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Study of a Nano-SiO_2 Microsphere-Modified Basalt Flake Epoxy Resin Coating

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Abstract: Basalt flakes (BFs) have been widely used in recent years as a novel anticorrosion material in the marine industry to prevent the corrosion of metal substrates. In this study, BFs were modified with 1–7‰ nano-SiO_2 microspheres, and a modified BF epoxy coating was successfully prepared. Experimental results showed that the BF epoxy resin coating modified with 3‰ nano-SiO_2 microspheres exhibited excellent chemical durability (surface weight loss rate of 2.2% in the alkali solution and only 1.1% in the acid solution at room temperature after 480 h), low water infiltration (water absorption of 0.72% after 480 h), and good mechanical performance (tensile strength of approximately 33.4 MPa). This study proves the feasibility of using nano-SiO_2 microspheres to modify BF epoxy resin coating and enhance the chemical durability and mechanical properties provided by the coating.

Keywords: basalt flake; nano-SiO_2 microspheres; coating; chemical durability; modification

1. Introduction

The marine industry has played a vital role in global economic integration and continues to develop rapidly, promoting the wide utilization of metals due to their excellent mechanical properties and durability [1]. However, metal components easily corrode and fail in marine environments with high salinity and oxygen-rich seawater [2]. Coating techniques that have advantages of easier operation, lower cost, and better protection have been widely applied in order to prolong the life of metals in the marine environment.

The corrosion resistance of a coating can be further enhanced by mixing flakes in the polymeric matrix. Glass flake (GF) coatings were the earliest to be utilized and are now the most widely used anticorrosion coatings [3]. They have a strong adhesion to base materials, thus providing strong resistance to seawater corrosion. GF fillers effectively increase the diffusion pathways of salt water and destructive ions in the coatings, thus significantly enhancing their anticorrosion properties [4]. Alhumade et al. [5] modified the surface of GFs with aminosilane groups, leading to a substantial enhancement in the corrosion protection and thermal stability of epoxy–GF composite coatings. Broughton et al. [6] found that GFs modified with aminosilane had higher stiffness and strength than GFs modified with titanate. Yan et al. [7] studied the alkali/acid resistance of epoxy/basalt flake coatings and concluded that good chemical durability will improve the anticorrosive property of epoxy coatings.

Basalt is one of the most earth-abundant and widely distributed minerals [8]. It has a good shielding performance, has strong acid and alkali resistance, and is therefore widely used in the preparation of composite materials [9,10]. Compared with glass, basalt has higher Fe_2O_3, TiO_2, Al_2O_3, and CaO contents, which can modify the network structure and enhance chemical stability of glass [11], As a result, basalt exhibits good corrosion resistance, weather resistance, dielectric properties, and thermal deformation. However, similar to other inorganic fillers, basalt flakes (BFs) are hydrophilic and oleophobic [12]. The compatibility of BFs and epoxy resin is rather poor, resulting in low corrosion resistance of coatings. Surface modification of BFs helps to reduce the difference in chemical structure and physical properties between the filler and the polymer, thus improving properties such as affinity, processing fluidity, dispersibility, and wettability [13].

Nano-SiO_2 microspheres are widely used in the modification and enhancement of composite materials because they possess many unique characteristics, such as high specific surface area, excellent surface adsorption, large surface energy, good dispersion properties, and good thermal resistance [14]. Nano-SiO_2 microspheres effectively enhance the bonding strength of carbon fabric and resin, improving the friction-reduction and anti-wear abilities of friction materials [15]. Zhang et al. [16] introduced nano-SiO_2 particles to the surface of carbon fibers by a sizing treatment, significantly improving the interfacial shear strength and interlaminar shear strength of carbon fibers.

Due to their natural abundance, low cost, energy-saving manufacturing, and excellent stability under extreme conditions (e.g., high temperature, high pressure, acidic and alkaline media), basalt flakes have a huge potential and promising properties to be applied as fillers for protective coatings [12]. The excellent properties of nano-SiO_2 microspheres motivated us to modify BFs with nano-SiO_2 microspheres and study the effects of nano-SiO_2 microspheres on the properties of modified BF epoxy resin coatings. In this study, BFs were modified with different percentages of nano-SiO_2 microspheres, and a modified BF epoxy resin coating was successfully prepared. The chemical durability and mechanical properties of the modified BF epoxy resin coating were examined.

2. Experimental Procedures

2.1. Materials

The chemical composition of the basalt flakes used in this work (measured by X-ray fluorescence (XRF), in wt%) was 53.56 SiO_2, 13.99 Al_2O_3, 12.39 Fe_2O_3, 7.64 CaO, 6.04 MgO, 2.45 TiO_2, 2.98 Na_2O, 0.56 K_2O, and 0.043 ZrO_2. The BFs used had an average thickness of 5 $\pm$ 2 μm, length of 10–50 μm, and density of approximately 2.9 g/cm^3.

2.2. Sample Preparation

Nano-SiO_2 microspheres with controllable particle sizes were prepared by the tetraethylorthosilicate (TEOS) hydrolysis method [17]. The surfaces of the microspheres were modified with the KH550 (supplied by Shanghai Macklin Biochemical Co., Ltd. Shanghai, China) silane coupling agent.

First, we prepared the nano-SiO_2 microspheres. The TEOS reactant (16 mL), ammonia hydroxide catalyst (8 mL), and deionized water (48 mL) were added to ethanol, which was used as the solvent (480 mL). Then, the TEOS solution was hydrolyzed by stirring at 25 °C for 2 h and centrifuged at 20,000 rpm for 1 h to obtain SiO_2 microspheres with an average particle size of 30 nm. Second, we used KH550 to improve the nano-SiO_2 microspheres (to avoid agglomeration). The nano-SiO_2 microspheres were dispersed in ethanol and deionized water. KH550 was hydrolyzed by reacting with deionized water and ethanoic acid at 25 °C for 1 h. Then, 5% KH550 hydrolysate was added to obtain the improved nano-SiO_2 microspheres. Third, we prepared the modified BFs. The BFs were added to xylene, and magnetic stirring was carried out for 20 min. The improved nano-SiO_2 microspheres were added at 65 °C and 75 drops/min with percentage by weight of 1, 3, 5, and 7‰. Then, the BFs, xylene, and nano-SiO_2 microspheres were mixed at 80 °C for 3 h and at 110°C for 1 h. Afterward, the modified BFs were centrifuged and washed with xylene and tetrahydrofuran. Finally, we prepared

the modified BF epoxy resin coating. The epoxy resin coating was prepared by adding epoxy resin, xylene, anhydrous ethanol, and hexamethylenetetramine (HMT) in a 10:4:2:1 mass ratio with magnetic stirring for 40 min. The modified BF epoxy resin coating was prepared by adding 25 wt% modified BFs to epoxy resin coating with magnetic stirring for 60 min and then solidifying at room temperature for 24 h.

2.3. Characterization Techniques

The modified SiO_2 microspheres were characterized using a Fourier transform infrared spectrometer (FTIR; Nicolet 8700, Waltham, MA, USA). The morphology of the samples was studied by scanning electron microscopy (SEM; SU8010, Tokyo, Japan), and energy-dispersive spectroscopy (EDS; X-MAX (50 mm^2), Tubney Woods, Abingdon, UK) was used to detect and analyze the elemental changes of the surface of the basalt flakes. Basalt flake epoxy resin coating samples with dimensions of 75 mm × 12.5 mm × 2.0 mm were prepared for tensile strength measurements carried out using a Universal Testing Machine (WDW3020, Changchun, Jilin, China) at a testing speed of 0.5 mm/min. The tensile strength can be calculated by $\sigma_M = F/A$, where F is the maximum force, and A is the original area of cross section.

2.4. Chemical Durability and Water Absorption Tests

The chemical durability of the modified BF epoxy resin coating (15 mm × 15 mm × 5 mm) was assessed by leaching tests [18] conducted at room temperature for 480 h in 3 mol/L HCl solution and 3 mol/L NaOH solution and shown by the surface weight loss rate. The surface weight loss rate can be calculated by $(w_0 - w_1)/w_0$, where w_0 is the initial weight of the modified BF epoxy resin coating, and w_1 is the weight after the leaching tests after washing by deionized water and drying. Each sample was measured five times by the Mettler Toledo AL204 balance (Shanghai, China) at room temperature, and the results reported are the average values.

The water absorption of the BF epoxy resin coating (50 mm diameter and 32 mm thickness) was assessed. First, the samples were immersed in deionized water at room temperature for 24, 240, and 480 h. The samples were then taken out of the water, dried completely with cloth, and weighed using the Mettler Toledo AL204 balance (Shanghai, China) as w_3. The water absorption rate can be calculated by $(w_3 - w_2)/w_2$ [4], where w_2 is the initial weight of the modified BF epoxy resin coating.

3. Results

3.1. Characterization and Properties of BFs

3.1.1. Surface Morphology Analysis of BFs

The surface morphologies of the unmodified BFs and modified BFs with different contents of nano-SiO_2 microspheres are shown in Figure 1. It can be seen in Figure 1a that the surface of the unmodified BFs was quite smooth. The amount of nano-SiO_2 on the surface of the BFs increased with increasing content of nano-SiO_2 microspheres. In Figure 1b, it can be seen that the 1‰ nano-SiO_2 microspheres were only scattered on the surface of the BFs. In contrast, as shown in Figure 1c, the 3‰ nano-SiO_2 microspheres were evenly distributed on the surface, and local accumulation occurred. It can be observed from Figure 1d that the density of the nano-SiO_2 microspheres on the surface increased dramatically when their content was 5‰. Lastly, Figure 1e shows that when the nano-SiO_2 microspheres content reached 7‰, the nano-SiO_2 microspheres were severely agglomerated on the surface of the BFs. This indicates that if the nano-SiO_2 microsphere content is too high (e.g., 7‰), nano-SiO_2 particles will agglomerate in a thermodynamically unstable state because of their extremely high surface energy.

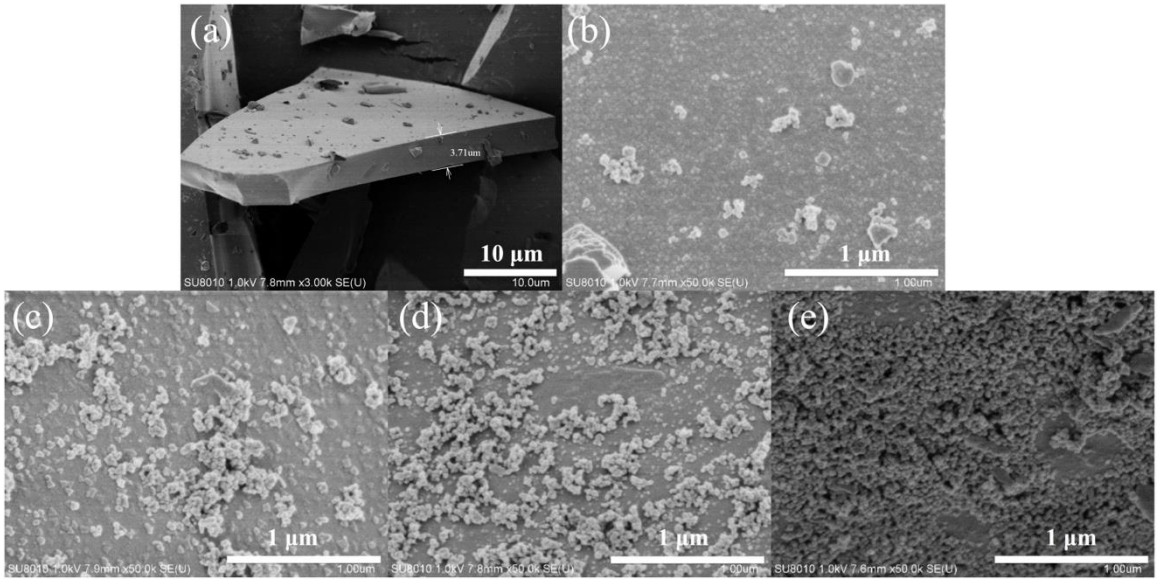

Figure 1. SEM images of (**a**) unmodified basalt flakes (BFs) and BFs modified with (**b**) 1‰, (**c**) 3‰. (**d**) 5‰, and (**e**) 7‰ nano-SiO_2 microspheres.

3.1.2. Surface Composition Analysis of BFs

Figure 2a,b shows the results of the EDS analysis of chemical elements present on the surface of unmodified BFs and BFs modified with 7‰ nano-SiO_2 microspheres.

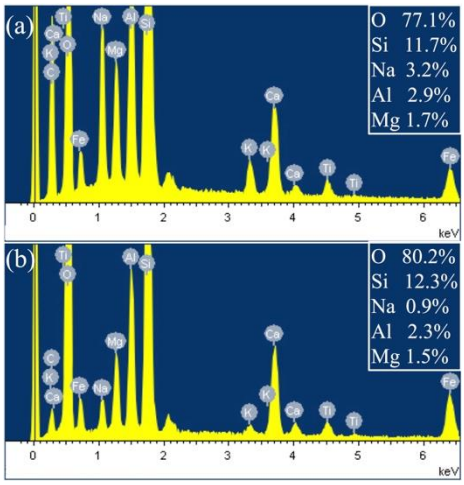

Figure 2. Energy-dispersive spectroscopy (EDS) images of (**a**) unmodified BFs and (**b**) BFs modified with 7‰ nano-SiO_2 microspheres.

According to Figure 2a,b, the contents of Si and O elements on the surface of the BFs increased after the nano-SiO_2 microsphere modification, while the contents of Na, Mg, and Fe were reduced significantly. The contents of the other elements showed no obvious changes, proving that the surfaces of the BFs were successfully covered by the nano-SiO_2 microspheres.

3.2. Characterization and Properties of the Modified BF Epoxy Resin Coating

3.2.1. Surface Morphology Analysis of the Modified BF Epoxy Resin Coating

The morphology of the cross section of the modified BF epoxy resin coatings, which is a fracture surface quenching by liquid nitrogen, is shown in Figure 3. It can be observed from Figure 3a that obvious cracks were present in the unmodified BF epoxy resin coating. However, as shown in

Figure 3b, in the modified BF (3‰ nano-SiO_2 microspheres) epoxy resin coating, the cross-linking of BFs and epoxy resin was significantly improved; additionally, many cracks were covered by the nano-SiO_2 microspheres.

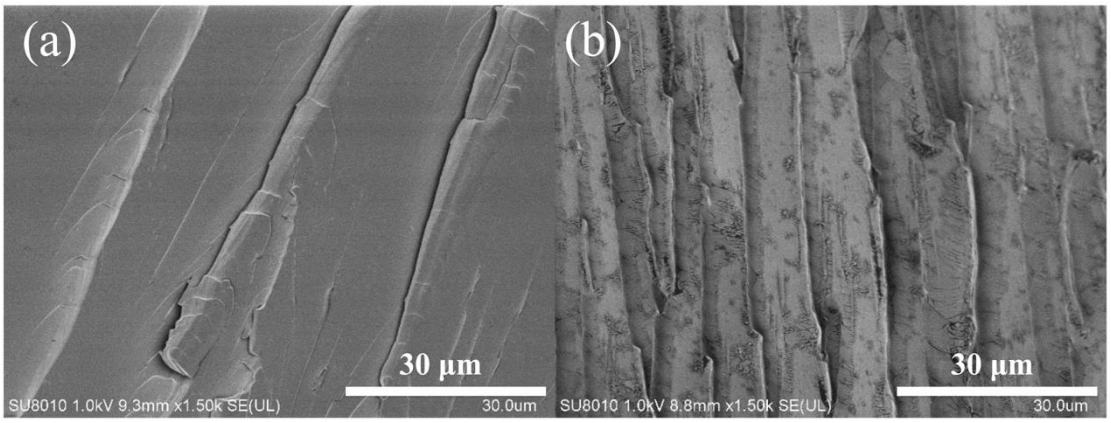

Figure 3. SEM images of the section morphology of (**a**) an epoxy resin coating with unmodified BFs and (**b**) an epoxy resin coating with BFs modified with 3‰ nano-SiO_2.

3.2.2. Chemical Durability of the Modified BF Epoxy Resin Coating

As shown in Figure 4, the surface weight loss rate of the modified BF epoxy resin coating was significantly smaller, both in acid and alkali resistance tests. The acid and alkali resistance reached the optimal values (with the surface weight loss rate of 2.2% in the alkali solution and only 1.1 % in the acid solution) when the nano-SiO_2 microsphere content was 3‰. Then, with the increase in the content of the nano-SiO_2 microspheres, the acid and alkali resistances of the coating decreased.

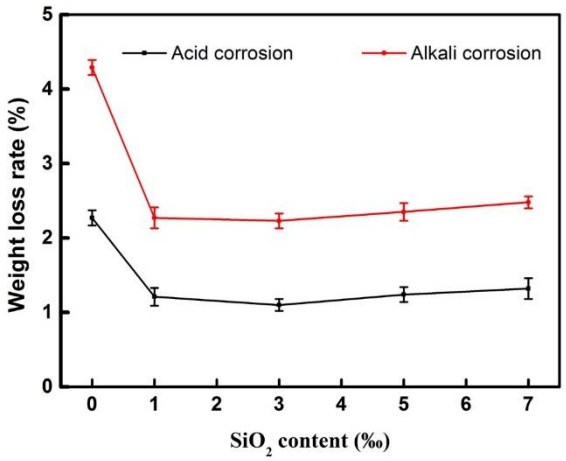

Figure 4. Weight loss rate of the modified BF epoxy resin coatings with different nano-SiO_2 contents in 3 mol/L HCl and 3 mol/L NaOH solutions.

3.2.3. Water Absorption of the Modified BF Epoxy Resin Coating

As seen in Figure 5, the samples modified with 3‰ nano-SiO_2 had the lowest water absorption after immersing the modified BF epoxy resin coating samples in water for 24, 240, and 480 h at room temperature. Then, with the increase in the nano-SiO_2 content, the water absorption rate of the samples increased slowly. Compared with the other coatings, the water blocking ability of the BF epoxy coatings modified with 3‰ nano-SiO_2 was the best.

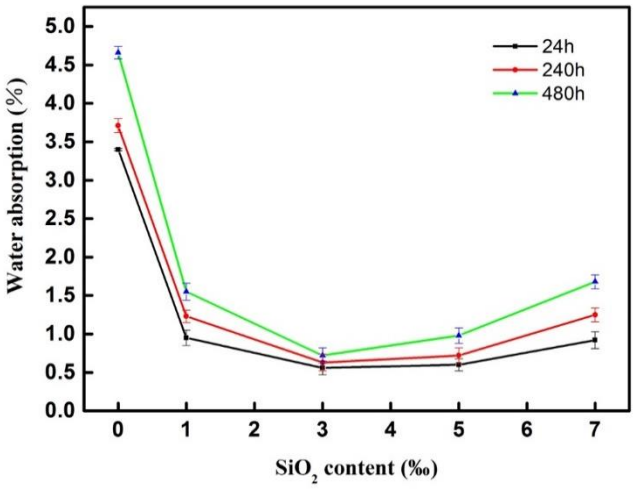

Figure 5. Water absorption of BF epoxy resin coatings.

3.2.4. Tensile Strength the Modified BF Epoxy Resin Coating

As seen in Figure 6, the tensile strength was significantly improved after the nano-SiO_2 microsphere modification of the BFs. The tensile strengths of the modified BF epoxy coatings were greater than 30 MPa, while the tensile strength of the unmodified BF epoxy coating was only approximately 20 MPa.

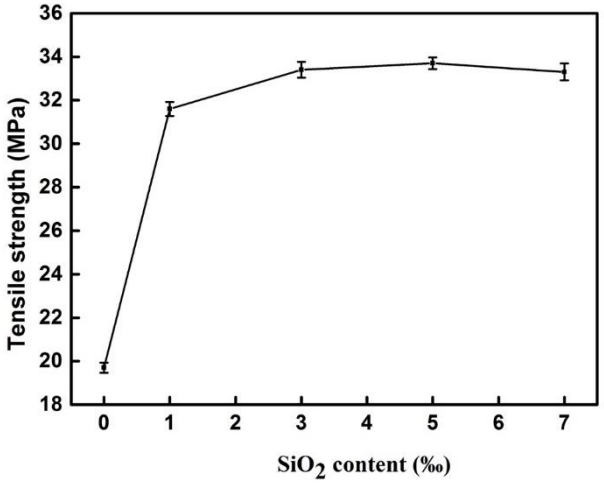

Figure 6. Tensile strength of the modified BF epoxy resin coatings.

4. Discussion

Nano-SiO_2 microspheres significantly improve the chemical durability of BFs and BF epoxy resin coatings. Nano-SiO_2 microsphere modification acts not only physically but also chemically. A compatible nature of nano-SiO_2 particles with organic matrices after the surface treatment of nano-SiO_2 microsphere with KH550 is commonly suggested [19]. As shown in Figure 7a, based on [19], we assume that nano-SiO_2 microspheres are closely linked to the resin and BFs, preventing the shedding and displacement of the flakes and resin. The epoxy resin shows strong adhesion to nano-SiO_2 microspheres due to the existence of a large number of hydroxyl groups and ether bonds in the molecular chain. This gives rise to the improved mechanical and chemical properties of the modified BF epoxy resin coating.

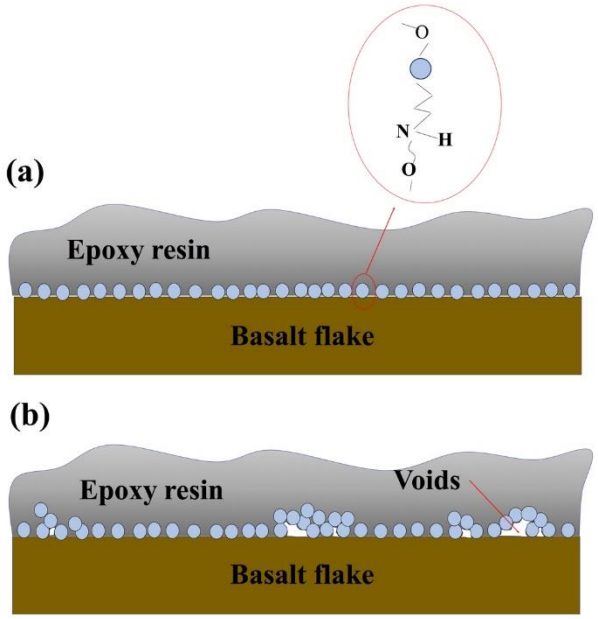

Figure 7. Schematic diagram of the agglomeration and stacking process of nano-SiO_2 microspheres on the surface of the modified BF epoxy resin coating. (**a**) For an appropriate amount of nano-SiO_2 microspheres and (**b**) for an excessive amount of nano-SiO_2 microspheres.

A small amount of nano-SiO_2 microspheres that partially modify the surface of BFs improves the interfacial compatibility to a certain extent; however, their effect is severely limited by their uneven distribution on the surface. Nano-SiO_2 particles have a large specific surface area, which indicates high surface energy, and thus they are in a thermodynamically unstable state. The existence of hydroxyls on the surface of nano-SiO_2 microspheres induces strong water absorption and causes agglomeration [20]. High water absorption can lead to cracking of the coating, which lowers the protection efficiency [12]. Another limitation is that an excessive amount of nano-SiO_2 microspheres aggregated on the surface of the BFs generates a large number of voids between the microspheres, weakening the binding between the BFs and epoxy resin, as shown in Figure 7b. Therefore, an excessive amount of nano-SiO_2 microspheres has a negative influence on the acid-based chemical durability, permeation resistance, and tensile strength of the coating. Additionally, the significantly improved chemical durability under alkali conditions compared with acid conditions is due to the relatively better anti-acid corrosion than anti-alkali corrosion properties of unmodified BF epoxy resin coatings.

Unmodified BFs have poor compatibility with epoxy resins. Therefore, the binding force between the flakes and the resin is rather weak. BFs are unevenly distributed in the coating sample and are easily deposited on one side, leading to a low spline tensile strength. The compatibility of modified BFs and epoxy resin is improved, thus increasing the binding force between the BFs and the epoxy resin. As a result, the tensile strength of the modified BF epoxy resin is greatly improved.

5. Conclusions

In this work, a nano-SiO_2 microsphere-modified basalt flake epoxy resin coating was successfully prepared. The nano-SiO_2 microspheres significantly improved the chemical durability and dispersibility of the BF epoxy resin coating. The BF epoxy resin coating sample modified with 3‰ nano-SiO_2 microspheres exhibited the best comprehensive performance with (1) excellent chemical durability (surface weight loss rate of 2.2% in the alkali solution and only 1.1% in the acid solution at room temperature for 480 h), (2) low water infiltration (water absorption of 0.72% for 480 h), and (3) good mechanical properties (tensile strength of approximately 33.4 MPa). This study proves the feasibility of using nano-SiO_2 microspheres to modify a BF epoxy resin coating and enhance the chemical durability and mechanical properties provided by the coating. Good chemical durability can

improve the anticorrosive property of BF epoxy resin coatings. The next step for this work will be to check the corrosion resistance of the coating in the marine environment and to further improve the properties of this new coating to meet commercial standards.

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Conflicts of Interest: The authors declare no conflict of interest.

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