



# Preparation of novel graphene oxide crosslinked azo polyurethane composite and its application in thermo-optic switch

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## ABSTRACT

A novel graphene oxide/azo polyurethane (GO/CBAPU) composite with 4,4'-bis(4-dihydroxy-phenylazo)-benzene (BDPB), R(-)-3-chloro-1,2-propanediol and IPDI as comonomers and functionalized with graphene oxide (GO), was prepared by polymerization reaction. The GO/CBAPU composite was characterized by FT-IR, UV-vis spectroscopy, <sup>1</sup>H NMR, SEM and TEM. The thermal and mechanical properties of GO/CBAPU composite were measured. Differential scanning calorimetry (DSC), thermo-gravimetric analysis (TGA) and mechanical properties of GO/CBAPU composite were investigated. Refractive index (n) of GO/CBAPU composite were measured at different wavelength (532 nm, 650 nm and 850 nm) and temperature by ATR technique; and the transmission loss of GO/CBAPU composite was characterized by CCD digital imaging devices. The results demonstrated that the thermo-optic coefficients (dn/dT) of GO/CBAPU are  $-19.400 \times 10^{-4}$  (532 nm),  $-8.660 \times 10^{-4}$  (650 nm) and  $-6.600 \times 10^{-4}$  (850 nm), and the transmission losses is only 0.1705 dB/cm. The Y-shaped and MZ-typed thermo-optic switches based on GO/CBAPU thermo-optic effect were simulated. The response times of the Y-shaped and MZ-typed thermo-optic switches are 0.2 ms and 0.01 ms, respectively. The conclusion has potential significance to provide an effective and promising method for preparing graphene oxide-based polymer composites.

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## 1. Introduction

Azobenzene, with two phenyl rings separated by an azo ( $-N=N-$ ) bond, serves as the parent molecule for a broad class of aromatic azo compounds. The p-electron delocalization of the extended aromatic structure can yield high optical nonlinearity, and azo chromophores have been extensively studied for nonlinear optical applications and second harmonic generation (SHG) [1,2]. Azo-polymers offer advantages over azo monolayers as superior materials in view of higher processability, the ability to form good free-standing films with a variety of thicknesses from nanometer to centimeter scales, in addition to

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flexibility in molecular design, and precisely controlled synthesis [3]. Hence, azo polymeric materials incorporating azobenzene moieties have attracted considerable attention owing to their potential technological applications, such as liquid crystal alignment, holographic image storage, micropatterning, optical switches and optical diffraction devices among many others [4]. However, the study found that the aromatic azo polymers of bis-azo the polymer shows more excellent performance than monoazo polymer, such as the better electrical storage function, the better optical performance, having ultra-high storage density and non-destructive readout characteristics [5–7].

Graphene is a two dimensional sheet of  $sp^2$  hybridized carbon atoms, arranged in a honeycomb fashion, and its sheets offer extraordinary electronic, thermal, mechanical properties [8]. In the molecular structure of graphite oxide (GO), there are plenty of hydroxyl and epoxy groups, which not only allow the good dispersion of graphite oxide in matrix, but also provide active sites to form chemical bonds, acting as an ideal interface between the graphene nanosheets and polymers [9]. Polyurethane (PU) is a flexible and elastic polymer, which is widely used in adhesives, thermoplastic elastomers and composites [10]. Due to the formation of chemical bond in the GO/PU composites, there is a strong interaction between the GO nanoplatelets and the hard segment of the PU, which allows effective load transfer [11,12].

Recently, optical switching devices, including electro-optic, magneto-optic and thermo-optic (TO) switches have received large attention for simple operation, large scalability and low cost [13–15]. Cao et al. [16] prepared graphene oxide-polyimide as waveguide material of TO switch and simulated power consumptions and response times of the Y-branch and Mach-Zehnder (MZI) interferometer polymeric TO switch. Yan et al. [17] designed a polymer/silica hybrid TO switch based on the MZI structure which can split light into two decoupled waveguides, a phase tuning section with 1 mm length in one of the waveguide, and the other 3 dB coupler acting as an output combiner. In this work, novel graphene oxide/azo polyurethane GO/CBAPU composite was prepared. The thermo-optic property, mechanical property, dispersion property and transmission loss of materials were investigated.  $1 \times 2$  Y-shaped and  $2 \times 2$  Mach-Zehnder (MZ-typed) polymeric thermo-optic switch were simulated and analyzed based on the GO/CBAPU composites.

## 2. Experimental

### 2.1. Preparation of graphene oxide/azo polyurethane (GO/CBAPU) composite

Graphene oxide was synthesized using the modified Hummers' method and was exfoliated by mild ultrasound for 5 h (Scheme S1, Supplementary data). A solution of  $\text{NaNO}_2$  in deionized water was slowly added to the solution of *p*-phenylenediamine in hydrochloric acid. Then, the diazonium salt solution was added to *m*-dihydroxybenzene and sodium hydroxide solution at  $0^\circ\text{C}$  and kept for 1 h. The dark-purple compound 4,4'-bis(2,4-dihydroxy-phenylazo)-benzene (BDPB) was obtained (yield: 72.3%; melting point:  $112.4^\circ\text{C}$ ).  $^1\text{H}$  NMR (DMSO- $d_6$ , ppm): 6.40–6.78 (ArH, 4H), 7.76–7.90 (ArH, 2H), 8.0–8.39 (ArH, 4H), 9.98 (–OH, 2H) and 11–12.26 (–OH, 2H).

A mixture of BDPB, R(-)-3-chloro-1,2-propanediol,  $\text{K}_2\text{CO}_3$  and KI dissolved in DMF was heated to  $105^\circ\text{C}$  and refluxed for 4 h. The resultant precipitate was filtered and the crude product was recrystallized twice with toluene. The azo chromophore compound 4,4'-bis[1,3-bis(1,2-dihydroxy-3-phenoxy)-4-diazenyl]-benzene (BBDPDB) was obtained (yield: 70.9%; melting point:  $115.6^\circ\text{C}$ ).  $^1\text{H}$  NMR (DMSO- $d_6$ , ppm): 3.45–3.58 (– $\text{CH}_2$ –, 16H), 3.76–3.87 (–CH–, 4H), 3.0–3.9 (–OH, 8H), 6.41–6.82 (ArH, 4H), 7.77–7.91 (ArH, 2H) and 8.0–8.39 (ArH, 4H).

GO and BBDPDB dissolved in DMF were added to flask at  $85^\circ\text{C}$ . IPDI and catalyst T-12 were added and the reaction mixture was stirred for 4 h. Then, DMF was evaporated under reduced pressure. The novel graphene oxide/azo polyurethane (GO/CBAPU) composite was obtained and filtered through a syringe with a 0.45 mm Teflon filter and spin-coated onto the hypotenuse face of a prism. The weight-averaged molecular weight ( $M_w$ ) and molecular weight distributions ( $M_w/M_n$ ) are 20,800 and 1.19, respectively (Scheme S2, Supplementary data).

### 2.2. Characterization

Ultraviolet-visible ((UV-vis)) spectra of samples were recorded with a Shimadzu (Japan) UV-2450 spectrometer at  $25^\circ\text{C}$ . The contents of GO, BBDPDB and GO/CBAPU composite in DMF were 3.0 mg/L. Fourier transform infrared (FTIR) spectra of samples were obtained on a KBr pellet with a Nicolet (USA) AVATAR 360 FT-IR spectrometer. A minimum of 32 scans was signal-averaged with a resolution of  $2\text{ cm}^{-1}$  in the  $4000\text{--}400\text{ cm}^{-1}$  range. Gel permeation chromatography (GPC) was performed in THF to determine molecular weights and molecular weight distributions,  $M_w/M_n$ , of polymer samples with respect to polystyrene standards using a WATERS SEC-244 system at  $25^\circ\text{C}$  in THF.  $^1\text{H}$ -NMR was recorded on an AVANCEII400MHz Bruker NMR spectrometer. Dimethyl sulfone- $d_6$  (DMSO) containing TMS as an internal standard were used as solvent. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out on a Netzsch (Germany) STA 449C instrument. The programmed heating range was from room temperature to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen atmosphere. The measurement was taken with 6–10 mg sample. The tensile strength and elongation at break testing for polymer film were carried out on a tensile tester (KY-8000A, Jiangdu Kaiyuan Test Machine, Jiangdu, China) at room temperature at a speed of 50 mm/min. All measurements had an average of three runs. The dumbbell-type specimen was 30 mm length at two ends, 0.2 mm thick and 4 mm wide at the neck. The hardness was measured with a sclerometer (KYLX-A, Jiangdu Kaiyuan Test Machine) (Jiangdu, China); measurements were done three times for the polymer sample, and the average value was calculated. The specific rotation was performed with an automatic polarimeter (Shanghai Precision

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