



Evaluation of scratch resistance of functionalized graphene oxide/polysiloxane nanocomposite coatings



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ABSTRACT

Functionalized graphene oxide (FGO) was synthesized with 3-glycidoxy-propyl trimethoxy silane (GPTMS) and subsequently incorporated into polysiloxane coatings to improve the mechanical properties, especially scratch resistance, through the sol-gel and epoxy/amino curing reactions. The surface functionalization of graphene oxide (GO) was evidenced by TEM, FTIR and XPS. FGO was found to have better compatibility and establish stronger interface with polysiloxane matrix than GO based on the observed microstructures using OM and SEM. Nanoindentation, macro scratch and progressive load scratch tests were employed to assess the mechanical performance of FGO/polysiloxane nanocomposite coatings, demonstrating significant improvement in comparison with either the pure polysiloxane or the GO/polysiloxane coatings. A 40% enhancement on microhardness (233 MPa), 83% improvement of scratch resistance (1100 g) and 144% increase in 1st scratch critical normal load (4.88N) are achieved by addition of only 0.75 wt% of FGO. Furthermore, elastic recovery and scratch damage morphology were investigated to provide insight into scratch behavior and reinforcement mechanism.

1. Introduction

Sol-gel derived organic-inorganic hybrid polysiloxane coatings attract increasing research interests, since their dense Si–O–Si network provides promising mechanical performance [1–3], weather durability [4,5], optical property [6–8] and anti-corrosion performance [9,10]. These polysiloxanes are usually synthesized by the co-hydrolysis/condensation of tetraalkoxysilane [Si(OR)₄] and trialkoxysilane [X-Si(OR)₃] [1,2,4,6,9]. However, their high inorganic fraction usually renders polysiloxane coatings hard and brittle with very low thickness of few microns, due to residual stresses [11]. In addition, these coatings typically require high curing temperatures for curing completely, which limits their application on immobile articles. To solve these problems, organic groups are incorporated into Si–O–Si network of polysiloxane coatings [11–13]. Introduction of a large organic fraction and reduction in density of Si–O–Si network improve ductility, alleviate brittleness and achieve thick films, whereas coating hardness and strength simultaneously reduce. This shortcoming limits coatings' usage in the electronic, optical, household and automotive applications, where they are strongly subjected to scrapes, scratches, impacts and have serious requirement in scratch resistance for long-term aesthetics. Therefore,

how to improve the scratch resistance of organic groups modified polysiloxane coatings becomes an urgent issue.

One of the most common routes to handle this problem is to introduce mineral fillers, such as SiO₂ [14], TiO₂ [15] and Fe₃O₄ [16], which often contributes to significant increase in hardness and corresponding enhancement on scratch resistance. Ting He et al. [17] improved the pencil hardness of polysiloxane coatings from 4H to 7H, by incorporating 10% surface modified silica alcosol. These composite coatings also demonstrated higher nanoscratch critical loads and lower residual indentation depths, which confirmed the better scratch resistance. Generally, composite coatings perform optimized performances when the content of mineral fillers are relatively high (> 10%). And sometimes, they bring about simultaneous reduction in flexibility. Considering the organic-inorganic hybrid property of polysiloxane coatings, graphene, the emerging nanomaterial, has potential to reinforce them more efficiently.

Graphene, known as two-dimensional (2D) atomically thin carbon material with superior mechanical strength [18], electronic and thermal conductivity [19,20] and barrier property [21], has received considerable attention in the range of polymer nanocomposites. However, a trend of graphene to form aggregates in the polymer matrix

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limits composites' performance, due to strong van der Waals force and ultrahigh specific surface area [22]. In order to ensure the effective reinforcement of the polymer nanocomposites, the homogeneous dispersion and strong interfacial bonding between graphene sheets and polymer matrix need to be guaranteed [23]. Therefore, chemically modified graphene derivatives, such as graphene oxide (GO), reduced and functionalized GO, are synthesized and introduced into polymer nanocomposites, as well as protective coatings, to reinforce their corrosion resistance [24,25], flame retardation [26], gas impermeability [27,28] and scratch resistance [29,30]. Massimiliano Barletta et al. [30] studied the graphene derivatives/epoxy composite coatings and found that reduced graphene oxide sheets could improve the modulus, stiffness as well as the anti-scratch performance of composite coatings. Although graphene based nanocomposite coating becomes an increasingly hot topic, the graphene's application in polysiloxane organic-inorganic hybrid coatings is rarely reported.

Hence, we employed functionalized graphene oxide (FGO) to improve the mechanical performance, especially scratch resistance, of polysiloxane coatings. Functionalization of GO with 3-glycidoxypropyltrimethoxysilane (GPTMS) was carried out by a facile process, which improved the compatibility of GO with polysiloxane matrix. FGO, polysiloxane oligomer and aminopropyltriethoxysilane (APS) were employed to fabricate nanocomposite coatings by the sol-gel and epoxy/amino curing reactions. Homogeneously dispersed FGO sheets were demonstrated to establish interfacial bonding with polysiloxane matrix and reinforce anti-scratch properties of nanocomposite coatings efficiently. Moreover, the progressive load scratch tests and corresponding damage morphology analysis were adopted to further investigate the role of FGO in the scratch behaviors.

2. Experimental

2.1. Materials

Graphene oxide (GO) was obtained from Nanjing Cangji Technology Development Co., Ltd. 3-Glycidoxypropyltrimethoxysilane (GPTMS, 98%), Phenyltrimethoxysilane (PTMS, 98%), Dimethyldimethoxysilane (DMDS, 98%), 3-Glycidoxypropyldimethoxymethylsilane (GPDS, 98%), aminopropyltriethoxysilane (APS, 98%), ammonia (25%) and absolute ethanol (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were used as received.

2.2. Preparation of functionalized graphene oxide (FGO)

120 mg of graphene oxide (GO) was added into a three-neck flask containing 90 ml of absolute ethanol and 30 ml of deionized (DI) water. The mixture was dispersed in a sonic bath for 0.5 h. Then 2 g of GPTMS in 10 ml of absolute ethanol was added into the mixture solution. The brown solution of homogeneously dispersed GO was stirred and heated at 70 °C for 24 h. After reaction, the color of the solution became dark brown, indicating the generation of FGO. The mixture was isolated by centrifugation and washed with ethanol and water for three times separately, in order to remove the unreacted GPTMS molecules. The FGO was collected and dried in a vacuum oven at 50 °C for 24 h.

2.3. Synthesis of polysiloxane oligomer

7.93 g of PTMS, 4.41 g of GPDS and 4.8 g of DMDS were added into a 50 ml round-bottom flask equipped with condenser and magnetically stirred. Then, 4 g of deionized water, 0.1 g of ammonia and 2 g of ethanol were mixed homogeneously and dropped into the flask. After that, the mixture was heated at 60 °C in an oil bath for 10 h to obtain the polysiloxane oligomer.

2.4. Preparation of FGO/polysiloxane nanocomposite coatings

In a typical operation, FGO was re-dispersed in 4.25 g of as-obtained oligomer solution with sonication for 0.5 h. 0.50 g of APS was added to the mixture functioning as the curing agent. The weight ratios of the FGO were made to be 0.25, 0.5, 0.75, 1.00 wt%. Then, the mixture was stirred for 30 min to obtain a homogeneous solution. Subsequently, it was coated on a tinplate sheet by a #9 drawdown rod (wet film thickness = 120 μm), and cured in ambient conditions for 7 days to form the nanocomposite coating films with an average thickness of $80 \pm 5 \mu\text{m}$. Herein, APS, on one hand, participates in the sol-gel reaction with polysiloxane oligomers, and on the other hand, their amino groups react with epoxy groups of polysiloxane oligomers and FGO. All the coating mechanical performance tests, including nanoindentation and progressive load scratch tests, are carried out directly on the sheets. The coating specimens were also removed from the tinplate sheets to get structure characterizations, such as optical microscopy and scanning electron microscopy. All tinplate sheets were polished with silicon carbide cloth and cleaned with acetone before coating. For comparison, the GO/polysiloxane nanocomposite coating and pure polysiloxane coating specimens were also prepared by the above experiment steps. The thickness of these coating films were also controlled to be $80 \pm 5 \mu\text{m}$. The preparation procedure and the structure of FGO/polysiloxane nanocomposite coatings are shown in Scheme 1.

3. Characterization

The transmission electron microscopy (TEM, Hitachi H-800, Japan) was conducted to observe the morphologies and dispersion of the GO and FGO sheets. Samples were prepared by dropping solutions, in which the sheets were dispersed in ethanol by sonication for 30 min, on copper grids and dried at room temperature. Fourier transform infrared (FTIR, Nicolet Nexus 470, USA) was performed to identify functional groups of GO and FGO. The powder was pressed into pellets with potassium bromide and scanned over the wavenumber ranging from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} and accumulation of 32 times. For X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ECSA, USA), all the binding energy values were calibrated using the reference peak of C 1s at 284.6 eV. Thermogravimetric analysis (TGA, TA instruments Q500, USA) of GO and FGO was carried out from room temperature to 800 °C at a linear heating rate of 10 °C/min under nitrogen flow. X-ray diffraction (XRD, Bruker D8 Advance, USA) was conducted at a scan rate of 4°/min between 3° and 45°, using a Cu-K α radiation ($\lambda = 0.15406 \text{ nm}$).

The morphologies and structures of composite coatings were examined by using both scanning electron microscopy (SEM, Philips XL30, USA) and optical microscopy (OM, Hirox KH7700, USA). The composite coatings were fractured in the liquid nitrogen to prepare the cross section samples. The pencil hardness of coatings was determined using CHUNG HWA pencils, according to National Standard Testing Method (GB/T6739-1996) of China. Flexibility was measured by a QTX paint flexibility tester (Shanghai Modern Environmental Engineering Technology, CN), according to National Standard Testing Method (GB/T1731-1993) of China. Coating panels were bent around the tester's mandrel bar with diameters of 15, 10, 5, 4, 3, 2 and 1 mm. The smallest bar diameter that did not cause cracking in the coatings denotes the flexibility of coatings. Higher mandrel diameters correspond to less flexible coatings. Macro scratch test was carried out with an Automatic Scratch Tester (Sheen Instrument Ltd, UK). This tester is composed of a 1 mm tungsten carbide ball ended tip and a series of poises with mass from 100 g to 2 kg. The tip with different loads was applied to the coatings to produce scratches. The lowest load which caused a remaining mark was justified by OM and noted as the scratch resistance.

Nanoindentation tests were carried out on a CSM nanoindentation instrument (CSM Instruments, Switzerland) using a Berkovich diamond indenter. By utilizing the optical microscope and positioning system of

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