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The tribological behaviors of polyacrylate/graphene oxide and polyacrylate/surfactant-modified reduced graphene oxide composite coatings on flexible leather substrates

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ABSTRACT

An anionic surfactant, linear alkylbenzene sulfonate (LAS), was used to modify reduced graphene oxide by in-situ reduction process to enhance its compatibility in polyacrylate latex. Polyacrylate/graphene oxide (PA/GO) and polyacrylate/surfactant-modified reduced graphene oxide (PA/LAS-rGO) were prepared to investigate their tribological behaviors on flexible leather substrates. The structure and morphologies of GO and LAS-rGO were investigated by XRD, FT-IR, Raman spectroscopy, SEM and TEM. The tribological behaviors of polyacrylate composite coatings were studied by mechanical properties, wear loss of coated leather and ESEM. The results of XRD, FT-IR and Raman spectroscopy confirmed that LAS-rGO was modified by LAS and had good dispersity in water. SEM and TEM images implied the layered structure of GO and LAS-rGO. The mechanical and tribological properties of polyacrylate/LAS-rGO are better than that of polyacrylate/GO. The analysis of ESEM show that LAS-rGO can form self-lubrication and barrier layer owing to its amphiphilicity and π-π stacking with water evaporating.

1. Introduction

The abrasion resistance of polymer-based coating material is one of the important indexes to evaluate the material properties. It directly determines the service life of the coating. At present, a wide range of investigations [1] showed that the wear loss of the material mainly depends on the hardness of the material and the load it carried. The previous studies [2] have mainly focused on the tribological behaviors of polymer-based materials on hard substrates. As an excellent polymer-based coating material, waterborne polyacrylate latex has been widely applied in leather coating [3], which enhances the mechanical properties of leather substrates and retains its softness. Due to their softness and low hardness, the coated leather is easy to wear. It greatly reduces the service life of leather products. The development of wear-resistant coatings based on flexible substrates especially for leather is very important. The tribological properties of waterborne polyacrylate latex need to be enhanced for higher performance in applications. One of the most common methods is to modify the polyacrylate with nanomaterials [4–7]. Numbers of studies suggest that nanomaterials can improve the mechanical properties of the coating and form self-lubrication layer to improve its tribological properties [8–10].

Graphene is an atomically thin layer of sp^2-bonded carbon atoms [11]. This special structure makes graphene have many excellent performances, such as high specific surface area and good mechanical properties [12]. It has been widely used as an excellent filler to enhance the mechanical properties of polymer materials [13–15]. The remarkable mechanical properties and extremely thin laminated structure of graphene also enable it to become one of the most promising nanomaterials in improving the tribological properties of polymer matrix by forming a self-lubricating transfer film between substrates and friction medium [16]. Lahiri [17] investigated the lubrication of graphene nanosheets in polyethylene. When the content of graphene added from 0.1 wt% to 1.0 wt%, the wear rate was reduced by 4 times which was caused by the good mechanical properties and shearing action of graphene. The unique layered structure of graphene makes it have anisotropy in wear resistence [18]. Yan et al. [19] introduced the aligned reduced graphene oxide-Fe_3O_4@polyphosphazene onto the specific surface of the composite where friction occurs via a directed magnetic field and obtained a great enhancement on tribological performance owing to the formation of self-lubrication layer.

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However, some researches [20] reported that the weak compatibility between graphene and polymer matrix is the main limitation for graphene to be a potential additive to improve the tribological properties of composites. The dispersion of graphene in water limits its use in waterborne polymers. Compared with graphene, graphene oxide (GO) has not only the 2-D structure of graphene, but also many oxygen functional groups, like epoxy, carboxyl and hydroxyl group, which may have stronger interaction with polymer matrix [21–24]. It could easily disperse in water and other solvents by ultrasonication. GO is also a promising additive to improve the mechanical and tribological properties of polymer [25,26]. Shen and his coworkers [27] studied the tribological properties of GO/epoxy resin. The results indicated that the wear rate was reduced by 94.1% as the content of GO was 0.5%. Results from Zhao et al. [28] reported that the anti-wear enhancement of GO reinforced epoxy resin depended on the interface adhesion strength between GO and polymer matrix. However, compared with graphene, it is more difficult for GO to significantly enhance the performance of polymer due to its inferior mechanical properties.

Firstly, in order to compare GO with rGO on the mechanical and tribological properties enhancement based on flexible substrates. An anionic surfactant was absorbed onto the rGO surface by in-situ reduction process to prevent rGO from aggregation and restacking in water. Then GO and LAS-rGO were incorporated into polyacrylate latex respectively to prepare polyacrylate/GO and polyacrylate/LAS-rGO composite latexes. The composite latexes were applied in leather coating. The influence of GO and LAS-rGO on the tribological properties of polyacrylate leather coating had been investigated. To the best of our knowledge, the tribological behaviors of waterborne polyacrylate/GO and polyacrylate/LAS-rGO composite coatings on flexible leather substrates have not been yet reported instead of in oil media [29].

2. Experimental

2.1. Materials

Graphite was purchased from Shanghai Macklin Biochemical Science and Technology Co., Ltd. Concentrated sulfuric acid (H_2SO_4, 98%), potassium permanganate ($KMnO_4$), hydrazine hydrate ($N_2H_4{\cdot}H_2O$), butyl acrylate (BA), methyl methacrylate (MMA), potassium bromide (KBr), sodium hydrate (NaOH), hydrogen peroxide (H_2O_2, 30%), ammonium persulfate (APS), sodium dodecyl sulfate (SDS), ammonia (25%) and hydrochloric acid (37%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Linear alkylbenzene sulfonate (LAS) was purchased from Guangzhou Li Sheng Chemical Co. Ltd. Glycidyl methacrylate (GMA) was purchased from Shanghai Yuan Ji Chemical Co., Ltd. Branched secondary alcohol ethoxylates (TMN-10) was purchased from Nanjing Gu Tian Chemical Industry Co., Ltd. All of the reagents were used as received.

2.2. Preparation of GO

GO was prepared according the methods in our previous work [21]. 2.5 g of natural graphite and 1.25 g of sodium nitrate were added to 100 mL concentrated sulfuric acid (98%) in a round-bottom flask. The flask was put into an ice bath to keep the temperature of the mixture less than 5 °C. Stirring with a speed of 200 rpm, 7.5 g of potassium permanganate was slowly added to the reaction mixture in 30 min. After that, the temperature of the reaction mixture was heated up to 35 °C and kept for 2 h. Deionized water (200 mL) was rapidly added to the reaction mixture. Then the temperature was heated up to 80 °C and kept for 15 min. Deionized water (600 mL) was added into the mixture to terminate the reaction. After the temperature cooled down to 30 °C, 30 mL hydrogen peroxide was added into the mixture. The mixture was centrifuged and washed with hydrochloric acid (5 wt%) and deionized water for four times. Finally, the GO dispersion was centrifuged at 3000 rpm for 20 min to remove the unexfoliated graphite. GO was prepared by ultrasonic treatment for 60 min. The final solid GO was lyophilized.

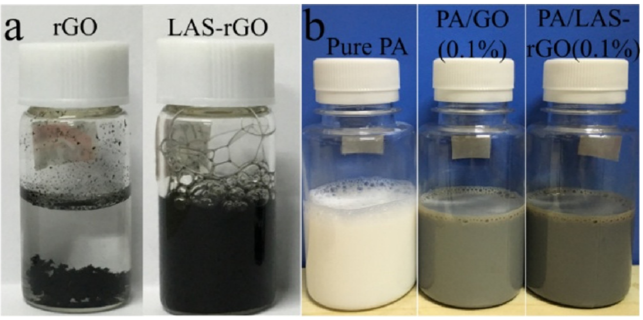

Fig. 1. Opitical images of rGO, LAS-rGO(a), pure polyacrylate, polyacrylate/GO and polyacrylate/LAS-rGO composite latexes(b).

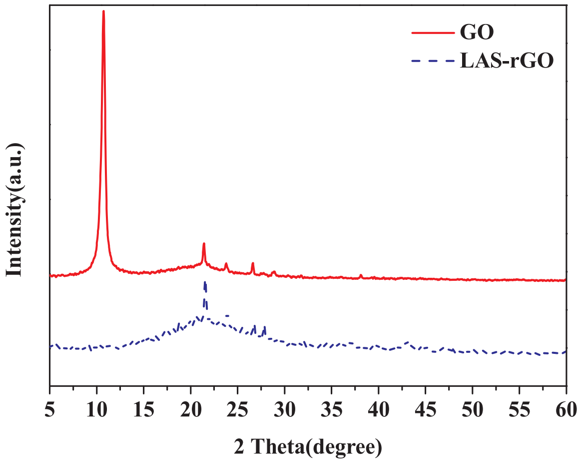

Fig. 2. XRD patterns of GO and LAS-rGO.

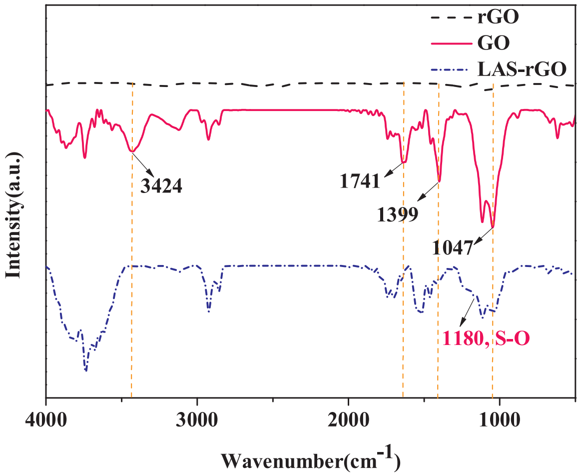

Fig. 3. FTIR spectra of GO, rGO and LAS-rGO.

2.3. Preparation of LAS-rGO aqueous dispersion

GO was reduced by $N_2H_4{\cdot}H_2O$ with the stabilization of LAS. Briefly, 0.5 g of GO, 1 g of LAS and 0.5 mL of $N_2H_4{\cdot}H_2O$ were placed in 50 mL distilled water with magnetic stirring. Hence, pH of the mixture was adjusted to 7 with NaOH aqueous solution (0.1 M). The mixture was heated to 98 °C for 90 min with reflux. At last, a stable LAS-rGO aqueous dispersion was obtained via ultrasonic treatment. A sample of rGO was prepared to be a contrast without the stabilization of LAS in the