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Graphene oxide-integrated high-temperature durable fluoroelastomer for petroleum oil sealing

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ABSTRACT

Two-dimensional one-atom thick graphene inspires intensive studies due to its great potentials in enhancing polymer's mechanical, gas/liquid barrier, and thermal properties. However, its poor dispersion within highly viscous rubber elastomers by conventional mill mixing posed significant technical challenges and hindered its vast applications. In this paper, graphene oxide (GO) enhanced fluoroelastomer (FKM) was solution-processed to enhance the mechanical and liquid barrier properties of FKM for the first time. Due to the chemical bonding, the GO/FKM performed 1.5-fold increment tensile strength compared with pure FKM and 1.2-fold increment tensile strength compared with Reduced Graphene Oxide/FKM at 150 °C. The reduced permeability of GO/FKM to organic solvent (such as methyl ethyl ketone) indicated the improved liquid barrier properties. This research provides a cost-effective solution process to efficiently enhance the thermal mechanical and liquid barrier properties of FKM with the addition of GO sheets through excellent dispersion techniques and strong GO-matrix bonding.

1. Introduction

During petroleum exploration and production, rubber-elastomer based oil seals are used widespread in assembling pipes and machinery to prevent oil leakage and gas infiltration. These rubber elastomers are required to exhibit excellent hardness, strength, chemical/water resistance, good elasticity and structural stability under both high and low temperatures and high pressures. Fluoroelastomer (FKM) has been widely used in those harsh environments due to their excellent heat and solvent resistance properties. Although the service life of most FKMs are theoretically up to thousands of hours even at 200 °C, they may still lose 30% of the tensile strength and 10% of the volume swell after exposure to oil for 70 h at 200 °C [1]. Water vapor and other gas adsorption could make them worse. Hence, new products of FKMs with enhanced performance is in needed.

In the recent years, different reinforcements, such as carbon black [2], silica [3], clays [4–6], and carbon nanotubes (CNTs) [5–7], have been added to enhance the mechanical, thermal, and electrical properties of FKMs. The reinforcement for FKM requires a high loading of the conventional filler, which introduced many side-effects in processing, curing, and applications. In contrast, significant enhancement of mechanical, and thermal properties can be achieved by adding novel nanomaterials at a small loading [7–10]. CNT-reinforced rubber elastomers as sealing materials in the oil industry have also been studied in the recent years and near-commercial products are currently available [7]. However, the low modulus and the prohibitively high processing cost of chemical vapor deposition (CVD) produced CNTs limits its application for mass consumption.

Graphene, a flexible one-atom-thick two dimensional graphite carbon nanostructure, has drawn a lot of attention due to its exceptional mechanical properties [8], electrical properties, and large surface area [9]. The recent research of mixing a small amount of graphene into natural rubber [10–12] proved that graphene is an excellent filler to improve the strength of rubber-elastomers. In comparison with other fillers, graphene offers the mechanical performance as high as CNTs at the price of clay fillers. Moreover, graphene demonstrates outstanding gas/liquid barrier properties [13]. Therefore, graphene is a very promising reinforcement material for novel elastomers with improved mechanical properties, thermal stability and gas/liquid barrier properties.

In order to reinforce the high-temperature mechanical properties of rubber elastomers [14], further functionalization on the plain 2D structure of graphene is commonly carried out to improve the dispersion and interfacial bonding. As the mechanical properties of vulcanized elastomer are mainly dependent on the crosslink density [15], the functional groups enable graphene to crosslink with different elastomers. Graphene oxide (GO) is a single-layer graphene with oxygen groups attached onto it. Different from the reduced graphene oxide (RGO), the allyl alcohol groups on the GO offer reactive sites with elastomers during vulcanization [16–18] and further provide a higher modulus and fracture

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strength in elastomer nanocomposites. Ultrasonic and subsequent co-coagulation approach has been proved to provide better dispersed fillers in silicate/rubber system [19], nanoclay/rubber composites [12,20] and graphene/natural rubber composite [11,21]. In this paper, different concentrations of graphene and GO nanoparticles were used to reinforce FKM. To the authors' knowledge, this is the first attempt to reinforce FKM by graphene or GO using the co-coagulation method. The effects of graphene or GO as fillers on the high-temperature mechanical properties and liquid barrier properties were investigated.

2. Experimental

2.1. Preparation of rubber nanocomposites

2.1.1. Preparation of graphene

The graphene oxide (GO) was produced by the modified Brodie's method, which is reported elsewhere [22]. In order to obtain reduced graphene oxide (RGO) powder, in which most of the oxygen groups were removed by reduction, the GO powder was first dispersed in pH 10.5 ammonia/water solution, then this solution was mixed with 50 μL hydrazine and stirred overnight. The resultant solution was dried at 70 °C to obtain RGO powder.

2.1.2. Solvent selection

Five different organic solvents (DMF: dimethylformamide, acetonitrile, Ethanol, DMSO: dimethyl sulfoxide, and NMP: N-methyl-2-pyrrolidone) were used for the solubility tests for both FKM and GO (or RGO). 1 g of FKM was dispersed in 30 ml of each organic solvent by stirring for 3 days. 1 mg of GO powder and RGO powder were dispersed into 30 ml of each organic solvent by 1 h tip-sonication, respectively. The theoretical analysis of the solubility was carried out according to the Hansen solubility parameter [23].

2.1.3. Mixing rubber nanocomposites

10 g of the FKM (FC 2260; Dyneon, 3M. Composition: di-polymer of vinylidene fluoride and hexafluoropropylene, plus cure site monomer. Fluorine content: 65.5%. Mooney Viscosity ML 1 + 10@121 °C: ~60 MV. Specific gravity: 1.80) and 1 g of GO (or RGO) was dispersed into acetonitrile separately. The GO (or RGO) suspension was prepared by tip-sonication for 1 h and the FKM suspension was prepared by stirring the suspension for 3 days. The FKM suspension was slowly poured into the GO (or RGO) suspension. After stirring for 4 h, the mixture was co-coagulated by pouring into large amount of DI water under strong mechanical stirring. In order to obtain the well-dispersed composites, the solids was collected by filtration and dried in an oven at 70 °C for 24 h. These composites were named as GO masterbatch or RGO masterbatch.

In order to achieve a better dispersion, the above-mentioned masterbatch were processed in a rheometer mixer (Haake Polylab with Rheomix Compounder, 450C). Different amounts of the GO/RGO masterbatch was mixed with neat FKM, 3 wt% $Ca(OH)_2$ and 2.5 wt% peroxide curatives (Luperox® 101XL45) to produce control (no master piece), 1 wt% GO/FKM, 2 wt% GO/FKM, 1 wt% RGO/FKM and 2 wt% RGO/FKM by weight fraction.

The commercial FKM, peroxide, and the masterbatch were mixed for 12 min at 80 °C and 80 rpm. Subsequently, the mixed pastes were compression molded and cured by hot press machine according to the ASTM D3182. The pastes were pre-cured on a hot-pressing machine at 177 °C, 5 MPa for 7 min. After that, the pre-cured pastes were post-cured at 235 °C for 24 h.

During pre-curing, the decomposition of the peroxide agency and crosslinking were initiated. Because the crosslinking is a diffusion-controlled process, it is not possible to achieve completed crosslinking at one temperature due at short curing period (normally less than 30 min). Because the increasing crosslinked network rising the glass transition temperature gradually and reducing the mobility of chains, the vulcanization slows down even if there are still non-reacted groups. In that case, the post-curing with elevated temperature and longer curing period (normally 16–25 h) is needed. During post-curing, the crosslink density further increased because polymer chains are re-activated to reach and react with the non-reacted groups.

2.2. Characterization

2.2.1. Characterization of GO and RGO

GO and RGO were characterized by Transmission Electron Microscopy (TEM, HITACHI T8100), Fourier-Transform Infrared (FT-IR, Nicolet iS10) and X-ray photoelectron spectroscopy (XPS, PHI5000 Versa Probe). The vulcanization was analyzed with an oscillating disc rheometer (ODR, Akron Rubber Development Laboratory, Inc.) at 177 °C according to ASTM D2084.

2.2.2. Measurement of crosslink density and barrier properties

The crosslinking densities of the vulcanized composites were measured by the swelling tests in MEK (methyl ethyl ketone). The mole percent uptake Q_t for solvent after t min immersion was determined using:

$$Q_t = \frac{(M_t - M_0)/MW}{M_0} \times 100 \tag{1}$$

where M_t is the mass of the sample after t min of immersion, M_0 is the initial mass of the sample, and MW is the molecular weight of the solvent. The sorption was plotted as the Q_t *vs.* $t^{1/2}$ and the diffusion and permeability coefficients were calculated according to the plot [24–26]. The crosslink density was calculated according to ASTM D6814 [27]. The polymer solvent interaction parameter (χ) was calculated to be 1.31 at 25 °C [28,29].

2.2.3. Measurement of mechanical properties

The tensile tests were performed on a Universal Tester (AGS-X, SHIMADZU) at room temperature (25 °C), 75 °C and 150 °C in a temperature control chamber. Five ASTM D412 type D specimens were measured to obtain the average value of tensile strength, elongation, and stress at 100%, 200%, and 300% strain (M100, M200, and M300) at 250 mm/min stretch rate until breakage. Each sample was kept in the constant temperature-controlled chamber before tests (for 20 min) and during tests (till breakage). The morphology and the element analysis of their rupture cross-section was also investigated using Scanning Electron Microscopy (SEM, HITACHI S4300).

3. Results and discussion

3.1. Characterization of GO and RGO

As-synthesized GO and RGO were characterized by TEM, FT-IR, and XPS. As shown in the TEM images in Fig. 1(a) and (b), the GO and RGO were mostly single-layer graphene based nanoribbons with the size of about 100 nm × 600 nm. The chemical structures of the GO and RGO were investigated by FT-IR. As shown in Fig. 1(c), epoxy groups (1390 cm^{-1}, 1060 cm^{-1} and 946 cm^{-1}), carboxyl group (1260 cm^{-1}, 1720 cm^{-1} and 3400 cm^{-1}), and aromatics (1560 cm^{-1}) exist in the as-prepared GO [30,31]. Compared with the GO, the intensity of above-mentioned oxygen functional groups were significantly reduced in the RGO. The similar situation was also confirmed by the XPS spectra. As seen in the survey (d) and the C1 of GO (e) and RGO (f). The C/O ratio of atomic