



# Constructing interconnected graphene network in fluoroelastomer composites by F-H polar interaction for enhanced mechanical and barrier properties



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## ABSTRACT

Graphene is one of the most promising fillers for functional nanocomposites due to its high strength, high conductivity and high specific surface area, etc. However, its poor interfacial compatibility makes it difficult to simultaneously satisfy high strength and low gas permeability of nanocomposites. Herein, we proposed a novel strategy to regulate interfacial adhesion by fluorine-hydrogen (F-H) polar interaction in the FKM composites. The F-H polar interactions effectively induce the graphene oxide (GO) interact with the chain of fluoroelastomer (FKM) in spatial arrangements on molecular-level, promoting the construction of interconnected GO network. Specifically, a 10-fold increase in tensile strength of FKM/GO-5 with the incorporation of 5 phr GO is realized compared with pure FKM, and the oxygen permeability of FKM/GO-5 decreases by 79%. At the same filler contents, FKM/GO-5 composites exhibit higher mechanical property and lower gas permeability compared with FKM/rGO composites. Such enhanced performances make FKM/GO composites with an interconnected network very competitive for potential applications as multi-functional structural materials. The proposed strategy provides a novel effective approach for developing and designing the high-performances fluorine-based polymer nanocomposites.

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## 1. Introduction

Functional elastomer composites with high strength and lower gas permeability have been widely used in seals, shock absorbers, electronic packaging and battery electrodes separation membrane et al. [1–4]. Generally, the incorporation of functional filler into the elastomer have been widely explored to achieve satisfactory performance for meeting the demands in practical application [5–7]. The challenge for obtaining the high-performance elastomer composites lies in the regulation of filler-polymer interfacial adhesion and the design of effective filler network in the elastomer matrix. V. Bocharova et al. reported the polarity covalent bond strongly influence the interfacial dynamics of polymer nanocomposites [8]. C. W. Macosko et al. incorporated the graphene in polyurethane with hydrogen bonds interaction [9]. These results illustrate that the polar interaction bonds can improve the filler-polymer interfacial interaction, contributing to the reinforcement of composites. Despite this interest, it should be noted that it is

difficult to simultaneously endue the elastomer with high strength and low gas permeability by the aforementioned strategies. However, M. Lavorgna and J. R. Potts et al. reported the filler network have higher performance on lower gas permeability with lower filler content, compared to the none-network structure [10,11]. Unfortunately, these filler network structures always exhibit inferior mechanical properties, poor interfacial interaction and highly difficult to organize the filler in spatial arrangement without defects [12–14]. Therefore, it is a great challenge to enhance adhesion of fillers in network composites and simultaneously realize high strength and low gas permeability.

Particularly, the polar interaction bonds contain covalent and noncovalent bond, while the covalent bond needs the rigorous reaction conditions and complicated process that limit its application [15,16]. Noncovalent bond including hydrogen bonds,  $\pi$ - $\pi$  interactions and dipole-dipole interactions have great advantages in simple condition and low-cost process to realize the network construction and regulate the interface interaction with high strength [17–19].

Graphene oxide, a single layer of carbon atoms with large numbers of hydroxyl, carbonyl and epoxy group, has been the

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subject of considerable interest and study because of its excellent mechanical flexibility and chemical/physical properties [20]. As expected, graphene oxide holds promising applications in advanced elastomers by virtue of its potential to efficiently endow neat elastomer with reinforcement and functional properties in different spatial arrangements.

In this contribution, we report a novel strategy to regulate the interfacial adhesion that GO sheets along with the FKM molecular chain arrangement by F-H noncovalent bond, further endowing the fabricated composites with high strength and low gas permeability. This unique interconnected network not only greatly reduce the agglomeration of GO, but also effectively improve the interfacial interaction, results of which are mainly attributed to the formation of the strong F-H polar interaction in the FKM/GO system. Additionally, the gas permeability interconnected network effected by the enhanced interfacial adhesion has also been investigated. This novel strategy exhibits highly competitive for developing advanced elastomer applying to seals, electronic packaging and battery electrodes separation membrane, etc.

## 2. Experimental section

### 2.1. Materials

Fluoroelastomer (vinylidene fluoride, hexafluoropropylene, and polytetrafluoroethylene, fluorine content: 66%. Mooney Viscosity ML1+10: 120 °C), was purchased from ChengDu SEEFAR Co. Ltd. The GO was synthesized from natural graphite powder by a modified Hummers method. DMAc: dimethylformamide, Magnesium oxide (MgO), Hexafluorobisphenol and benzyl triphenyl phosphorus chloride were provided by sigma.

### 2.2. Self-assembly process

Self-assembly process of FKM/GO nanocomposites by F-H strong polar interaction is displayed in Scheme 1. Graphene oxide (GO) suspensions were firstly obtained by the modified Hummer method and ultrasonic assisted process previously reported by our group [21]. And the FKM completely dissolve in DMAc with weight ratio of 2:3 under reflux at 105 °C for 4 h [22]. Then the GO suspensions (1 mg mL<sup>-1</sup>) were dropwise added into mixture and stirred for 24 h at 105 °C, to obtain the FKM/GO, FKM/GO-x, herein, x denotes the GO content in the composites. In the experiment, x was controlled to be 0.5 phr, 1 phr, 3 phr, 5 phr. Subsequently, all the rubber additives and 300 mL water were subjected to the ball milling, and the stable and homogeneous aqueous dispersions were poured into the mixture and stirred for 1 h at 105 °C. Finally, the obtained reaction compounds were transfer into an oven at 60 °C for 48 h for completely removing the DMAc and deionized water.

### 2.3. Preparation of FKM/GO composites

The obtained FKM/GO composites were vulcanized by hot press machine according to the ASTM D3182. The composites were prepared at 177 °C, 10 MPa under the cure time (T90). After that, the procured samples were post-cured at 235 °C for 24 h, and the thickness of all the samples are about 220–235 μm. For comparison, the GO was reduced to remove functional groups for preparation of the reference FKM/rGO-x, herein, x was also controlled to be 0.5 phr, 1 phr, 3 phr, 5 phr under the same conditions.

### 2.4. Characterization

Fourier transform infrared spectroscopy (FT-IR) spectrum was tested on a Bruker Vertex Fourier Transform Infrared Spectrometer.

The X-ray photoelectron spectroscopy (XPS) was measured on Axis Ultra DLD using a Mono Al K $\alpha$  radiation of 1486.6 eV. Scanning electron microscopy (FESEM) was analyzed by a Nova NANOSEM 430. Transmission electron microscopy (TEM) was conducted on a JEOL2100 microscope. The crosslinking rate was determined using a U-CAN UR-2030 vulcameter (Taiwan). The crosslinking density was obtained via an equilibrium swelling experiment based on the Florye-Rehner equation with toluene as the solvent. The dynamic mechanical analysis was employed to analyze the interfacial interaction by a TA DMA Q800 instrument under a tensile Mode with a dynamic strain of 0.5%. The samples were scanned from -115 to 95 °C and the frequency and heating rate were fixed at 5 Hz and 3 °C/min, respectively. The characteristics of mechanics were carried out by high precise tensile machine (KJ-1065A), with tensile strain rate from 0.01 to 500 mm/min, and detection precision reach to 0.01 N. The gas barrier property was measured by on the gas transmittance tester (PSG-66) by the pressure-difference method.

## 3. Results and discussion

### 3.1. The confirmation of F-H polar interaction

To confirm the F-H polar interaction, FTIR spectroscopy was employed to analyze the chemical characteristics on surface of GO and FKM/GO composites, as shown in Fig. 1a and b. Compared with pure GO and FKM, FKM/GO exhibit characteristic vibration peaks at 1725 cm<sup>-1</sup>, 1182 cm<sup>-1</sup> [23], 2847 cm<sup>-1</sup> and 3450–3300 cm<sup>-1</sup>, which are attributed to -COOH, F and C-H, -OH stretching vibration under the electron acceptor (F) and electron donor (H) interaction on self-assembled process, respectively. Because F shows the strong electro negativity, while the H shows contrary electro positivity, once the electron acceptor (F) and electron donor (H) gain enough energy and adequate distance, which enables the formation of stabilizing electrostatic interaction, and the Hartree-Fock calculations and Mulliken partial charge data suggest that there is a large electrostatic interaction between the electro negativity and electro positivity on hydrogen bonds and  $\pi$ - $\pi$  interactions et al. [22,24,25] Furthermore, the heat treatment was adopted to rupture electrostatic interaction, as expected, the characteristic vibration peaks of FKM/GO were returned to the normal vibration (-COOH at 1720 cm<sup>-1</sup>, C-H at 2852 cm<sup>-1</sup>, and -OH at 3350–3150 cm<sup>-1</sup>) [26]. These features indicate the presence of electron donor (H) of -COOH and -OH potential bond with the electron acceptor (F), which promotes the formation of the F-H polar interaction.

In order to further verify the F-H interaction, XPS was conducted to evaluate the variation of fluorine electronic energy. The F1s deconvolute spectra for neat FKM and FKM/GO were shown in Fig. 1c and d, respectively. For neat FKM, the characteristic peak of C-F located at 686.25 eV is observed [27]. After self-assembly process, a new peak raise at the binding energy of 687.6 eV, which indicates that the F electronic energy is intensely affected by electron donor (H) originated from GO.

### 3.2. Morphology and structure

The effect of F-H polar interaction on the self-assembly behavior between the GO and FKM was further investigated by the SEM. In Fig. 2a, the glazed surface of pure FKM is different from the self-assembled composites, indicating the intrinsic morphology of FKM. As shown in Fig. 2b, it is clear that the surface of the FKM/GO-3 composite is rough, which are attributed to the FKM molecules wrapped with GO sheets. It is noteworthy that the self-assembly behavior derived from the strong F-H polar interaction effectively contributes to that GO nanosheets spread along the FKM chains,

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