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Preparation and lubricating properties of poly(vinylidene-fluoride) particles wrapped by reduced graphene oxide

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ABSTRACT

Graphene-based composites are good candidates for improving tribological performances. This study describes preparation process and mechanisms of poly (vinylidene-fluoride) (PVDF) particles wrapped by reduced graphene oxide (RGO) in a solution. Meanwhile, characterization techniques combining SEM, TGA, FT-IR, XRD, and XPS revealed reduction of PVDF diameters and successful integration between PVDF particles and RGO sheets. Tribological properties of RGO/PVDF nanocomposite as lubricating additive were investigated, and control experiments were performed by respectively adding PVDF, RGO as well as the mixture of PVDF and RGO. It is found that RGO/PVDF nanocomposite exhibits the best lubricating performances among all the samples and that the average friction coefficient as well as wear rate decreased by 44.4% and 98.7% compared with that of paraffin oil.

1. Introduction

Nano scaled particle additives are becoming very promising lubricant additives due to many advantages including their special size. Generally, they can enhance tribological behaviours by tribofilm formation, rolling between friction pairs, mending effect and polishing effect [1,2].

Over the past few decades, the studies about micro and nano particles as lubricant additives are mainly focused on inorganic substance. Since Novoselov et al. firstly found graphene in 2004 by micromechanical cleavage method [3], many researchers have put attention on graphene-related fields because of its excellent thermal and mechanical properties. These wonderful properties of graphene enable it become a promising candidate in various applications such as sensors, solar cells, electrodes, nanocomposites and electrical devices [4–8]. Moreover, graphene has been regarded as a remarkable candidate as lubricant additives for reducing friction, adhesion, and wear [9–12]. Furthermore, various graphene-based composites are reported to hold better tribological properties as lubricant additives than individual components [13–18]. For example, Song et al. synthesized α-Fe2O3 nanorod/GO composites and found that the oil with α-Fe2O3 nanorod/GO composites showed better tribological properties [13].

Graphene-wrapping composite is a kind of graphene-based composites and holds some potential merits for tribological application. For instance, graphene-wrapping nanoparticles can confine nanoparticles within individual carbon shells, thus tackling the aggregation problem and improving the tribological properties [19–22]. PVDF is a kind of functional semi-crystalline polymer [23–25], which has been used as membranes [26,27] and lubrication materials [28]. PVDF holds some advantages such as lightweight, flexible, biocompatible and electroactive [29]. Some efforts have already been payed to synthesize poly (vinylidene-fluoride) (PVDF)/functionalized graphene nanocomposite [26,30] and PVDF nano-spheres [31–33]. However, to our best knowledge, research about graphene wrapping PVDF has not been reported yet. Since both RGO and PVDF hold good lubrication property, RGO wrapping PVDF nanocomposite is expected to show excellent tribological properties.

Herein, a highly flexible technique is proposed to fabricate encapsulated RGO/PVDF composite in a solution. For encapsulated structure, RGO sheets function as carbon shells for PVDF particles and trace amounts of acetanilide (AA) was utilized as special adhesives between RGO and PVDF. AA with imino groups is a key intermediation during many chemical syntheses [34–36]. The refined PVDF particles were wrapped by graphene successfully via crystallization under hydrogen bond aiding. Trace amounts of AA were adhesive on PVDF particles, improving the connection between RGO sheets and PVDF as

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well as blocking the growth and accumulation of PVDF particles. Subsequently, the prepared RGO/PVDF nanocomposite was used as additives in paraffin oil for steel/steel contacts to explore its tribological properties.

2. Experimental

2.1. Materials

PVDF (FR905, molecular weight, 524 kD) was purchased from Shanghai 3F New Materials Co., Ltd. (Shanghai, China). AA was purchased from Tianjin FuYu Fine Chemical Co., Ltd. (Tianjin, China). THF and hydrazine hydrate were purchased from Tianjin FuChen Chemical Regents Factory (Tianjin, China). All the materials used in the research were analytic reagent grade (AR).

2.2. Preparation

2.2.1. Preparation of RGO/PVDF composite

In a typical procedure, GO was prepared from natural graphite by the Hummers method [37]. GO (100 mg) and deionized water (100 mL) was loaded in a 250-mL round bottom flask. The mixtures was dispersed using a sonification (300 W; Cotohoto (Beijing) Science and Technology Co., Ltd) until it became homogeneous dispersion. Hydrazine hydrate (80%, 1 mL) was then added and the mixture was stirred for 24 h at 100 °C, a black solid was gradually precipitated out. The mixture was centrifuged (10000 rpm, 15 min) to obtain precipitate, which was washed 3 times with alcohol–water solution. And then the precipitate was dried for 24 h at 80 °C in a vacuum oven. The RGO held lateral dimension of 1–6 μm and the thicknesses of 1–3 nm.

In the next step, encapsulated RGO/PVDF composite were fabricated. Firstly, 0.05 g PVDF whose diameter was at 500 nm was added in 50 mL THF and stirred at 50 °C for 15 min until PVDF powder was completely dissolved. Secondly, 30 g AA was added in the mixture and stirred for 15 min at 50 °C. Thirdly, above 5 mL solution was taken into a beaker. After that, 0.2 mL RGO solution was added into that beaker and the mixed solution was stirred for 15 min. The concentration of RGO solution was 3.25 mg mL^{-1}. Finally above mixed solution was added into 400 mL deionized water under vigorous stirring, then light grey crystalline mixture appeared in the solution, and continue stirring for 2 h at room temperature.

PVDF and RGO cannot be dissolved in ethanol, but ethanol is a good solvent to AA. Therefore, dialysis bags with 1000 molecular weight placed in ethanol were used to remove majority of AA in above crystalline mixture. The dialysis bag was placed in ethanol and the solution underwent seven times dialysis for seven days. After dialysis, the solution was dried at 60 °C through drying oven, and the RGO/PVDF composite was obtained.

2.2.2. Control exams

In order to elucidate the role of AA in preparing the RGO/PVDF composite, two control exams were conducted. One is without AA, the other one is without RGO. The experimental steps of the control exams are basically the same as the above steps, except without addition of AA or RGO. The products of the control exam without AA were called RGO/PVDF hybrid. And the products of the control exam without RGO were named as AA/PVDF hybrid.

2.3. Stability tests of oil with RGO/PVDF composite

Paraffin oil was used as the base lubricant in this study. The reason why we choose paraffin oil is that it can directly reflect the lubrication effect of RGO/PVDF composite and avoid the affection of other additives. The concentration of nanoparticle additive in base oil is mostly range from 0.05 wt% to 2 wt%. Generally speaking, high concentration could bring better lubrication effect but cause more serious aggregation problem [1]. Based on friction screen test results (Fig. S1), 0.5 wt% is selected as the addition concentration for RGO/PVDF composite. RGO/PVDF composite was added in liquid paraffin oil and ultra-sonicated to obtain hybrid lubricants. The hybrid lubricants respectively with 0.5 wt % RGO, with 0.5 wt% PVDF as well as with 0.25 wt% RGO and 0.25 wt % PVDF were obtained in the same way.

The dispersion stability of the paraffin oil with RGO/PVDF composite was evaluated by a 721 visible light spectrometer. Based on the Lambert–Beer law, absorbance is proportional to concentration. Fig. S2 shows the relative concentration of the RGO/PVDF composite at different time. A value of 1.0 represents the initial concentration intensity of the suspension without particle sedimentation. It shows that the relative concentration of RGO/PVDF composite approaches to 1.0 at the initial 2 h, meaning very few particle sedimentation. It suggests that RGO/PVDF composite nanoparticles can keep excellent dispersion stability during the friction tests (1 h).

2.4. Friction tests

The tribological properties were investigated using a ball-on-disk tribometer (UMT-2, CETR Corporation Ltd, USA) in reciprocating friction mode. Experiments were performed at room temperature (25 °C) and ambient humidity (30 ± 2%). The ball was sliding against the disk with the load of 5 N. The experimental time was 60 min, and sliding speed was 24 mm/s. The disk specimen was Φ30 × 5 mm AISI52100 bearing steel plate with hardness of 700 Hv and surface roughness of Ra 0.020 ± 0.002 μm. And the ball specimen was Φ9.5 mm AISI52100 steel with hardness of 780 Hv and surface roughness of Ra 0.008 μm. The average contact pressure was 661 MPa, which was calculated by Hertzian formula. The lubricants adopted in tests were parrifin oil (S1), parrifin oil with 0.5 wt% PVDF (S2), parrifin oil with 0.5 wt% RGO (S3), parrifin oil with the mixture of 0.25 wt% RGO and 0.25 wt% PVDF (S4) as well as parrifin oil with 0.5 wt% RGO/PVDF nano-composites (S5), respectively. In order to ensure the repeatability of the results obtained, all tests were repeated three times with lubricants produced by the same preparation procedure.

Moreover, in order to specify the wear rates (k) for each experiment, we have calculated the wear volumes (V) based on the corresponding wear scar radiuses (r) of the balls through the following equations.

$$h = R - \sqrt{R^2 - r^2} \tag{1}$$

$$V = \pi \cdot h^2 \left(R - \frac{h}{3} \right) \tag{2}$$

$$k = \frac{V}{F \cdot S} \tag{3}$$

Where h is the height of spherical cap, R is the original radius of the ball, F is the normal load in the experiment and S is the total sliding distance. For all experiments, we took three radiuses of each wear scar and adopted the average value.

2.5. Characterizations

X-ray diffraction (XRD) patterns were obtained on a D8 Advance X-ray diffractometer with a wavelength (λ) of 0.15418 nm (D8 advance, Bruker, Germany). Fourier transform infrared (FT-IR) was carried out between 400 and 4000 cm^{-1} using a Bruker spectrophotometer (TENSOR27, Bruker, Germany). Scanning electron microscopy (SEM) was utilized to observe the morphology of nano-composite (Gemini SEM 500, ZEISS, Germany) and the disk surface (SU3500, HITACHI, Japan). X-ray photoelectron spectroscopy (XPS) was adopted to analyze the surface of nano-composite (AXIS Ultrabld, Kratos, England). Thermogravimetric analyzer (TGA) was under an oxygen atmosphere from 25 to 800 °C (STA449C, NETZSCH, Germany). SEM, EDS and optical microscope (OM) were also used to analysis the worn sufaces.