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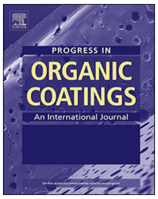

Silicone/graphene oxide sheet-alumina nanorod ternary composite for superhydrophobic antifouling coating

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ABSTRACT

Superhydrophobic silicone fouling-release (FR) nanocomposite coatings have gained considerable interest as an eco-friendly and economic solution to combat biofouling problems of ship hulls. In this work, graphene oxide anchored with alumina nanorods (GO-Al_2O_3 NRs) sheet hybrids were fabricated via a two-phase method. A ternary nanocomposite series of elastomeric silicone/GO-Al_2O_3 hybrid NRs sheet coating was developed via solution-casting method. γ–Al_2O_3 NRs of 150 nm in length and 20 nm in diameter were fastened between GO nanosheets and conformably coated with silicone layers. Different concentrations of GO-Al_2O_3 hybrid NRs sheet fillers were inserted in the silicone composites to study the structure property relationship. Nanocomposites' surface characteristics, such as superhydrophobicity, surface free energy (SFE), and rough topology were investigated here. The physical and mechanical characteristics of the coating materials were also considered. Selected micro-foulants were used for the investigation of biological inertness. Laboratory assessments were performed on coated specimens for up to 28 days. A rigorous field trial was carried out for the fabricated model in natural marine water for 3 months. Well-dispersed GO-γ-Al_2O_3 NRs sheets hybrids of up to 1 wt.% increased the contact angle (151°), decreased the SFE (13.25), and provided micro-nano roughness. Thus, a promising FR nanocomposite coating was approved with superhydrophobicity, high thermal stability, and economic savings for marine coating applications.

1. Introduction

Superhydrophobic, nanostructured surfaces have caused a worldwide concern in various industrial applications [1]. These surfaces are candidates for various engineering applications, including self-cleaning, anti-biofouling, anticorrosion, and textiles [2]. Biofouling is a complex problem that causes serious negative economic and ecological impacts in the marine environment and shipping industry [3,4]. Biofouling on ship hulls results in the increase in drag resistance and hydrodynamic weight and thus causes the reduction of shipping velocity, increase in fuel consumption, and emission of harmful compounds to the environment [5]. Substantial environmental toxicity issues and increased global restrictions on the applications of traditional biocidal antifouling (AF) paints have motivated research in an eco-friendly direction with a particular focus on silicone foul-release (FR) technology [6]. Non-stick polydimethylsiloxane (PDMS) FR paints rely on a technology that 1) inhibits fouling settlements and 2) weakens fouling adhesion strength by providing low friction and self-cleaning performance [7]. PDMS possesses several merits, such as its nonleaching property, low porosity, low surface free energy (SFE), high molecular mobility, repellency against water and dirt, and good thermal and UV stability [8]. The fabrication of PDMS surfaces with superhydrophobicity involves the controlled generation of a rough morphology with low-energy molecules [9]. High water contact angles (WCAs) > 150° and low sliding angle and self-cleaning effect result in the so-called superhydrophobic surfaces [10]. Superhydrophobic organic/inorganic hybrid nanocomposites represent a creative solution to develop novel nanomaterials with innovative self-cleaning and FR paints [11–13].

Carbonaceous nanofillers, especially graphene-based nanomaterials, play a promising role in the development of self-cleaning surfaces [14]. Among various shapes, sheet-like structures demonstrate the most outstanding barrier effects [15]. Graphene oxide (GO), one of the most important derivatives of graphene, is characterized by a layered structure with oxygen functional groups bearing on the basal planes and edges [16]. Many GO nanocomposites were reported because of the large and tortuous path produced by GO sheets and their reactions with

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polymer chains [17]. GO sheets have closely packed layered structures due to vacuum filtration and intrinsic van der Waals interaction [18]. Thus, although the sheets can be used as nanofillers, their applications remain limited as these structures cause poor dispersion and exfoliation in polymeric resins [19]. The aggregation of GO sheets can be prevented and a homogeneous dispersion and compatibility of nanocomposite can be ensured by decorating sheets with organic NPs [20,21]. γ-Al_2O_3 NRs possess many advantages, such as extremely high surface area, unparalleled morphology and self-cleaning properties [22,23]. γ-Al_2O_3 single-crystalline NRs with controlled size and morphology were facilely prepared by the thermal decomposition of boehmite (γ-AlOOH) precursor synthesized by solvothermal technique [24].

Considerable efforts have been spent to investigate non-noble catalysts as a substitutional approach to minimize the cost that can improve the commercialization efficiency of any technology, among many types of non-noble catalysts; carbon-based materials have elicited widespread attention as promising substitutes for catalysts [25]. GO nanosheets with the numerous hydroxyl, carboxyl and epoxy-containing groups provide a fertile opportunity for the formation of GO-Al_2O_3 NR hybrids by the physical interactions (π–π interactions and hydrogen bonding) [26]. Yu et al. [27] reported the fabrication of epoxy/GO–Al_2O_3 sheet hybrid coatings where a low nanofiller content (2 wt.%) improved the anticorrosion and durability properties. Such results indicated that GO–Al_2O_3 exhibited better dispersion than pure GO and Al_2O_3 nanomaterials. Fan et al. [28] fabricated a dense graphene nanosheets-Al_2O_3 composite by ball milling and spark plasma sintering. However, such conventional techniques require relatively long processing time at high temperatures that may result in degradation of nano-carbons. Ruoff et al. [29] have reported a pressure-less sintered GO-Al_2O_3 composite with improved mechanical properties and wear-resistance. GO nanosheets anchored with γ-Al_2O_3 have recently been the objective of several research papers and demonstrate great reinforcement property at very low nanofillers [30,31]. However, to the best of our knowledge, no report has been conducted so far on the use of GO-Al_2O_3 hybrid NR sheets as nanofillers for silicone FR paints. Fabrication of superhydrophobic surfaces based on exfoliated GO-Al_2O_3 hybrid NR sheet arrays depends on the combination between surface roughness and low SFE. Eco-friendly and non-leachant PDMS enriched with the large surface area, roughness, well-dispersion and antibacterial properties of GO-Al_2O_3 hybrid NR sheets represents a promising FR coating material.

In this study, we introduces for the first time a ternary nanocomposite series of a sheet coating of PDMS/exfoliated GO-Al_2O_3 hybrid NR as a robust surface material for self-cleaning FR surfaces. A stable GO-γ-Al_2O_3 NRs hybrid sheets was synthesized via a two-phase method. The controlled synthesis of GO/γ-Al_2O_3 hybrid NR sheets is necessary to afford outstanding superhydrophobic features. Surface characteristic variations are the main features of well-dispersed hybrid nanofillers. Chemical reactivity and surface self-cleaning characteristics were monitored via quantitative measurements, such as WCA and SFE, by using mathematical viewpoints. The mechanical and physical performance levels of the ternary nanocoatings were investigated. This work introduces several merits, such as facility, durability, ecological and economic impacts, thermal stability, and powerful applications in marine FR nano-coatings.

2. Experimental

2.1. Chemicals

Octamethylcyclotetrasiloxane (D_4, [–$Si(CH_3)_2O$–]$_4$, 98%), Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene known as Karstedt catalyst (Platinum ∼2%), 1,3-Divinyltetramethyldisiloxane ($C_8H_{18}OSi_2$, 97%), Poly(methyl siloxane) (PMHS; weight average molecular weight (Mn) = 1700–3200), Graphite powder (< 20 μm, synthetic), Aluminum chloride hexahydrate ($AlCl_3{\cdot}6H_2O$, 99%), Sodium dodecyl benzene sulfonate (SDBS, 98%), Sodium nitrate ($NaNO_3$, 99.0%) were all delivered from Sigma–Aldrich Chemical Co. Ltd., USA. Sulfuric acid (H_2SO_4, 95.0%), Potassium permanganate (KMnO4, 99%), and hydrogen peroxide (H_2O_2, 35%), Sodium hydroxide (NaOH, extra-pure; 98%) and anhydrous ethanol (AR) were delivered from Acros Co., Belgium. All the chemicals were used as received without further purification.

2.2. Preparation methods

2.2.1. Preparation of exfoliated GO nanosheets

Using a modified Hummer's approach, we prepared GO nanosheets via graphite powder oxidation. Briefly, 1 g of graphite powdered flake and 1 g of $NaNO_3$ were added into 48 mL of H_2SO_4 under constant stirring until dissolved. While preventing the temperature of the suspension from exceeding 20 °C, we slowly added 6 g of $KMnO_4$ and then continued stirring the mixture for 1 h at 35 °C. We slowly diluted the suspension with 80 mL of distilled water and raised the temperature to 90 °C. We slowly added 10 mL of H_2O_2 to reduce residual permanganate and manganese dioxide into colorless soluble manganese sulfate and filtered the suspension with distilled water until pH 7.0. The exfoliation of the yellow-brown suspension obtained was conducted using a sonicator to produce single-layer GO, followed by centrifugation to remove un-exfoliated precipitates. Finally, a brown dispersion of homogeneously exfoliated GO was obtained.

2.2.2. Preparation of γ-Al_2O_3 NRs

Distinct γ-Al_2O_3 NRs were synthesized via a simple hydrothermal method to generate ϒ-AlOOH nanorods, followed by thermal decomposition of the prepared γ-AlOOH precursor under air atmosphere. In a typical reaction, $AlCl_3{\cdot}6H_2O$ (4.82 g) was dissolved in a 90 mL solution of water and dimethyl benzene at 2:1 mixing ration by volume under vigorous magnetic stirring at RT for 15 min. Under continuous stirring, SDBS (2 g) was added to the above solution followed by 1 M NaOH solution (50 mL) to obtain a suspension solution. A separating funnel was used without shaking to separate the obtained suspension and form two liquid phases. The upper organic liquid phase was transferred into a 50 mL Teflon-lined stainless steel autoclave, which was sealed and maintained at 200 °C for 24 h and then allowed to cool naturally to RT. The product was centrifuged (4233EC+ laboratory centrifuge, Italy) at 5000 rpm for 20 min, washed with a mixture of water and ethanol (50:50 by volume) for several times, and dried in vacuum oven at 80 °C for 12 h. The obtained white powder consisting of γ-boehmite nanostructured powder was put into an alumina crucible in a tube furnace and heated in air to 550 °C for 3 h at a heating rate of 5 °C/min.

2.2.3. Preparation of GO sheets/γ-Al_2O_3 NRs hybrids

GO nanosheet/γ-Al_2O_3 NR nanocomposites were synthesized using a two-phase method. In this technique, GO (50 mg) and deionized water (100 mL) were added into a 250 mL bottle and sonicated for 1 h. γ-Al_2O_3 NRs (50 mg) with different weights (5, 10, and 15 mg) dispersed in 50 mL of toluene were added into the GO water solution. The mixtures were continuously stirred for 12 h such that the GO and γ-Al_2O_3 NRs coordinated with the GO sheets at the water/toluene interface. The GO/γ-Al_2O_3 NRs nanocomposites were purified with acetone and centrifuged. The obtained hybrid nanocomposites were then washed with tetrahydrofuran to remove residual surfactants. The final GO/γ-Al_2O_3 NRs nanocomposites were freeze-dried at −50 °C for 24 h.

2.3. Modelling of self-cleaning FR composite coatings

2.3.1. Preparation of virgin and GO/γ-Al_2O_3 NRs hybrid nanocomposites

The anionic ring opening polymerization of D_4 was performed to fabricate vinyl-ended PDMS with high molecular weight [32]. Following a typical polymerization reaction, we added 30 g of vacuum-