



# Identical steady tribological performance of graphene-oxide-strengthened polyurethane/epoxy interpenetrating polymer networks derived from graphene nanosheet



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## ABSTRACT

Graphene-oxide-hybridized polyurethane/epoxy interpenetrating polymer networks (PU/EP IPNs) are prepared through an *in-situ* polymerization. The results showed that the mechanical performance of graphene-oxide-hybridized PU/EP IPNs is improved due to the formation of chemical bonds between graphene oxide nanosheet and polyurethane/epoxy segments, affording the loading transfer from polymer matrix to graphene oxide nanosheet. The average friction coefficient in the steady stage is decreased about 30.2% from neat PU/EP IPN to graphene-oxide-hybridized PU/EP IPNs. Especially, the specific wear rate is decreased about two orders of magnitude from neat PU/EP IPN to graphene-oxide-hybridized PU/EP IPNs. Interestingly, graphene-oxide-hybridized PU/EP IPNs have the same friction coefficient in the steady stage, independent of graphene oxide content. The identical steady friction coefficients are derived from the same friction bodies in three-body friction model, such as graphene-oxide-strengthened PU/EP IPN surface, metallic counterpart and graphene-oxide-wrapping polymer particles as wear debris in the transfer film.

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## 1. Introduction

The tribology, being involved in friction, lubrication and wear, is being paid much attention because the most of energy exhaustion takes place in the process of friction. It is well known that polymer materials have been widely applied as an important material category. Out of question, the polymer tribology will become more and more significant subject, not only in the macroscopic scale [1–3] but also in the microscopic nanoscale [4,5]. Usually, the polymer friction depends on the dynamic rearrangement of outermost polymer segments at shearing interfaces [6]. Accordingly, the modification on the polymer surface will become an important issue to improve the tribological performance of polymer materials [7] by regulating the fundamental surface energy dissipation [8]. Notably, the low friction efficient [9–11], even negative friction efficient [12], has been achieved through the application of carbonaceous materials, such as carbon nanotube,

graphite and graphene. Therefore, the effect of carbonaceous materials on the tribological performance of polymer materials becomes an interesting subject, which is also studied in metal-on-metal tribology [13].

Graphene is being widely studied in recent years owing to its outstanding properties [14,15], such as large surface area, superior tensile strength, high flexibility, good thermal conductivity and remarkable electron-transporting property. The tribological characteristics of mechanically exfoliated monolayer graphene have been carefully investigated at the nanoscale by friction force microscopy [16]. Nevertheless, the effect of graphene on the tribological property of bulk polymer materials has a crucial significance for practical application. At present, graphene has been applied to prepare the polymer composites by combining with epoxy (EP), polymethylmethacrylate, polypropylene, polyethylene, polystyrene, Nylon and silicone rubber [17]. Considering the compatibility between graphene and polymer matrix, graphene oxide (GO) is more preferred at this occasion instead of pristine graphene on account of the potential interaction/reaction of hydroxyl, epoxy, carboxyl and ketone groups on the GO nanosheet with the polymers [18–21]. The current investigations exactly showed that GO is

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remarkably able to improve the mechanical property of polymer composites [22–25]. Due to Lancaster–Ratner correlation between mechanical property and wear resistance [26], GO should also have an evident improvement on tribological property of polymer composites. For example, the wear resistance is significantly enhanced by the addition of GO into epoxy with the specific wear rate reduced about 90.0–94.1% at the GO content of 0.5wt% comparing with the neat epoxy [27]. In addition, GO is also used as a wear-resistant nanofiller for ultrahigh molecular weight polyethylene [28], polymethylmethacrylate [29], monomer-casting nylon [30], nitrile rubber [31], poly(ether ether ketone) [32], thermosetting polyimide [33]. Usually, the formation of interpenetrating polymer networks (IPNs), which consist of two polymer networks holding together by permanent covalent entanglement, is an effective way to combine the respective outstanding properties of different polymer materials. The excellent synergistic effect in mechanical properties has been achieved in PU/EP IPNs due to their good compatibility between polyurethane (PU) and epoxy (EP) [34,35]. The wear resistance of PU/EP IPNs can be also improved a lot by the addition of nanodiamond comparing with neat PU/EP resin or PU/EP IPNs [36,37]. To the best of our knowledge, the effect of GO on the tribological property of PU/EP IPNs is not yet reported up to now although the mechanical and thermal properties of PU/GO/EP composites has been investigated [38].

In this work, GO-hybridized PU/EP IPNs are prepared through an *in-situ* polymerization on the GO nanosheet. The GO effect on the wear resistance of PU/EP IPNs is investigated in detail. Interestingly, GO-hybridized PU/EP IPNs with different GO contents have an approximately equal friction coefficient, which come from the same friction bodies in three-body friction model, such as GO-strengthened PU/EP IPN surface, metallic counterpart and GO-wrapping polymer particles as wear debris in the transfer film. Simultaneously, the friction coefficient is also decreased about 30.2% and the specific wear rate is reduced about two orders of magnitude from neat PU/EP IPN to GO-hybridized PU/EP IPNs.

## 2. Experimental

### 2.1. Materials

Graphite powders is purchased from J&K Chemical Co. Ltd. Phosphoric anhydride ( $P_2O_5$ ) and biphenol A are obtained from Sinopharm Chemical Reagent Co. Ltd. Potassium persulfate ( $K_2S_2O_8$ ), sulfuric acid ( $H_2SO_4$  98%), potassium permanganate ( $KMnO_4$ ) and hydrogen peroxide ( $H_2O_2$ ) are purchased from Tianjin Chemical Reagent Factory. PU with the NCO content of 4% is supplied by Institute of Chemistry, Henan Academy of Sciences. 3, 3'-Dichloro-4, 4'-diamino-diphenyl methane (MOCA) is purchased as curing agent from Suzhou Xiangyuan Special Fine Chemical Co. Ltd. Dimethyl silicone is purchased as defoaming agent from Shandong Dayi Chemical Co. Ltd. All the materials are technical grade and used without further purification.

### 2.2. Testing methods

Graphene oxide (GO) is respectively analyzed by scanning electron microscope (SEM, Quonxe-2000) and atom force microscope (AFM, SPA-9500J3). FT-IR is employed to investigate the curing reaction of PU/EP IPNs. Its sample is prepared as following: the mixture of PU, GO/EP precursor and MOCA are diluted with acetone and then evenly spread on the surface of KBr sheet. Thermal stability is tested by thermogravimetric analysis (TGA, Peking Optical Instrument Factory, WCT-2) with a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  in air condition ( $10\text{ ml}/\text{min}$ ). Dynamic thermomechanical analysis

(DMA, NETZSCH, DMA242C) is detected to investigate the dynamic mechanical properties by using the compassing mode at a frequency of 1 Hz and at a heating rate of 3  $^\circ\text{C}/\text{min}$ . Tensile strength is measured by tensile instrument (Jinan Faen Instrument Factory, WDW-S) according to GB/T 528-1998. Wear resistance is studied by a pin-on-disc friction wear testing machine (Lanzhou Zhongke Co. Ltd., QG-700) at room temperature without any lubrication [23]. The counterpart pin is fabricated by steel with a diameter of 5 mm. The normal load and sliding speed are 0.4 MPa and 0.5 m/s, respectively. Experimental data are collected within 120 min in wearing the disc-like samples with a diameter of 60 mm and a thickness of 5 mm. The worn surface and fracture morphologies of GO-hybridized PU/EP IPNs are observed by SEM.

### 2.3. *In-situ* synthesis of GO/EP precursor [38].

GO is synthesized from graphite through a modified Hummers method according to our previous procedure and kept in deionized water as a suspension form [39]. The GO suspension is directly mixed with biphenol A (44.0 g) and epoxy chloropropane (55.9 g) according to different GO contents, such as 0.05wt%, 0.1wt%, 0.15wt% and 0.2wt%. The mixture is stirred for 1.5 h, followed by 30-min ultrasonication. Then, the mixture is heated to  $75\text{ }^\circ\text{C}$ . After biphenol A is completely dissolved, 28wt% sodium hydroxide (NaOH) hydrous solution is dropped under stirring within 40 min. Continuously, the reaction is carried out for 1.5 h. Distilled water (60 ml) and benzene (120 ml) are added in turn to extract the unreacted substances when the resultant mixture is cooled to room temperature. By static settlement, the water layer is removed. Then, the remainder is washed by deionized water until no chloride ion could be detected. GO-hybridized EP (GO/EP) precursor is obtained after removing the residual solvents under a reduced pressure. The epoxide number of resultant precursor is determined to be 0.43.

### 2.4. Preparation of GO-hybridized PU/EP IPNs

The stoichiometric amount of GO/EP and PU precursors, melt MOCA, defoaming agent are added in turn and then homogenized, degassed, cured by two stages according to the previous preparation procedure of PU/EP IPNs [23]. The first stage is carried out at  $70\text{ }^\circ\text{C}$  for 3 h for prepolymerization and the second stage at  $120\text{ }^\circ\text{C}$  for 4 h for complete curing. The EP content in PU/EP IPNs is fixed to 30wt% according to our previous work [36]. The neat PU/EP IPN is also presented by the similar procedure for comparison.

## 3. Results and discussion

GO-hybridized PU/EP IPNs are herein prepared through an *in-situ* polymerization with an aim to improve the mechanical and friction properties of PU/EP IPNs. First of all, GO is synthesized through a modified Hummers method according to our previous work [39]. The atom force microscope (AFM) and scanning electron microscope (SEM) observations in Fig. 1 respectively show the monolayer structure (0.65 nm) and wrinkled texture of GO nanosheet, providing a precondition for oxygen-containing groups (epoxy, carboxyl, hydroxyl, etc. [18–21,38]) on the ample large surface area to react with biphenol A and epoxy chloropropane affording GO/EP precursor with an epoxide number of 0.43 as shown in Fig. 2. Here, the GO content is set to be 0.05wt%, 0.1wt%, 0.15wt% and 0.2wt% in order to adjust the amount of reactive GO surface, which will affect to a large extent on the outcome of mechanical and tribological improvement. Finally, the resulting GO/EP precursor stoichiometrically react with PU precursor under the action of melt 3, 3'-dichloro-4, 4'-diamino-diphenyl methane (MOCA) as a curing agent, producing a series of GO-hybridized PU/EP IPNs with different

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