 mg) in the mixture of water and ethanol (50:50 by volume) (30 mL) was realized by ultrasonication for 1 h at room temperature. APTMS (1 g) was added and the mixture was refluxed at 70 °C for 24 h under  $\text{N}_2$ . After cooling to room temperature, the product was centrifuged and washed with absolute ethanol to remove the residual APTMS. The resulting APTMS-GO was dried at 60 °C for 24 h in a vacuum oven.

### 2.3. Preparation of APTMS-GO/PAA precursors

Typically, 2.0 mg of APTMS-GO was re-dispersed in 24 mL of DMF for 1 h by ultrasonication. The above suspension was added to a 100 mL three-necked flask followed by introducing 2.0 g of ODA. After ODA was dissolved completely, 2.2 g of PDMA was added. The mixture was stirred vigorously in an ice bath for 6 h under nitrogen to obtain viscous APTMS-GO/PAA solution with a solid content of 15 wt%. The precursors APTMS-GO/PAA solution was poured onto a clean glass plate and a film was cast using a doctor blade. For comparison, GO/PAA was also prepared using the same process. The intrinsic viscosity of all APTMS-GO/PAA and GO/PAA solutions was controlled at about 2.2 to avoid the negative effect of molecular weight to the mechanical properties of composites.

### 2.4. Preparation of APTMS-rGO/PI composite films

The cast films first were dried in a vacuum oven at 60 °C for 12 h to remove the residual solvent, and then heated to 100, 200 and 300 °C at a rate of 3 °C/min, respectively, and finally retained for 1 h to complete the imidization of PI and thermal reduction of GO. APTMS-rGO/PI film with a homogenous thickness of 50  $\mu\text{m}$  was obtained, and it was assigned to 0.05 wt% APTMS-rGO/PI, 0.1 wt% APTMS-rGO/PI, 0.3 wt% APTMS-rGO/PI, and 0.5 wt% APTMS-rGO/PI, respectively.

### 2.5. Characterization and instruments

FT-IR spectra were recorded using a spectrometer (Bruker Vector 22) in the transmission mode. The morphology of GO, APTMS-rGO and the fracture surface of PI composite was observed by field emission scanning electron microscopy (FE-SEM, S4800 Hitachi,

Japan) with an accelerating voltage of 10 kV. All samples were sputtered with gold prior to SEM analysis. Transmission electron microscopy (TEM, JEM-2100) was used to observe the dispersion state of rGO/PI and APTMS-rGO/PI composites under an acceleration voltage of 20 kV. Thin sections for the TEM observations were cut from the as-prepared films using a Leica ultramicrotome with a diamond knife. The thermal stability of PI composites was measured by thermal gravimetric analysis (NETZSCH STA 409, Germany) under a nitrogen atmosphere with a heating rate of 10 °C/min and a scanning range from room temperature to 800 °C. The tensile testing of the films was carried out on SANS-20 kN (China) with a crosshead speed of 5 mm/min at room temperature. Samples were cut into rectangular sheets with a dimension of 80 × 10 × 0.05 mm<sup>3</sup> and the tensile properties reported here were obtained from the average values of five testing results for each sample. Dynamic mechanical analyses (DMA) were performed on a DMA242C analyzer (NETZSCH, Germany). All the specimens were performed under a tension mode from 100 to 500 °C at a heating rate of 5 °C min<sup>-1</sup>, a frequency of 1 Hz, and static compressive stress of 4 N. Wide-angle X-ray diffraction (XRD) was carried out with a D8 DISCOVER (Cu K $\alpha$  radiation with  $\lambda = 1.54 \text{ \AA}$ , BRUKER AXS, US) at an accelerated voltage of 40 kV and a current of 150 mA. X-ray photoelectron spectroscopy (XPS) was conducted on a 60 (GENESIS EDAX, US) with Al K $\alpha$  radiation ( $h\nu = 1486.4 \text{ eV}$ ). Raman spectra for the graphite, GO and APTMS-rGO powders were obtained using a Renishaw 1000 Raman microprobe system (Renishaw, UK) with an Argon ion laser of wavelength 532 nm. To avoid PI matrix fluorescence, in situ dynamic Raman measurements of PI composite were performed (DXR Raman Microscope, USA) using the 780 nm of a 15 mW He–Ne laser. The laser power was 2 mW in order to avoid the down shift of G band of APTMS-rGO resulted from the heating effect of laser. Strains were applied to the samples by using a home-made actuator that was able to precisely stretch the samples to a predetermined length. Raman spectra were obtained at each strain level. A Gaussian profile was used to fit Raman bands.

## 3. Results and discussion

### 3.1. Structure analysis of APTMS-GO

Fig. 1 gives the detailed synthesis process of APTMS-GO, and FT-IR spectroscopy is used to characterize the structure of APTMS-GO (Fig. 2). The GO bands appear at 1726 cm<sup>-1</sup> (C=O stretching), 1623 cm<sup>-1</sup> (C=C stretching), 1226 cm<sup>-1</sup> (C–OH stretching), 1059 cm<sup>-1</sup> (C–O of epoxy stretching), respectively [25,26]. For APTMS-GO, the bands at 3432, 2921 and 2851 cm<sup>-1</sup> appear, arising from the N–H in amine groups and C–H in methylene groups in APTMS, respectively. The appearance of N–H deformation and twisting vibration at 1571 and 765 cm<sup>-1</sup> and the formation of Si–O–C band at 1076 and 691 cm<sup>-1</sup> demonstrate the reaction success of APTMS with GO [27,28]. Fig. 3 presents XPS result of APTMS-GO. GO only gives C1s and O1s peaks, however, C1s, O1s and Si2p peaks are shown in APTMS-GO. Furthermore, the curve-fitted peaks in Fig. 3b, where the peak at 285.6 eV and 283.7 eV is attributed to Si–O–C and Si–C, respectively, indicate the success reaction of APTMS with GO sheets. As shown in Fig. 4, graphite (Fig. 4a) shows a sharp diffraction peak 26.6°, corresponding to the graphitic face, while GO exhibits a broad diffraction peak at 10.2° ( $d = 0.86 \text{ nm}$ ) (Fig. 4b) [29]. After modified by APTMS, a smaller angle at 5.9° ( $d = 1.5 \text{ nm}$ ) in Fig. 4c is observed. The increased interlayer spacing of APTMS-GO sheets illustrates the successfully grafting reaction of APTMS with GO. Note that, however, a residual broader diffraction peak at 11.6° indicates the existence of partially unreacted GO.

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