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Nanosheets of MoS_2 and reduced graphene oxide as hybrid fillers improved the mechanical and tribological properties of bismaleimide composites

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ABSTRACT

The hybrid nanoparticles composed of reduced graphene oxide and MoS_2 nanosheets with active amino groups (NH_2-rGO/MoS_2) were fabricated by a facile and effective method. Then the bismaleimide (BMI) composites filled with the as-prepared NH_2-rGO/MoS_2 nanoparticles were obtained by a casting method. The microstructure and morphology of NH_2-rGO/MoS_2 nanoparticles, the mechanical properties, thermal property and tribological properties of NH_2-rGO/MoS_2/BMI composites were investigated. The results show that the interlaminar distance of MoS_2 nanosheets in the hybrid nanoparticles is 0.71 nm, which is much larger than that of bulk MoS_2 (0.62 nm); and the NH_2-rGO/MoS_2/BMI composites possess better friction-reducing and anti-wear performances (the friction coefficient and volume wear rate are about 0.2 and 2.9×10^{-6} $mm^3/(N \cdot m)$, respectively) compared to the neat BMI resin. This is mainly attributed to the enhanced toughness of the nanoparticles, good interfacial adhesion between NH_2-rGO/MoS_2 and BMI matrix as well as the synergistic effect between rGO and MoS_2 nanosheets.

1. Introduction

In recent years, the tribology, including friction, lubrication and wear, is acquiring increasing attention since the most of the energy exhaustion takes place in the process of friction. Bismaleimide (BMI) resins are widely used as matrixes of high-performance composites in the fields of aerospace, transportation, machinery, and electronics [1,2]. However, the cured resin is extremely brittle because of its high cross-link density, resulting in poor mechanical properties and friction performance which restrict its further property in the advanced industrial applications. Therefore, many modified BMI resin systems have been developed to meet the requirement of various applications [3,4].

It is well known that graphene has been widely studied owing to its outstanding properties, such as superior tensile strength and high flexibility [5], good thermal conductivity [6], mechanical property [7] and remarkable electron-transporting property [8–10]. Thus, graphene can be used as a solid lubricant to significantly improve the friction and wear properties of composites [11]. Kim et al. [12] prepared graphene oxide nanosheet coatings, which showed better surface protection ability and friction property in contrast to single-layer graphene coatings; Wang et al. [13] prepared multi-layer graphene filled poly (vinyl chloride) composites and discovered that the presence of multi-layer graphene could greatly decrease the friction coefficient and wear rate of the composites. Especially, in our previous work, Yan et al. [14] prepared hyperbranched polysiloxane grafted reduced graphene oxide composites and found that the addition of a low content of fillers can greatly improve tribological and mechanical performances of BMI resin. Therefore, graphene or modified graphene are widely used as a solid lubricant to improve the friction and wear properties of polymeric matrix [15,16].

More recently, MoS_2 nanosheets have gained renewed interests thanks to their crystallographic structure consisting of the covalently bonded S–Mo–S tri-layers in analogy to graphene [17–20]. MoS_2 is organized in two layers of sulfur atoms forming a sandwich structure, with a layer of molybdenum atoms in the middle [21]. Due to the weak van der Waals interaction between the sheets, MoS_2 shows a low friction coefficient and thus gives rise to its superior lubricating property with numerous potential applications, such as lubricating fluid additives [22], self-lubricating coatings [23] and solid lubricants [24]. Tang et al. [25] synthesized MoS_2 flower-like microspheres, which possess superior anti-wear and

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friction-reducing properties as a lubrication additive compared to pure base oil. Xu et al. [26] prepared hollow spheres-like nano-MoS_2 precipitated in TiO_2 particles and found that the tribological properties were greatly improved due to the decreased size of MoS_2 and the synergistic effect between MoS_2 and TiO_2.

Because the both exfoliated-MoS_2 (exf-MoS_2) and graphene have the similar morphology and layered structure, hybrid rGO/MoS_2 nanoparticles can maximize their structural compatibility and synergize the exf-MoS_2 and rGO interaction, and thus result in the excellent tribological property better than the sum of individual components [27]. Motivated by the above consideration, a facile and scalable approach to produce NH_2-rGO/MoS_2 hybrid nanoparticles from nanosheets of MoS_2 and reduced graphene oxide is reported in this paper. Furthermore, we have used the as-synthesized NH_2-rGO/MoS_2 as a lubrication additive to evaluate the tribological properties of BMI resin. The results indicated that the NH_2-rGO/MoS_2/BMI composites exhibited improved anti-wear and friction-reducing properties in contrast to the pure BMI resin.

2. Material and methods

2.1. Reagents and materials

MoS_2 (99%, particle size <2 μm, #234842 Sigma–Aldrich) and NaCl (≥99.5%, #S7653 Sigma–Aldrich) were used as received. Natural graphite flakes (325 mesh) was obtained from Qingdao Hensen Graphite Co., Ltd (Shandong, China). The graphene oxide (GO) nanosheets were produced from natural graphite flakes by the modified Hummers method [28]. γ-aminopropyltriethoxysilane (APS) was purchased from Jingzhou Jianghan Fine Chemical Co. Ltd (Hubei, China). N-methylpyrrolidone (NMP), ethanol, ammonia water and hydrazine hydrate were purchased from Tianli Chemical Reagents Co. Ltd (Tianjin, China). The BMI was provided by Rongchang Ning research group at Northwestern Polytechnical University. Dially Bisphenol A (DBA) and 4,4′-bismaleimidodiphenylmethane (BDM) were purchased from Sigma–Aldrich. All reagents were of analytical grade and used as received without further purification.

2.2. Experimental section

2.2.1. Synthesis of graphene oxide/MoS_2 nanosheets (GO/MoS_2)

MoS_2 nanosheets were prepared from commercial bulk MoS_2 by a mechanochemical treatment method [29]. In a typical procedure, 0.5 g MoS_2 and 5.0 g NaCl were added to the agate grinding bowl of planetary ball mill with the ball feed ratio of 1:7, grinding for 2 h at the rotation rate of 560 rpm. In this process, MoS_2 was uniformly mixed with NaCl, and became nanostructured after ball milling. The solids were thoroughly washed for several times using deionized water. Finally, the resulting product was dried under vacuum at 60 °C for 8 h to obtain the exf-MoS_2. Then, the exf-MoS_2 was dissolved in NMP and dispersed with ultrasound disintegration. The dispersions of MoS_2 nanosheets were purified by centrifugation, and the upper half of its volume was collected.

Then, the excess water from 200 mL GO aqueous suspension was removed by rotary evaporation, and the GO was re-dispersed in NMP under ultrasonication. The GO suspension and MoS_2 nanosheets were blended and sonicated for 1 h, and then vigorously stirred at 25 °C for 2 days. Then, two drops of concentrated hydrochloric acid were charged into the reaction mixture, which was stirred in the sealed flask at 80 °C for 1 day. The black product, recorded as GO/MoS_2, was filtered and washed with deionized water and absolute ethanol for three times, respectively, and then freeze-dried for further reaction.

2.2.2. Preparation of hybrid nanoparticles with active amino groups (NH_2-rGO/MoS_2)

Hybrid nanoparticles of NH_2-rGO/MoS_2 were achieved by two reaction steps: (1) the reaction of APS with GO/MoS_2, and (2) reducing the resultant with hydrazine hydrate to obtain NH_2-rGO/MoS_2.

The first step of the reaction was carried out as follows: 0.60 g GO/MoS_2, 8 mL distilled water and 175 mL ethanol were added into a beaker, and then treated under ultrasonication for 30 min. Then, the mixture was transferred to a 250 mL three-necked flask holding a mechanical stirrer, reflux-condenser and constant-pressure funnel. Subsequently, a mixture of 2.5 mL APS and 25 mL ethanol was added into the flask dropwise. After that, the reaction mixture was heated to 78 °C and maintained for 4 h. The synthetic route was shown in Fig. 1. After the reaction, the mixture was filtrated and washed with ethanol for several times. Finally, the resulting product, recorded as NH_2-GO/MoS_2, was collected and dried in a vacuum oven at 60 °C for 12 h.

The second reaction step was conducted as follows: the obtained NH_2-GO/MoS_2 was dispersed in 180 mL distilled water under ultrasonication for 30 min. Then, the mixture was transferred to a 250 mL three-necked flask holding a mechanical stirrer and reflux-condenser. Subsequently, 2.5 mL hydrazine hydrate and 7.5 mL ammonia water were added when the reaction mixture was heated to 98 °C and maintained for 6 h. After the reaction, the resulting product, abbreviated as NH_2-rGO/MoS_2, was filtered and washed with distilled water and ethanol for several times, and dried in a vacuum oven at 60 °C for 12 h.

2.2.3. Preparation of NH_2-rGO/MoS_2/BMI composites

The NH_2-rGO/MoS_2/BMI composites were prepared by a casting method. DBA and BDM with a mass ratio of 3:4 were mixed in a beaker under 140 °C and kept at this temperature till totally melting. The appropriate amount of NH_2-rGO/MoS_2 was then carefully mixed with the pre-polymer and stirred for about 30 min to disperse uniformly. After that, the mixture was put into a pre-heated mold coated with release agent and degassed in a vacuum oven at 150 °C for about 1 h. Then the mixture was cured and post-cured following the schedule of 150 °C × 2 h, 180 °C × 2 h, 220 °C × 4 h and 250 °C × 4 h. Finally, the mold was cooled to room temperature and demolded to get the samples of NH_2-rGO/MoS_2/BMI composites.

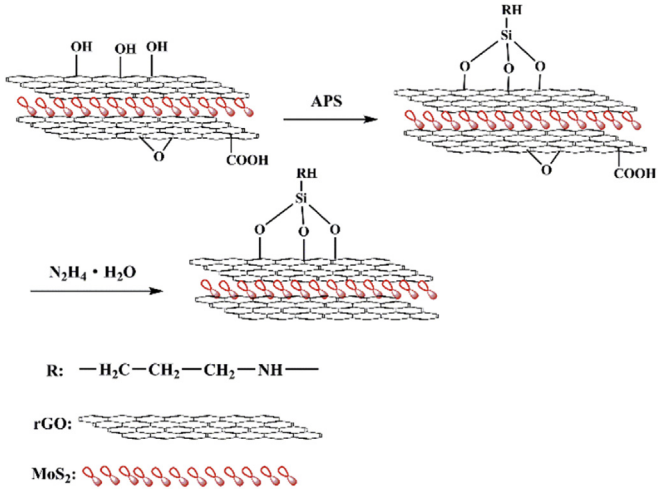

Fig. 1. The synthesis route of APS grafted rGO/MoS_2.