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Synthesis of ultrahydrophobic and thermally stable inorganic–organic nanocomposites for self-cleaning foul release coatings

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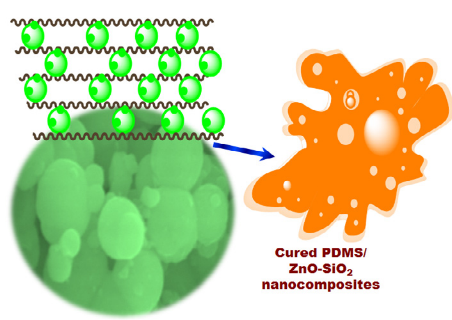
HIGHLIGHTS

- Low cost nanofiller of polydimethylsiloxane/SiO_2-ZnO nanocomposites were synthesized.
- The nanofiller featured stable, well-dispersed, uniform particle morphology.
- Ultra-smooth surface, well-dispersion nanoparticles lead to potential nanocomposite fillers.
- Surface wettability, hydrophobicity, roughness and free energy are a key of self-cleaning FR.
- The nanofiller showed potential as FR self-cleaning via a physical repelling mechanism.

GRAPHICAL ABSTRACT



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ABSTRACT

A conformal novel and low-cost series of elastomeric high-molecular weight polydimethylsiloxane (PDMS)/controlled SiO_2-doped ZnO nanocomposites were accurately synthesized via hydrosilation curing. Different concentrations of doped nanospheres were inserted in the nanocomposite via in situ technique. The synergetic effect of micronanobinary scale roughness and controlled fouling on different kinds of substrates was determined. The hydrophobicity, roughness, and free-energy properties were investigated as self-cleaning and fouling release (FR) factors. The nanocomposites were also subjected to various tests on surface adhesion and mechanical properties, such as impact, T-bending, crosscut, and abrasion resistance. The anticorrosive features of nanocomposites were investigated through salt spray test. The mechanical tests and salt spray test exhibited the most profound effect by incorporation of 0.5% SiO_2-doped ZnO nanospheres, indicating well distributed SiO_2-doped ZnO nanofillers (0.5%). Results indicate that the nanocomposites retained the nanostructure characteristics under thermal and irradiation treatments. Furthermore, microfoulants of chosen bacterial progenies were applied on vinyl-ended PDMS/spherical SiO_2-doped ZnO nanocomposites for about one month of laboratory assessments. These studies indicated the importance of good distribution of doped nanofillers on enhancing FR ability in the modeled nanocoatings. A particular increase in contact angle (CA, $167^{\circ} \pm 2$) and the decrease in free energy of surface (9.24 mN/m) and microroughness indicated the FR functionality of these nanocomposites. Our findings show evidence that the developed nanocomposites demonstrated inert and

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nonwettable properties, superior physical characteristics, surface innerness and lotus effect, long-term durability under UV radiation, and thermal stability and resistance against a wide range of pH solutions, making them promising as efficient environment-friendly self-cleaning for coating of ship hulls.

1. Introduction

Biofouling is a major problem of material surfaces in shipping industry and causes substantial costs because of increased fuel consumption, maintenance costs, and negative ecological impacts [1–3]. Traditional antifouling (AF) paints can kill potential fouling organisms through leaching biocides [4]. Widespread utilization of these toxicants presents negative environmental consequences on marine environment [5]. The international embargo on tin-based biocidal AF paints by the International Maritime Organization in 2001 directed recent studies toward nonleachant fouling release (FR) surfaces as ecological alternatives [6,7]. Self-cleaning surfaces with low-surface free energy, low microroughness, and ultrasmooth topology prevent fouling settlements [8,9]. The hierarchical nature and layer of waxes covering the lotus leaf produce a superhydrophobic self-cleaning and water-repellent surface called "lotus effect" [10,11]. Lotus effect is a common phenomenon for some plants that possess high water repellency and self-cleaning ability. The water repellency of a coated film is fundamentally based on the following: (i) nano-micro-binary structure and (ii) chemical functionality of nanocomposite coatings [12,13]. Water contact angle (CA) larger than 150° and a considerably low roll-off angle are crucial for self-cleaning and surface inertness [14]. However, superhydrophobic surface of substrates is attained through different methods, such as chemical vapor deposition, electrospinning, electrowetting, lithography, etching; sol–gel method is more conventional among these methods because of its easy process and acceptable treatment conditions [15,16].

A superhydrophobic FR nanosurface exhibits many advantages, such as low fouling adhesion, low friction, low surface tension, and high restitution coefficient [17]. Environmental exposures of nanomaterials are inevitable because of their various applications in technological and biological fields [18]. Silicone paints, particularly polydimethylsiloxane (PDMS), possess nonleachant properties and ultrasmooth topology, environmental friendliness, stability in water, low free energy, optimum molecular mobility, water and fouling repellency, stability against heat and oxidation, and good adhesion on different substrate materials [19]. These superior characteristics of vinyl-ended PDMS over hydroxyl-terminated PDMS enable its applications in FR technologies [20]. Recently, PDMS elastomers and their nanofiller reinforcements have attracted worldwide interest because of their unparalled characteristics possessed from organic/inorganic hybrid components [21,22]. High surface reactivity is obtained through nanofiller intercalation and bond to the polymer matrix chains [23]. Thus, this reaction generates new physical properties and improves the self-cleaning and nonwettability performance of AF coatings [24]. The present research introduces a novel series of self-cleaning FR coating models based on ZnO–SiO_2 nanocomposites.

ZnO particles possess various advantages, such as low cost, environmental friendliness, antibacterial activity, and anticorrosive properties, which enable their utilization in physics, chemistry, materials, and solar cells [25,26]. Changing the morphology from microrods to nanospheres through changing pH provides efficient bacteriostatic activity [26]. In nanostructured materials, surface reactivity, functionality, and charge can be altered by doped nanoparticles (NPs), which can also ameliorate durability and immutability. Moreover, these factors can improve the stability and dispersive ability of core material [27]. ZnO-doped nanostructures exhibit excellent antibacterial properties than undoped structures [27]. SiO_2 is one of the most studied material because of its eminent stability and environmental compatibility with other materials. These outstanding features prompted our research to prepare SiO_2-doped ZnO-structured nanocomposites with novel FR performance resulting from synergetic interaction of composite materials [28]. Vinyl-ended silicone composites enriched with SiO_2-doped ZnO nanofillers were synthesized. Several nanofiller concentrations were also utilized for comparison. The volume fraction, nanofiller type, morphology, and interfacial properties of individual constituents are the main factors in determining PDMS composite behavior. Therefore, this research focused on applying a hin, environment-friendly, inert, water repellent, low cost, and nonleachant nanocomposite coatings with low surface free energy in an in situ process to produce self-cleaning FR phenomenon. Stable ZnO doped with SiO_2 nanospheres with 25 nm average diameter was elaborated via a facile sol–gel technique.

Newly developed nonstick FR composites of silicone filled with SiO_2–ZnO NPs were successfully prepared and studied. The changed surface features, which can ameliorate lotus effect and develop ultrasmooth surface, resulted mainly from the well-dispersed nanocomposites' fillers. We hypothesized that the water repellency of self-cleaning FR nanosurfaces can be monitored through improved chemical reactivity and surface topology. The CA, microroughness, and free energy of modeled surfaces were quantitatively measured mathematically. The designed nanosystem could be potentially applied in ideal self-cleaning FR via a physical repelling mechanism. This research obtained promising findings about facility, economic returns, durability, stability against UV irradiation, wide range of pH solutions, environmental impacts, and effective applications in marine FR nanocoatings.

2. Experimental

2.1. Chemicals

Octamethylcyclotetrasiloxane (D_4, 98%, utilized as vinyl-ended PDMS source), tetramethyldivinyldisiloxane (97%), polymethylhydrosiloxane (PMHS; Mn = 1700–3200), platinum catalyst (Karstedt catalyst), diethylene glycol (DEG, AR), polyethylene glycol (PEG) (400, AR), cesium hydroxide (99.95%), ammonium hydroxide (NH_3-·H_2O; 33 wt% in water), toluene (AR), and anhydrous ethanol (AR) were all purchased from Sigma–Aldrich Chemical Co. Ltd. (USA). Zinc acetate dehydrate (AR; Acros Company, Belgium) was used as ZnO precursor. All solvents were of analytical reagent grade; they were all purchased from Merck, Mumbai, India and used as received.

2.2. Fabrication of SiO_2-doped ZnO nanospheres

Distinct ZnO nanospheres doped with SiO_2 were synthesized without any additional surface modification.

SiO_2-doped ZnO was prepared by a simple sol–gel procedure using Stöber method (Scheme 1) [29–31]. NPs finally appeared as white precipitates; they were filtered, washed several times with ethyl alcohol and 2-propanone (50:50 by volume), and finally