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Amine-modified graphene oxide as co-curing agent of epoxidized polysulfide prepolymer: Thermophysical and mechanical properties of nanocomposites

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ABSTRACT

Amine-modified graphene oxide (GO) nanosheets were used to co-cure epoxy-terminated polysulfide pre-polymer and fabrication of polysulfide polymer/graphene nanocomposites. GO was modified with ethylenediamine (EDA) to obtain amine-functionalized reduced GO-EDA nanosheets. Besides, epichlorohydrin reacted with disodium tetrasulfide (Na_2S_4) to prepare epoxide-terminated polysulfide prepolymer. Different amounts of GO-EDA nanosheets were used to fabricate EDA-cured nanocomposites. Different properties of nanocomposites were investigated consisting of structural, thermophysical, thermal and mechanical properties. Also, in-plane tensile properties of samples were evaluated by a peel approach where a film of nanocomposites was exerted onto the surface of aluminum and adhesion was evaluated via ASTM D3039. Results showed that glass transition temperature (T_g), melting temperature (T_m) and enthalpy of melting (ΔH_m) of nanocomposites increased by increasing the amount of GO-EDA nanosheets up to 0.7 wt% whereas they were not changed significantly by more increase of nanosheets. Also, using 0.7 wt% GO-EDA led to the highest thermal stability, hardness and in-plane tensile properties of nanocomposites. In this field, variation of crystallinity of samples played the most important role in determining thermophysical and mechanical properties.

1. Introduction

Polysulfide polymers as sealants [1] and adhesives [2] have gotten much attention due to their excellent adhesion to different surfaces [3], resistance against to fuels and solvents due to S-S linkages [4], and high resistance to ozone and UV [5]. They are cured by various mechanisms utilizing their thiol functional groups consisting of curing via addition mechanism [6], oxidation curing [7], and curing via addition to epoxide groups [8]. Among epoxide compounds, epoxy resins with high Young's modulus and tensile strength have been widely used in industrial applications [9,10]. However, their brittleness and low resistance to formation of cracks restrict their applications in many industries [11]. To toughen epoxy resins, rubbers have been generally used as soft segments [12,13]. Polysulfide polymers are generally compatible with epoxy resins and physical mixing method has been widely used to prepare their blends [14,15]. However, an extra curing is necessary to fabricate blends with desired properties because reaction of thiols with epoxides has lower rate compared to other curing methods such as oxidative curing [16]. Moreover, epoxy resins are generally cured with amines in an appropriate reaction rate [17]. In this field, reaction of epichlorohydrin with disodium polysulfides leads to synthesis of epoxide-terminated polysulfide pre-polymers those can be cured with amine-containing compounds.

Among different nanostructures, graphene is one the most interesting nanostructures used in fabrication of nanocomposites [18,19]. Due to planar structure, graphene acts as barrier against different gases and improves thermal properties of polymeric matrices [20,21]. However, to avoid aggregation of graphene nanosheets, it is mostly used in oxidized form named graphene oxide (GO) [22,23]. To have better interactions with epoxidized structures, GO can be modified by amine-containing structures those can chemically react with epoxide rings to obtain a cured structure [24,25].

The aim of this work is synthesis of epoxy-terminated polysulfide pre-polymer which can be cured via amine groups instead of complicated curing methods of polysulfide polymers. Also, amine-modified GO nanosheets are used to co-curing pre-polymer to chemically introduce them into structure of nanocomposites. Briefly, GO nanosheets are modified with ethylenediamine (EDA) to obtain amine-functionalized reduced GO-EDA nanosheets. Also, epichlorohydrin reacts with disodium tetrasulfide (Na_2S_4) to prepare epoxide-terminated polysulfide prepolymer. Different amounts of GO-EDA nanosheets are used to fabricate EDA-cured nanocomposites. Due to existence of amine

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groups on the surface of nanosheets, they act as co-curing agents and covalently bonded to the polymeric matrix. Different properties of nanocomposites are investigated consisting of thermophysical, crystallinity, and thermal properties and hardness. Also, in-plane tensile strength of samples is measured by a peel approach where a film of nanocomposites was exerted onto the surface of aluminum and adhesion was evaluated via ASTM D3039.

2. Experimental section

2.1. Materials

Disodium polysulfide solutions were prepared by reaction of elemental sulfur (S, Merck, 98%) and sodium hydroxide (NaOH, Fakhr-Razi, 98%) as described previously [26]. Graphene oxide (GO) was produced by oxidation of graphite via improved Hummers' method [27]. Epichlorohydrin (ECH, DaeJung, 99%), ethylenediamine (EDA, Sigma-Aldrich, 99%), triethylamine (TEA, Sigma-Aldrich, ≥99.5%), *n*-hexane (Millipore, EMPLURA®), ethanol (Sigma-Aldrich, ≥99.8%), tetrahydrofuran (THF, Merck, 99%) were used as received.

2.2. Synthesis of epoxy-terminated polysulfide pre-polymer

Epoxy-terminated polysulfide pre-polymer named 1,4-bis(oxiran-2-ylmethyl)tetrasulfane (BOMTS) was synthesized by reaction of epichlorohydrin with Na_2S_4. Briefly, epichlorohydrin (6.2 mL, 0.079 mol) was added to Na_2S_4 solution (0.033 mol) under nitrogen atmosphere. After 1 h, synthesized pre-polymer was separated by filtration and washed with water several times. Finally, pasty yellow product was vacuum-dried at 40 °C for 24 h.

2.3. Modification of GO with EDA

To modify GO with EDA and prepare GO-EDA, GO (2.0 g) was dispersed in ethanol (100 mL) by sonication for 30 min. EDA (16.5 mL, 0.247 mol) and TEA (34.4 mL, 0.247 mol) was added and reaction was carried out for 72 h at 70 °C under nitrogen atmosphere. The obtained mixture was precipitated in *n*-hexane (300 mL) and GO-EDA nanosheets were separated by centrifugation. For further purification, GO-EDA nanosheets were washed several times with distilled water and finally dried at 60 °C under vacuum for 48 h. It is noteworthy that high amount of EDA is necessary to prevent the stitching of GO nanosheets to each other [28].

2.4. Fabrication of GO-EDA-containing nanocomposites

To fabricate nanocomposites, BOMTS (3.000 g, 0.0125 mol) was dissolved in THF (7.5 mL). Different amounts of GO-EDA nanosheets (0.1, 0.3, 0.5, 0.7 and 1 wt%) were added to the pre-polymer solution and completely dispersed using sonication for 30 min. After adding EDA (0.84 mL, 0.0125 mol), reaction was carried out for 24 h at 55 °C under nitrogen atmosphere. Resulting nanocomposites were vacuum-dried at 50 °C for 24 h. The resulting nanocomposites were named EDy where y is the wt% of GO-EDA nanosheets.

2.5. Instrumentation

FT-IR spectroscopy was utilized to investigate the presence of specific chemical groups in the materials. FT-IR spectra were recorded on a Bomem FT-IR spectrophotometer, within a range of 500–4000 cm^{-1} using a resolution of 4 cm^{-1}. An average of 32 scans has been reported for each sample. Cell pathlength was kept constant during all the experiments. The samples were prepared on a KBr pellet in vacuum desiccators. Raman spectroscopy as nondestructive method can be used to study the ordered and disordered structure of carbonaceous structures. Raman spectra were collected in the range from 700 to 3000 cm^{-1} using Bruker Dispersive Raman Spectrometer fitted with a 785-nm laser source, a CCD detector, and a confocal depth resolution of 2 μm. The laser beam was focused on the sample using an optical microscope. X-ray diffraction (XRD) was used to evaluate d-spacing of graphene nanosheets. XRD spectra were collected on an X-ray diffraction instrument (Siemens D5000) with a Cu target ($\lambda = 0.1540$ nm) at room temperature. The system consists of a rotating anode generator which operated at 35 kV and 20 mA. The samples were scanned from $2\theta = 2$ to 30° at the step scan mode; the diffraction pattern was recorded using a scintillation counter detector. Thermal gravimetric analysis (TGA) was used to investigate modification of GO nanosheets and thermal stability of nanocomposite. TGA was carried out with a PL thermo-gravimetric analyzer (Polymer Laboratories, TGA 1000, UK). The thermograms were obtained from ambient temperature to 600 °C at a heating rate of 10 °C/min. A sample weight of about 10 mg was used for all the measurements, and nitrogen was used as the purging gas at a flow rate of 50 mL/min. X-ray photoelectron spectroscopy (XPS) results were recorded on a Gammadata-Scienta Esca 200 hemispherical analyzer equipped with an Al Ka (1486.6 eV) X-ray source in an ultrahigh vacuum at pass energies of 20 eV for survey scan spectra. Differential scanning calorimetry (DSC) was used to study the thermophysical properties of nanocomposites. DSC was carried out using a DSC instrument (NETZSCH DSC 200 F3, Netzsch Co., Bavaria, Germany). Nitrogen at a rate of 50 mL/min was used as the purging gas. Aluminum pans containing 3 mg of sample were sealed using the DSC sample press. The sample was heated from −20 °C to 180 °C at a heating rate of 10 °C/min. T_g was obtained as the inflection point of the heat capacity jump. Surface morphology of powder samples was examined by scanning electron microscope (SEM, Philips XL30, Netherlands) with acceleration voltage of 25 kV. The Shore A hardness test is a fast and suitable method to evaluate the hardness of rubbers. The operation applied the force to the sample (12.5 N). The hardness tester (Shore durometer, Zwick/Roell-Germany) operated according to the ISO 7619-1: 2010 standard. The tested samples were 0.6 cm thick. The measured hardness for each sample was the average of five measurements at five different positions. Tensile tests were conducted via a peel test approach according to ASTM D3039 standard. To this end, a universal test machine (Zwick/Roell z010-Germany) was used and each test was repeated three times.

3. Results and discussion

GO nanosheets were modified with EDA to obtain GO-EDA nanosheets. Also, BOMTS as epoxide-terminated polysulfide prepolymer was synthesized via reaction of epichlorohydrin with Na_2S_4. Using different amounts of GO-EDA nanosheets, EDA-cured nanocomposites were achieved. Due to presence of amine groups on the surface of GO-EDA nanosheets, nanosheets can also react with pre-polymer to obtain matrix-grafted nanosheets. Therefore, both free chains obtained from reaction of EDA and pre-polymer and attached chains obtained from reaction of GO-EDA and pre-polymer present in structure of nanocomposites. The synthetic route to fabricate nanocomposites is shown schematically in Scheme 1.

3.1. Modification of GO nanosheets to prepare GO-EDA

GO nanosheets were modified with EDA to obtain GO-EDA nanosheets. Different characterizations were performed to investigate success of modification as results are shown in Fig. 1. In FT-IR spectrum of GO, stretching vibrations of oxygen-containing groups consisting of epoxide (C—O—C) at 1050 cm^{-1} [29], hydroxyl (—OH) at 1224 cm^{-1} [30], and carboxyl (—COOH) at 1724 cm^{-1} [31] are obvious. During reaction with GO nanosheets, EDA acts as a reducing agent for epoxide and hydroxyl groups in addition to reacting with —COOH groups [28]. Thus, the peak of C═O shifts to lower wavenumber and is merged with the peak of aromatic C═C bonds at 1640 cm^{-1} [32]. The peak of