

Supporting Information (SI)

Interactions, Morphology and Thermal Stability of Graphene-Oxide Reinforced Polymer Aerogel Derived from Star-Like Telechelic Aldehyde- Terminal Benzoxazine Resin

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1. EXPERIMENTAL SECTION

1.1. Reagents

Graphite powder (micro 850) was kindly obtained from Asbury Graphite Mills, Inc. polyetheramine (Star-like jeffamine T-403, $M_n = 403$ g/mol) was kindly supplied by Huntsman. Tetraethylenepentamine (TEPA), 4-hydroxybenzaldehyde, 4HBA, (98%), and paraformaldehyde, (96%) were purchased from Sigma-Aldrich Chemicals (USA). Concentrated sulfuric acid (H_2SO_4 , 98%), potassium permanganate ($KMnO_4$ crystal), hydrogen peroxide (H_2O_2 , 30% aqueous solution), concentrated hydrochloric acid (HCl), and glacial acetic acid (CH_3COOH), 1,4-dioxane, chloroform, and dimethylsulfoxide (DMSO) were purchased from Fisher Scientific (USA). All chemicals were used without further purification.

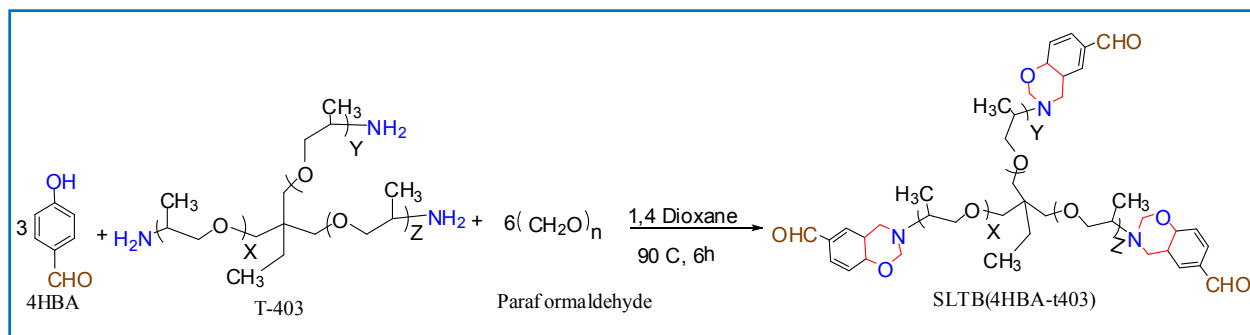
1.2. Preparation of Graphene Oxide (GO)

Graphene oxide was synthesized from natural graphite powder by the modified Hummer's method, as described in the literature.^{1,2} In brief, 3g natural graphite powder was added to 120 ml concentrated H_2SO_4 (98%) under stirring in an ice-bath (0 °C). Next, 15 g of $KMnO_4$ was added slowly under stirring. To control the temperature below 20° C, $KMnO_4$ was added gradually. The ice-bath was then taken-off and the system was heated at 35 °C for 2 h. Then, 250 ml deionized water was gradually added into the system and left under stirring for another 2 h. Then a solution of 700 mL deionized water with 120 mL 30 % H_2O_2 aqueous solution was added gradually to reduce the residual $KMnO_4$ till no bubble appeared. The color of mixture changed into brilliant yellow along with bubbling. The mixture was filtered and washed twice with 1:10 HCl aqueous solution (1L) to remove metal ions followed by 1 L of deionized water to remove acid. Finally, the solution was filtered resulting in a yellow-brown filter cake, which was washed by deionized

water until the pH value of the suspension reached near 7, and then graphene oxide was dried under vacuum for 48 h at 60 °C.

1.3. Preparation of Benzoxazine Precursor, SLTB(4HBA-t403)

The star-like telechelic benzoxazine (SLTB(4HBA-t403)) based on 4HBA and T-403 as shown in Scheme S1. Typically, T-403 (15 g, 34.09 mmol), 4-hydroxybenzaldehyde, 4HBA, (12.75 g, 102.27 mmol), paraformaldehyde, PF, (6.398 g, 204.55 mmol), and 1,4-dioxane 170 mL were introduced into a round 500 ml glass flask equipped with a condenser and a magnetic stirrer. The mixture was stirred at 90 °C for 6h. The product was precipitated in deionized water and filtered. The product was dissolved in chloroform and washed three times with 0.3 M NaHCO₃, and then washed three times with deionized water. The collected solution was dried using sodium sulfate anhydrous, and then the solvent evaporated using a rotary evaporator at 60 °C to give brown product of the benzoxazine monomer which is abbreviated hereinafter as SLTB(4HBA-t403) (24.68 g).



Scheme S1. Synthesis of star-like telechelic benzoxazine monomer, SLTB(4HBA-t403).

1.4. Characterizations

Fourier-transform infrared (FT-IR) spectroscopy was used to investigate the oxidation of graphene, polymerization of benzoxazine and the interactions between benzoxazine and graphene oxide. FT-IR spectra were obtained using a Bomem Michelson MB-100 FT-IR spectrometer with a dry air purging unit and a deuterated triglycine sulfate detector at a resolution of 4 cm^{-1} .

Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopy was used to conform the benzoxazine structure. $^1\text{H-NMR}$ spectra were taken on a Varian Gemini 2000 NMR operating at a proton frequency of 300 MHz. Deuterated chloroform was used as a solvent and tetramethylethylsilane was used as an internal standard.

2. RESULTS AND DISCUSSION

2.1. Preparation of Graphene Oxide, GO

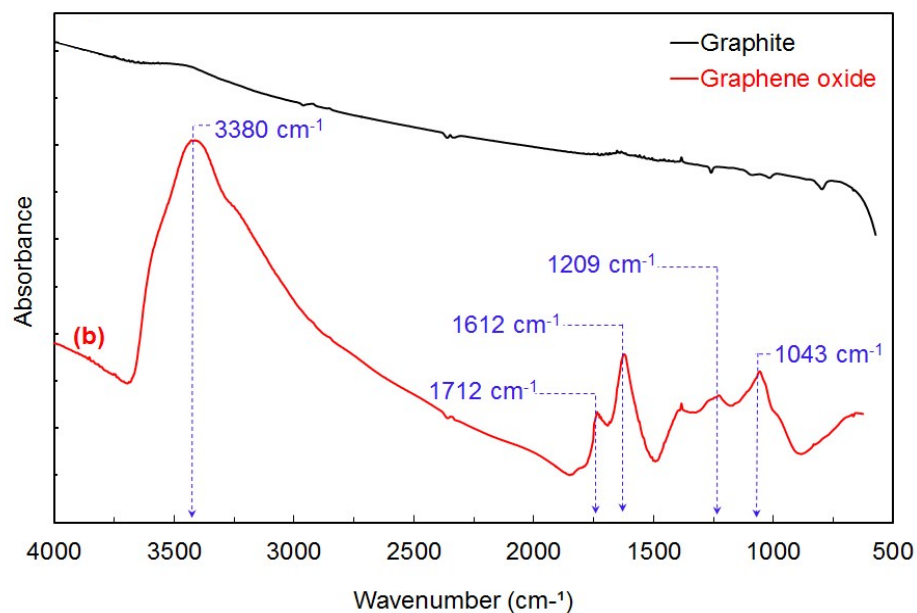


Figure S1. FT-IR spectra of: (a) graphite and (b) graphene oxide.

2.2. Confirmation and Polymerization of Benzoxazine Precursor, SLTB(4HBA-t403)

The structure of SLTB(4HBA-t403) has been confirmed by $^1\text{H-NMR}$ and FT-IR spectra. $^1\text{H-NMR}$ spectra depicted in Fig. S2 shows the characteristic resonances assigned to oxazine structure at 4.08 ppm (Ar-CH₂-N) and 4.98 ppm (N-CH₂-O).³⁻⁵ The aromatic protons were observed as multiple signals from 6.88 to 7.69 ppm.^{4,5} The resonance at 7.25 ppm is assigned to a solvent peak (chloroform) [4]. The resonance peaks in the range 3.3-3.7 ppm were assigned to the methylene of (O-CH₂-) groups of the poly(propylene oxide) structure. The signals from 1.1 to 1.3 ppm are due to the methyl group (-CH₃) in the poly(propylene block).^{6,7} The resonance at 9.83 ppm is assigned to the proton of the aldehyde group.^{8,9}

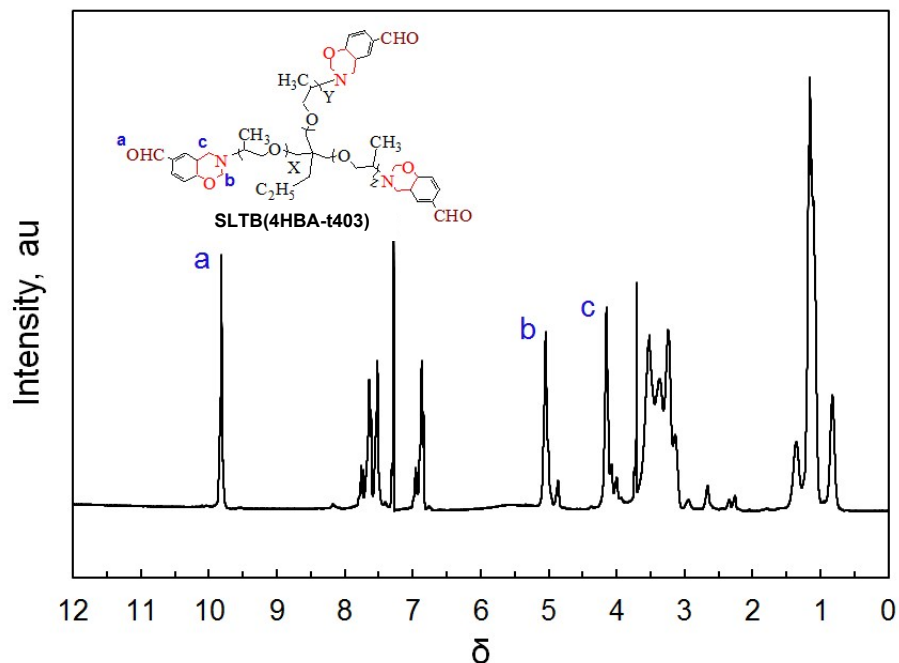


Figure S2 $^1\text{H-NMR}$ spectra of aldehyde star-like benzoxazine monomer, SLTB(4HBA-t403).

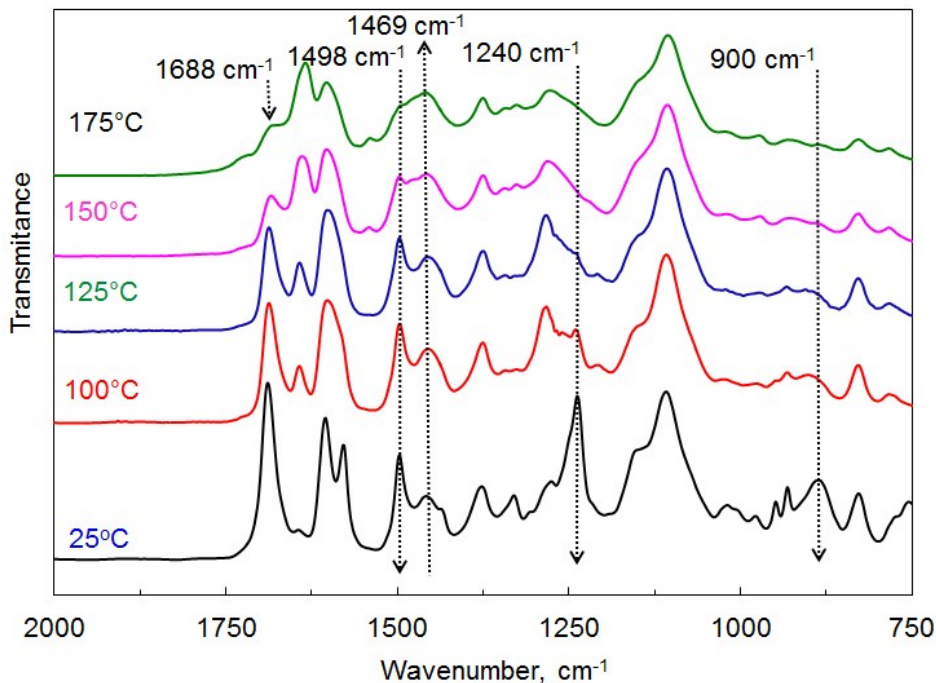


Figure S3 FT-IR spectra of aldehyde star-like benzoxazine monomer, SLTB(4HBA-t403). The FT-IR spectra were taken of casting a film from solution of monomer in chloroform onto a KBr crystal after each thermal treatment of 25, 100, 125, 150, and 175 °C for 2h/each.

FT-IR was used to confirm the formation and ring-opening polymerization of SLTB(4HBA-t403). Fig. S3 illustrates the room temperature spectrum of SLTB(4HBA-t403) along with the spectral evolution at various thermal treatments. The room temperature spectrum shows characteristic absorption bands of benzoxazine structure at 930 cm^{-1} due to the out-of-plane bending vibration of the benzene ring that is attached to the oxazine ring (C-H),³ and the bands at 1240 cm^{-1} due to antisymmetric stretching of C-O-C, and the wave-numbers at 1336 cm^{-1} (CH_2 wagging). Also the band at 1498 cm^{-1} that is attributed to the trisubstituted benzene ring was observed.^{4,5} In addition, the characteristic peak at 1688 cm^{-1} is due to the aldehyde groups on the monomer structure.^{8,9} Further, the strong absorption band can be detected at 1114 cm^{-1} , which is

ascribed to the antisymmetric (C-O-C) stretching vibration in polyether chain.^{6,7} As a result of thermal treatment of SLTB(4HBA-t403), the ring opening polymerization of benzoxazine led to the formation of cross-linked structure of poly(SLTB(4HBA-t403)) and the typical adsorption bands of benzoxazine were gradually reduced and almost disappeared with heat treatment, while tetra-substituted benzene mode at 1469 cm⁻¹ increased as shown in Fig. S3.³⁻⁵ Therefore, the change from tri-substituted to tetra-substituted benzene ring during the ring opening polymerization was confirmed.

2.2.1. Effect of GO on polymerization behavior of benzoxazine monomer

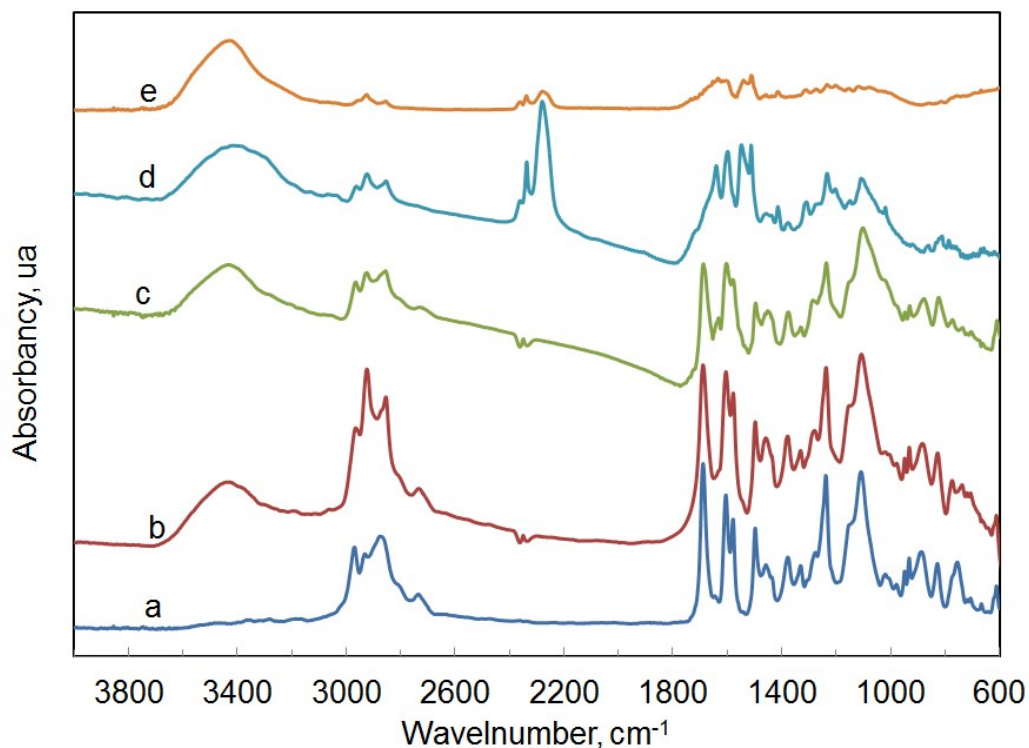


Figure S4 FT-IR spectra of SLTB(4HBA-t403)/GO-5% at various heat treatments: **(a)** neat SLTB(4HBA-t403) at 75 °C, **(b)**, **(c)**, **(d)**, and **(e)** SLTB(4HBA-t403)/GO-5% after heat treatment up to 60 °C, 160 °C, 175 °C, and 900 °C, respectively.

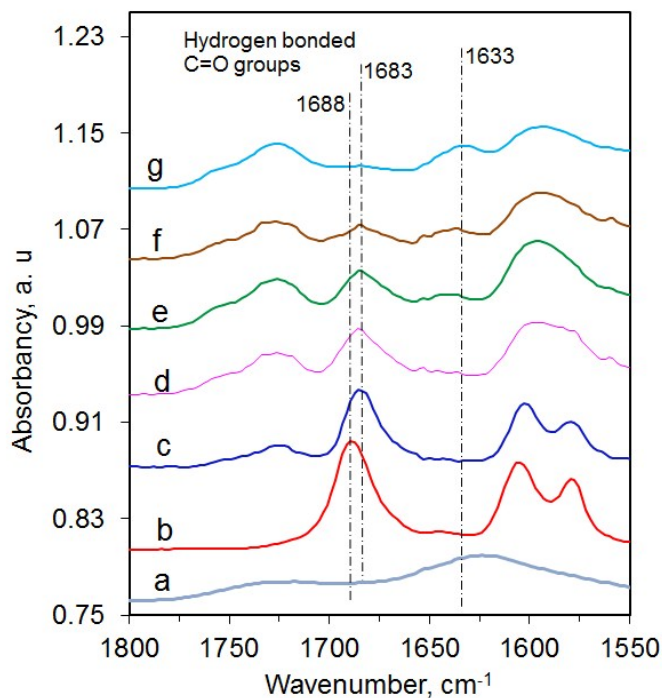


Fig. S5 FT-IR spectra of hydrogen-bonding of GO and SLTB(4HBA-t403) recorded at various temperatures between 1550 and 1800 cm^{-1} : (a) neat GO, (b) neat SLTB(4HBA-t403), (c), (d), (e), and (f) SLTB(4HBA-t403)/GO (40/60 weight percent) at 25, 100, 125, and 175 $^{\circ}\text{C}$, respectively.

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