Progress in Organic Coatings 116 (2018) 21–34

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Eco-friendly design of superhydrophobic nano-magnetite/silicone composites for marine foul-release paints

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ARTICLE INFO

Keywords:
Fouling release
Nanocomposites
Nano-magnetite fillers
Lotus effect
Bacterial progenies
Good-distribution

ABSTRACT

Advances in nanomaterials science are associated with developments fabrication methods in terms of energy saving, environment friendliness, and low cost. Self-cleaning nanocoatings with fouling release (FR) mechanism have been extensively investigated because of their non-stick, non-leachant, ecological, and economic advantages. Herein, we successfully modeled a series of self-cleaning technologies by using elastiometric siloxane polymer/nano-magnetite composites. The nanocomposite systems are dynamic non-stick surfaces and deter any fouling attachment through physical anti-adhesion. A series of superhydrophobic nanocomposites were synthesized through solution casting using different concentrations of nano-magnetite fillers. The fillers Exhibit 10–20 nm particle diameter range and spherical shape facet mainly with the {311} crystal lattice plane. The composites were dispersed in linear ά,ώ-dihydroxy polydimethylsiloxane (PDMS). Wettability characteristics, such as hydrophobicity, roughness, and free energy, were investigated by water contact angle analysis, field emission scanning electron microscopy, atomic force microscopy, X-ray photoelectron spectroscopy to evaluate self-cleaning and FR features. The nanocomposites were also subjected to various tests on surface adhesion and mechanical properties, such as tensile modulus, impact, T-bending, crosscut, and abrasion resistance. The anticorrosive features were investigated through salt spray test in 5 wt.% NaCl. Microfoulants of diatoms and bacterial progenies were selected and used to assess the anti-adhesion performance of the tailored nanosurfaces. The biological tests in laboratory was confirmed with a 3-month natural seawater field trial which indicated excellent inhibition of diatoms and bacterial growth and approved superior antifouling FR potential of the polymer/nano-magnetite (0.5%) composite hybrid coatings. This study provides insights into how structure–property relationship can enhance biological antiadhesion and FR performance. The uniform distribution of the nano-magnetite particles improved their water repellency, smoothness, and biological inertness. The particles also exhibited high static contact angle of about 153° ± 2° and low surface free energy with the lotus effect. The bulk properties and durability as well as anticorrosive properties were improved. The PDMS/magnetite nanomodels possess numerous advantages, such as simplicity, non-toxicity, environmental sustainability, commercial feasibility, low fuel consumption, and desirable self-cleaning surfaces with durability characteristics.

1. Introduction

Controlling fouling via environment-friendly and cost-effective paint technologies is of universal interest [1,2]. This market is worth billions of dollars annually [3]. Increased friction resistance and hydrodynamic weight lead to increase in fuel consumption and reduction in shipping velocity [4]; these outcomes increase the financial costs and harmful emissions of marine transportation to the environment [5]. Considering these adverse effects, researchers aim to design different coating solutions [6]. The increased international prohibition on the application of biocidal AF paints has encouraged the development of environment-friendly options [7]. Fouling release coating (FRC) technology is used worldwide particularly in the shipping industry because of their superior fouling resistance properties [8]. FRC works through hindering the attachment of fouling community by providing self-cleaning behaviour [9]. FRC is categorized into main subclasses of

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https://doi.org/10.1016/j.porgcoat.2017.12.008
Received 20 February 2017; Received in revised form 7 December 2017; Accepted 8 December 2017

organo-silicones and fluro-polymers. Organo-silicone polymers, especially polydimethylsiloxane (PDMS), are superior to and can overcome the limitations of fluro-polymer [10–12]. As non-leachant and non-stick FRC, PDMS possesses a structure with Si-O backbone and methyl side chain; this structure confers outstanding features, such as high smooth topology, water repellency, high structure mobility, low surface free energy (SFE), and porosity [12,13]. The incorporation of inorganic boosting nanofillers has become inevitable [14]. Increasing the interaction of PDMS–nanoadditive enhances cost savings and improves the mechanical, self-cleaning, and lotus effect characteristics [15]. The lotus effect is related to superhydrophobicity and water repellency caused by the hierarchical nature and the waxy layer that covers the leaves of the lotus plant [16]. This effect is a common natural phenomenon that allows the plant to easily clean themselves by water repellency. Self-cleaning nanosurfaces with the lotus effect and superhydrophobic performance exhibit potential for fouling prevention and microfluidic systems [17,18]. For a coated film, the lotus effect is achieved by obtaining micro–nano dual binary construction and surface chemical functionality [19]. Increase in water contact angle (WCA) and decrease in SFE are essential parameters to prevent bacterial and fouling detachments. Thus, the design of nano–micro surface with extra-high WCA and low SFE according to Baier curve are promising for FRC on ship hulls [20]. At present, number of publications on implications and applications of nano-magnetite (Fe_3O_4) increases [21,22]. Nano-magnetite possesses superior biological and physicochemical characteristics because of the Fe(II) and Fe(III) contents in its structure [22,23]. At the nanoscale, magnetite acts as super paramagnetic and is applied in various fields, such as biosensors, cell tracking, tissue engineering, and cancer treatment [24]. Magnetite nanoparticles (MNPs) possess large surface-to-volume ratio, which provides abundant sites for high chemical activity in biological applications [25]. Chemical stability and non-toxicity are key factors considered in the preparation of an MNP system [26]. This state-of-the-art technology inevitable presents dominant morphology and average diameter of the designed MNPs. Hollow spherical MNPs possess shell-like particles with controllable shape and size and chemical stability. These particles exhibit several advantages, such as large surface area and internal space. Nano-magnetite spherical morphology contains large surface area and internal spacing, low density, and polarity with improved chemical, mechanical, and thermal stability [27,28].

Spherical NPs can be produced through several techniques, such as hydrothermal, solvothermal, sol–gel, sonochemical, chemical vapor deposition, and co-precipitation methods [29]. Co-precipitation is the most widely used because of its products exhibit high purity, homogeneity, symmetrical order, small particle diameter, and single-step processing; in addition, this technique is environment friendly because only water is used for salt dissolution [30]. MNPs can also be prepared using template-assisted techniques; however, these approaches suffer from high cost, complex procedures, low yield, and difficulty in washing the produced PDMS/magnetite nanocomposites [31]. Enriched linear ά,ώ-dihydroxy PDMS with magnetite nanospheres were modeled, and different nanofiller percentages were utilized. The attributes of the individual constituents, volume fraction, nanofiller type and morphology, and interfacial properties are main factors considered in determining the behaviour of the PDMS nanocomposites. The composites should exhibit cost-effectiveness, inertness, low-SFE, self-cleaning through water repellency, and nano-leachant property.

In this work, we synthesized non-stick and nontoxic PDMS/magnetite nanosphere composite coating through an ex-situ method to obtain eco-friendly FR nano-paints. A one-step, template-free hydrothermal technique was conducted to synthesize MNPs with spherical shape and diameter range of 10–20 nm; the crystal growth of the particles follows Ostwald ripening. This research is the first to use PDMS/nanospherical MNPs for FR coating of ship hulls. Tensile modulus, impact, T-bending, and cross-hatch tests were performed to evaluate bulk mechanical properties. WCA, SFE, and micro-roughness were determined to evaluate surface properties. Nano-magnetite spheres stabilized with negatively charged citrate ions were chosen due to their enhanced dispersion property and better chemical compatibility with PDMS hosts. Incorporation of a specific nanofiller percentage of 0.5 (of nano-magnetite spheres) provided good dispersion, high surface-to-volume ratio, resulting in maximum water repellency, minimal free energy of the surface, and fouling immunity characteristics of the tailored PDMS composite nanocoatings. The topological, chemical, and mechanical characteristics confer the nanocomposite surface with inertness. The fouling cohesion characteristics were inhibited through this eco-friendly technique by using the failure adhesion mechanism of fouling. Comparative studies reflected the promising features introduced by these newly developed well-dispersed nanocomposites as compared with other commercial and previously reported AF coatings.

2. Experimental

2.1. Chemicals

Octamethylcyclotetrasiloxane ($C_8H_{24}O_4Si_4$, D4, 98%) which was utilized as HTPDMS source, Tetraethylorthosilicate (TEOS, 98%), Dibutyltindilurate Catalyst ($((CH_3CH_2CH_2CH_2)_2Sn[OCO\text{-}(CH_2)_{10}CH_3]_2$, 95%), Iron (II) chloride tetrahydrate, ($FeCl_2{\cdot}4H_2O$, Merck); Iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$,), ammonium hydroxide ($NH_3{\cdot}H_2O$; 33 wt.% in water) were all purchased from Sigma–Aldrich Chemical Co. Ltd., USA. anhydrous ethanol (AR), hydrochloric acid, (HCl, 37%); acetone was delivered from Acros Company (Belgium). Potassium hydroxide (KOH, 98%), Tetrahydrofuran (THF) and all solvents are analytical reagent grade and were purchased from Merck, Mumbai, India and used as received.

2.2. Synthesis of linear ά,ώ-dihydroxy PDMS

Linear ά,ώ-dihydroxy PDMS was successfully prepared through chain-growth polymerization by using anion reactive species obtained from the strong base catalyst KOH. Previous works were taken in consideration [9,32].

A definite amount of D4 (15 g) was injected in the reaction vessel and mixed with a small amount of ground KOH (0.08 g) at room temperature (RT) under continuous stirring. The sample was placed in a thermodynamic oil bath at temperature increased to 120 ± 5 °C in the presence of inert nitrogen under stirring for 4 h. The reaction mixture was cooled to approximately 50 °C and degassed to remove the unreacted monomer for frothing prevention. The temperature was increased to 180 ± 5 °C for 3 h. The temperature was gradually decreased to RT with overnight stirring to terminate the reaction. Finally, THF was used to solubilize the obtained macromolecule. A specific amount of glacial acetic acid was added to neutralize the unreacted source of anion (KOH) until the pH reaches 7 and stirred overnight. The formed salt was precipitated, the solution was filtered, and THF was evaporated. The product exhibits the following characteristics: molecular weight (Mw) ~139520 g/mol, dispersity (D) = 2.6, viscosity = 900–100 cp at 25 °C, and yield: 79%; ^{1}H NMR (300 MHz, $CDCl_3$): 1.1 (CH_3-side chain) and 4.6 (OH terminal end group).

2.3. NP growth and structure

Spherical MNPs were prepared through an easy coprecipitation method under inert nitrogen [33]. Briefly, 0.30 mol $FeCl_3{\cdot}6H_2O$, 0.15 mol $FeCl_2{\cdot}4H_2O$, and 2 mol aqueous HCl solution were added to 20 mL of deionized water. An aqueous solution of 2 M NH_4OH was used as alkali source and added dropwise. The reaction was carried out under vigorous stirring for 45 min, followed by a gradual increase in the temperature up to 80 °C ± 2 °C under nitrogen atmosphere with a flow rate of 4 sccm (standard cubic centimetre per minute). for 2 h. The color started to change to orange and became darker, ultimately