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The leaching behavior of phenylmethylsilicone oil and antifouling performance in nano-zinc oxide reinforced phenylmethylsilicone oil–Polydimethylsiloxane blend coating

Miao Ba[a,b], Zhan-ping Zhang[a,b,*], Yu-hong Qi[a,b]

[a] Key Lab of Ship-Machinery Maintenance & Manufacture, Dalian Maritime University, Dalian, 116026, China
[b] Department of Materials Science and Engineering, Dalian Maritime University, Dalian, 116026, China

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ABSTRACT

In order to figure out the influence of nano-zinc oxide (NZO) on the properties of the fouling release (FR) coating based on polydimethylsiloxane (PDMS) with the incorporation of phenylmethylsilicone oil (PSO), NZO reinforced PSO-PDMS blend coatings were prepared by adjustments to the particle size and pigment-binder ratio (P/B). The surface properties, the mechanical properties, the PSO leaching behavior and the biofilm adhesion assay of the reinforced coatings were investigated. Results indicated that with the increase of particle size and P/B value, surface roughness of the reinforced coatings increased and the mechanical properties of the reinforced coatings were enhanced. The addition of NZO caused PSO to migrate first inside the reinforced coating to form the oil storage sac, then migrate to the reinforced coating surface. Finally, PSO was leached on the reinforced coating surface. Meanwhile, the addition of NZO increased the crosslink density of the reinforced coatings, which caused the decrease of the leaching efficiency of PSO. When the P/B value was more than P/B_M, PSO still could not be observed on the reinforced coating surface after 1 year of exposure. And the anti-biofilm adhesion performance of the reinforced coatings decreased due to the increase in difficulty of leaching PSO.

1. Introduction

Marine biofouling is the undesirable growth and accumulation of marine organisms onto objects submerged in seawater [1–4]. It is a complex phenomenon in multiple stages due to more than 4000 different species of fouling organisms [5–7]. Coatings used to prevent the biofouling are divided into antifouling (AF) and fouling-release (FR) coatings [8–10]. Compared to AF coatings, FR coatings work by reducing the adhesion of biofouling to the surfaces submerged in seawater, instead of killing adherent organisms by releasing toxic components [11], which will not pollute the marine environment. Now, it has been widely used.

The first FR coating based on polydimethylsiloxane (PDMS) was tested in 1972 [12], and it has become a more widely mentioned topic since 1990. The practical using results show that it is the most effective FR coating [13–15], which the prevention of fouling organism adhesion mainly depends on the physicochemical property for PDMS elastomer. The low surface energy and elastic modulus of PDMS coating decrease the adhesion strength of fouling organism [16]. By seawater shear, the adherent fouling organisms can be released into the marine environment. It is conducive to the stability of the marine food chain. In addition, it cannot cause imposex, intersex, and sterility for marine organisms [17].

Incorporation of non-reactive silicone oils into PDMS coatings was the earliest reported in 1977 [18]. Related studies indicated that it can obtain improved fouling release properties by reducing the attachment strength of fouling organisms [19,20]. Further research shows that the antifouling performance improvement of related coatings is depended mainly on the leaching of silicone oils onto the coating surface, which improves the lubricity of the coating surface [21–23]. Meanwhile, the analysis of the kind of non-reactive silicone oil also confirms that methylsilicone oil (MSO) and phenylmethylsilicone oil (PSO) can be widely used in the FR coatings [21,22]. Especially PSO, it can effectively decrease the adhesion of barnacle and oyster [24]. And a clear report confirms that the incorporation of PSO into the coating can reduce the amount of substratum strain required to detach barnacles [8]. These research results show great prospects on improving the antifouling performance of FR coatings based on PDMS. Although some researchers worry the possibility that silicone oil may be harmful to the marine environment [24]. Incorporation of silicone oil into PDMS

* Corresponding author at: Key Lab of Ship-Machinery Maintenance & Manufacture, Dalian Maritime University, Dalian, 116026, China.
E-mail address: zzp@dlmu.edu.cn (Z.-p. Zhang).

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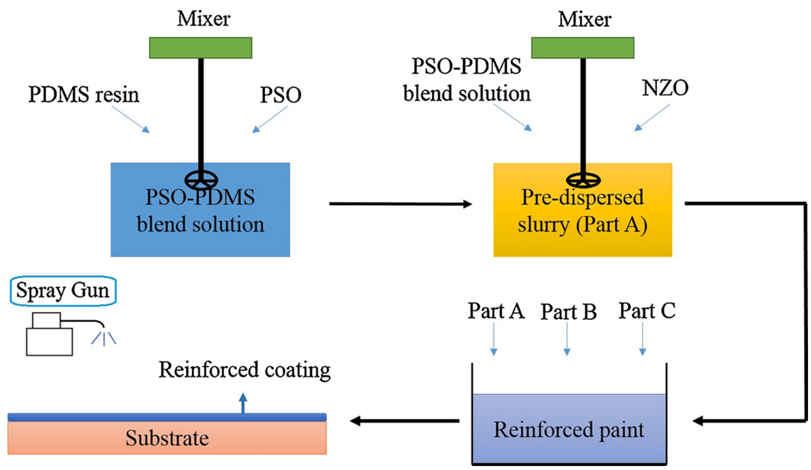

Fig. 1. The process of the coating preparation.

Table 1
The surface properties of the reinforced coatings.

Sample	Contact Angle (°)		Surface Free Energy (mJ/m^2)	Surface Roughness, Sa (μm)
	Water	Diiodomethane		
CS	116.5 ± 0.17	68.4 ± 0.32	25.3 ± 0.56	0.009
Z30-1	117.0 ± 0.33	69.2 ± 0.71	24.9 ± 0.47	0.015
Z50-1	117.2 ± 0.41	70.0 ± 0.52	24.4 ± 0.66	0.016
Z100-1	117.6 ± 0.33	70.3 ± 0.71	24.3 ± 0.47	0.020
Z100-2	117.9 ± 0.55	70.7 ± 0.24	24.1 ± 0.28	0.024
Z100-3	118.8 ± 0.71	72.7 ± 0.54	22.9 ± 0.68	0.028
Z100-4	119.5 ± 0.71	73.4 ± 0.21	22.5 ± 0.66	0.032

coatings demonstrate that no statistical evidence supports these concerns, and there is no direct threat to organisms given the extremely low toxicity of silicone oil [21,24]. And this kind of coatings can be considered as the Silicone Oil – PDMS blend coating

However, FR coatings based on PDMS have the following disadvantages: mechanical damage is susceptible to happen and also displays poor adhesion strength with substrates [10]. Therefore, it needs to be modified. As an important part of FR coating, particles, especially inorganic nano-particles are one of the promising solutions for superior PDMS-based composite coatings [17,25,26]. Various nanocomposites have been used to modify the FR coatings based on reinforcing the physical and the mechanical performance [26]. For example, nano-zinc oxide (NZO) is widely used in the field of antifouling coatings for shielding the ultraviolet rays, improving the attachment the mechanical properties of the coating [27,28]. However, it lacks the research for the effect of particles on the FR coating based on PDMS with the incorporation of non-reactive silicone oil. In order to figure out the influence of particles on the leaching behavior of non-reactive silicone oil, NZO reinforced blend coating will be prepared. By changing the pigment-binder ratio (P/B) between NZO and PDMS resin, as well as the particle size of NZO, the surface properties and mechanical properties of the coatings will be conducted. And the focus of this study will be on the analysis of the leaching behavior of PSO influenced by NZO. Subsequently, biofilm adhesion assay of the coatings will be evaluated, confirming the influence of NZO on the antifouling performance of the coatings with the incorporation of PSO.

2. Materials and methods

2.1. Materials

Hydroxyl-terminated polydimethylsiloxane (PDMS) with a viscosity of 10,000 mPa s was obtained from Dayi Chemical Industry Co., Ltd. (Yantai, China). Phenylmethylsilicone oil (PSO) with a viscosity of 100 mPa s from Hualing Resin Co., Ltd. (Shanghai, China) was used as non-reactive silicone oil. Tetraethylorthosilicate (TEOS) from Kemiou Chemical Reagent Company (Tianjin, China) was used as crosslinking agent. Toluene, xylene, and acetylacetonate from Yongda Chemical Reagent Company (Tianjin, China) were used as solvents. The effective catalytic component was Bismuth neodecanoate (BiND) from Deyin Chemical Co., Ltd. (Shanghai, China). All chemicals and reagents were used as received without any further purification. Nano-zinc oxide (NZO) from Aladdin (Shanghai, China) with 30 nm, 50 nm, and 100 nm of particle size was dried at 120 °C before the experiment.

2.2. Preparation of the coating

The coating consisted of three parts. Pre-dispersed slurry (Part A) included PDMS (100 g), PSO (5 g) and NZO. TEOS mixed with xylene to make the curing agent (Part B), and the catalytic agent (Part C) was composed of BiND and ethyl acetate. The two-stage method of preparation process was as follows: PDMS and PSO were added into a 500 mL stirring tank at 3000 rpm for 10 min, then NZO was added in the mixture for 30 min to make Part A. Subsequently, Part A was ground using cone mill, and afterward, Part A, Part B, and Part C were mixed well. Glass slides with dimensions of 75 mm × 25 mm × 1 mm, Teflon molds with dimensions of 150 mm × 150 mm × 2 mm, and glass Petri dishes with a diameter of 60 mm and a thickness of 2 mm were used as the substrate for casting coatings. The curing process was at room temperature for at least 4 h to form a cross-linked elastomer. Thereafter, the record of the exposure time began. The slide samples were used for surface properties and antifouling tests, the cast coatings with Teflon molds were used for mechanical properties, and the cast coatings with glass culture dishes were for morphology observation. The coating without NZO was used as a control sample (CS), and it was defined as the blend coating. The whole process was also shown in Fig. 1. Experimental coating number is Zx-y, where x represents the particle size value of NZO and y is equal to P/B value multiplied by 100. Correspondingly, they were defined as the reinforced coating. All measurements were conducted at room temperature.

2.3. Characterization

A JC2000C contact angle measurement system (Zhongchen Co., Ltd., Shanghai, China) was used. And 3-μL droplets of deionized H_2O and CH_2I_2 were placed on the sample surface using a syringe. Digital images of the droplet silhouette were captured with a charge-coupled device camera and the contact angles were evaluated using the measuring angle method. Six droplets for each sample were calculated for