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Effect of Emulsifier on the Structure and Properties of Waterborne Silicone Antifouling Coating

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Received: 2 January 2020; Accepted: 10 February 2020; Published: 12 February 2020



Abstract: Three-component waterborne silicone antifouling coatings, which could cured at room temperature, were prepared, respectively, with cationic (stearyl trimethyl ammonium bromide) or anionic (sodium dodecyl benzene sulfonate) silicone emulsion as a film-forming substance, γ -methacryloxypropyltrimethoxysilane as a curing agent and dibutyltin dilaurate as a catalyst. The effect of emulsifier on the structure and properties of silicone coating was studied. The results showed that the coating with cationic silicone emulsion had high crosslinking density, and its surface is smooth. The surface of the coating prepared by the anionic silicone emulsion is rough. Emulsifier type had no obvious effect on the surface free energy of the waterborne silicone coating. The coatings have the characteristics of low surface energy and excellent bacterial desorption properties. Stearyl trimethyl ammonium bromide in the cured coating can reduce the adhesion of marine bacteria on the coating prepared by cationic silicone emulsion has better comprehensive mechanical properties and antifouling performance.

Keywords: waterborne coatings; silicone emulsion; low surface energy; emulsifier; antifouling

1. Introduction

Marine fouling organisms adhere to the hull, which will reduce the ship's speed, increase fuel consumption (up to 30%), and cause blockage of marine pipelines. Therefore, biological fouling brought huge economic losses [1–3]. Antifouling coatings play an important role in preventing fouling organisms from attaching. Due to its low surface energy, silicone antifouling paint causes marine organisms not to attach firmly. Fouling organisms are easy to remove under the action of water flows [4]. Silicone antifouling coatings have been widely studied and applied because of their excellent environmental friendliness. Major coating companies have put their products on the market [5]. Current research is still focused on solvent-based antifouling coatings [6,7]. However, traditional organic coatings use a large amount of organic solvents and release volatile organic compounds during their production and application, which not only causes harm to human health, but also consumes a large amount of fossil energy. Therefore, water-based coatings have become the development direction of silicone coatings. Water-based coatings use water instead of organic solvents as the dispersing medium for film-forming materials, which meets the current requirements of low-carbon economy and energy saving. There are few related research reports, so further research is needed.

As the main film-forming substance of the aqueous silicone coating, the silicone emulsion requires an emulsifier to be added during the preparation process. According to the different emulsifiers used, silicone emulsions can be divided into cationic, anionic, non-ionic, and complex ionic [8]. Cationic and anionic silicone emulsions encounter problems such as poor compatibility with counter ions, while non-ionic emulsions have strong adaptability and better stability. However, anionic and cationic silicone coating applications.

emulsions are easier to produce and more economical. Water-based silicone coatings have gained some research and application in some industries such as architecture. Xu [9] mechanically blended the silicone emulsion and TiO₂ dispersion to prepare an aqueous silicone nanocomposite coating. Sun [10] prepared a silicone emulsion using polysiloxane as a monomer and sodium dodecylbenzenesulfonate as an emulsifier, then it dried in an oven at a high temperature for 3 h to obtain a superhydrophobic coating. It was found that as the amount of SiO₂ increased, the water contact angle of the hydrophobic coating first increased and then decreased. The highest water contact angle reached 156.1°. However, these silicone emulsions can only be formed at high temperatures, which is not conducive to practical

In order to obtain a more excellent film-forming performance and lower film-forming temperature of water-based silicone coatings, the use of other resin-modified silicone emulsions was explored. Naghash [11] synthesized a polyoxane-urethane emulsion so that it could be cured under a lower temperature and prepared coatings suitable for marine environments. He then studied the antifouling performance of the coating by soaking the sample in the marine environment for 90 days. It was found that the greater the silicone content, the smaller the fouling area. Jaber [12] used cationic silicone emulsions and acrylic emulsions to product coating. By adding acrylic emulsions with a relatively low glass transition temperature T_g , the minimum film-forming temperature of the mixed emulsions was changed, so that the blended emulsions could be cured at room temperature. The coating has good hydrophobic properties, so that the water contact angle could reach 96°. The use of other emulsion-modified silicone emulsions can change the minimum film-forming temperature to achieve low-temperature curing, but the compatibility and amount of the emulsion need to be considered, as well as the final film-forming properties of the coating.

Adding a cross-linking curing agent to the aqueous system can not only reduce the curing temperature, but also increase the cross-linking density of the film-forming material, so that the formed coating has a better performance. In this paper, two kinds of silicone emulsions are selected as film-forming products, and a KH-570 silane coupling agent (γ -methacryloxypropyltrimethoxysilane) is used as a cross-linking curing agent to explore the preparation of aqueous silicone coatings that can be cured and filmed at room temperature. The water-based silicone coatings meet the needs of the marine industry for energy conservation as new antifouling coatings. We focusanalyze the influence of cross-linking curing agents and emulsifiers on the properties of silicone coatings, and provide a scientific basis for the research and development of water-based silicone antifouling coatings for industrial applications.

2. Materials and Methods

2.1. Materials

The cationic silicone emulsion DY-OH5011 and anionic silicone emulsion DY-OH5012 were obtained from Shandong Dayi Chemical Company in Yantai, China. They are made from octamethylcyclosiloxane through emulsion polymerization. In the information provided by the supplier, we can see that both ends of the two aqueous emulsion molecules have a hydroxy functional group, and the aqueous emulsion solid content was about 30%. The curing agent (silane coupling agent KH-570) was produced by Nanjing Liansi Chemical Co., Ltd., Nanjing, China. The catalyst is dibutyltin dilaurate (analytical AR), produced by Kemiou Chemical Reagent Company in Tianjin, China. *Navicula Tenera* was produced by Algae Germplasm Bank of Chinese Academy of Sciences at Qingdao, China.

2.2. Preparation of Coating

A curing agent KH-570 (Component B) and catalyst dibutyltin dilaurate (Component C) were added into cationic silicone emulsion DY-OH5011 (Component A) or anionic silicone emulsion DY-OH5012 (Component A), respectively. Component A:B:C mass ratio is 10:0.5:0.1. Mixed liquid

room temperature, the mixture was cured for

was stirred evenly with a glass rod about 5 min. At room temperature, the mixture was cured for 4 h to form a film. After being cured, the coatings were recorded as coating 5011 and 5012. The mixture was brushed to a 76.2 mm \times 25.4 mm \times 1 mm glass slide for contact angle measurement and bacterial adhesion test. The mixture was cast into a Teflon mold to get a 120 mm \times 240 mm \times 2 mm cast film, which can be used for tensile tests, cross-link density measurement and infrared spectral analysis.

2.3. Characterization

2.3.1. Contact Angle Measurement

The water contact angle and diiodomethane contact angle were tested by a JC2000 contact angle measuring instrument (Shanghai Zhongchen Co., Ltd., Shanghai, China). A total of 3 μ L of deionized water or diiodomethane was directly placed onto the coating surface, then the contact angles were evaluated using JC2000D contact angle measurement software (1.0.0.1). Three test points were randomly selected for each sample and the average value was used as the contact angle of the coating. In order to eliminate the interference of the emulsifier on the coating surface, the sample was first ultrasonically cleaned in ethanol solution for 5 min and then ultrasonically cleaned in deionized water for 5 min. After the sample was completely dried, the contact angle test was performed. The surface free energy of the coatings was calculated with the formula proposed by Owens and Wendt [13].

2.3.2. Tensile Test

The dumbbell-shaped sample was prepared according to the national standard, GB/T 528-2009 (ISO 37:2005 [14]); the length of the sample was 75 mm and the guage length was 25 mm, the width was 4 mm. The tensile curve of the coating was measured using a UTM5105 computer-controlled electronic universal testing machine (Jinan Wantest Electric Equipment Co., Ltd., Jinan, China) with a tensile rate of 50 mm/min. The tensile data with a strain less than 0.01 mm/mm were selected to linear fitting and the corresponding curve slope was obtained as the elastic modulus of the tensile sample.

2.3.3. Determination of Crosslinking Density

The swelling equilibrium method was used to measure the crosslinking density of the coating. The crosslinking density of the silicone elastomer was expressed by the relative molecular mass (M_c) between adjacent crosslinking points of the polymer. A 1 cm² slice was cut from the PTFE cast film sample, and its mass was measured using an AB204-S precision electronic balance (Mettler Toledo Co., Ltd., Zurich, Switzerland). The density of the sample was measured by a MH-300A densitometer (Kunshan Creator Testing Instrument Co., Ltd., Kunshan, China). The weighed sample was put into a centrifuge tube filled with 50 mL toluene in a 25 °C constant-temperature water bath environment. The sample was taken out every 3 h and the residual solvent on the surface was blotted with filter paper. The sample was weighed immediately, then the sample was continued to swell in the solvent. Until the difference between the two adjacent weighing results did not exceed 0.1 mg, the sample reached a swelling equilibrium. The relative molecular mass between adjacent cross-linking points of the coating was calculated by the Flory–Rhener relationship [15]. In order to ensure the accuracy of the experimental data, three samples were tested for each studied coating, and the average value of the final calculated results was used to represent M_c .

2.3.4. Infrared Spectrum Analysis

The chemical structure of the coating was analyzed by Fourier Transfer Infrared Spectrometer (FTIR) (PerkinElmer Co., Ltd., Waltham, MA, USA) using the Attenuated Total Reflection (ATR) method. The scanning range was from 4000 to 650 cm⁻¹ for 32 scans at a spectral resolution of 2 cm⁻¹.

2.3.5. Marine Bacterial Attachment Test

The solid-medium culture method was used to evaluate the resistance of the experimental coatings to bacterial biofilm adhesion. In order to reasonably characterize the antibacterial adhesion performance of water-based silicone coatings, a solvent-based silicone coating was selected as the controlled sample. Solvent-based silicone coatings also contain three components: hydroxy-terminated polydimethylsiloxane (Component A), ethyl orthosilicate (Component B), and dibutyltin dilaurate (Component C). The number of bacteria attached to the surface of the solid medium was calculated by IMAGE PRO PLUS software (5.1.0.20). The sample was immersed in fresh seawater for 24 h, then half of the sample were washed. The attached bacteria on the sample was brushed into sterilized seawater, then the seawater was diluted 10^6 times. A total of $10 \ \mu$ L bacterial solution was applied to 2216E solid media. The bacterial colonies were observed and counted after the culture medium was put in the incubator for 48 h. The composition of 2216E solid medium is shown in Table 1.

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Ingredients	Peptone	Yeast Extract	FePO ₄	Agar	Sterilized Seawater
Content	2 g	0.4 g	0.004 g	8 g	400 mL

2.3.6. Surface Morphology Observation

A laser confocal microscope OLS4000 (OLYMPUS (China) Co., Ltd., Beijing, China) was used to observe and analyze the surface of the silicone coating. The surface roughness (S_a) of the coating was measured using the LEXT analysis software version 2.2.4.

2.3.7. Navicula Tenera Adhesion Test

Firstly, we took six slide samples of each coating and put them into fresh Navicula Tenera culture solution with an algae concentration of 105 to 106/mL, breed and control the light ratio at 22 °C for 12 h:12 h. Then, samples were taken to determine the chlorophyll a mass concentration ρ_a of *Navicula Tenera*. The specific method for the culture of *Navicula Tenera* can be found in the literature [16,17]. In order to evaluate the true adhesion amount and removal performance of the Navicula Tenera on the surface of the silicone antifouling coating, the samples were divided into two groups: rinsed and washed. Three pieces of each sample were taken and rinsed gently in sterilized seawater. The other three pieces were put into a 50 mL test tube with 45 mL sterilized seawater, and oscillated on a HY-4 speed-controlled multi-purpose oscillator for 15 min. The frequency was 130 r/min. After rinsing or washing, each sample was placed in 45 mL of 90% acetone solution with magnesium carbonate, then placed in a biochemical incubator at 8 °C in a dark environment for 24 h. A total of 10 mL of the supernatant was then removed. The solution was placed in a 15 mL centrifuge tube and centrifuged at a rate of 4000 r/min for 15 min. Finally, 3 mL of the supernatant was loaded into a quartz cuvette with a path length of 10 mm and a volume of 3.5 mL, and UV-2000 was used. A UV-visible spectrophotometer (Labtech Co., Ltd., Beijing, China) measured the absorbance at wavelengths 750, 663, 645, and 630 nm, respectively, calculated ρ_a according to Equation (1) [17]. The higher this value is, the higher the concentration of Navicula Tenera. This can evaluate the ability of coatings to resist Navicula Tenera.

$$\rho_a = 11.64 \times (\text{OD663}) - 2.16 \times (\text{OD645}) + 0.10 \times (\text{OD630}) \tag{1}$$

In the formula, OD663, OD645, and OD630 represent the corrected absorbance, obtained by subtracting the absorbance at 750 nm from the absorbance at 663, 645, and 630 nm, respectively.

3. Results

3.1. Chemical Structure

Figure 1a is the structural formula of the cationic emulsifier stearyl trimethyl ammonium bromide, Figure 1b is an emulsifier sodium sodium dodecyl benzene sulfonate structural formula, which has –SO₃ group in the structural formula.



Figure 1. Molecular structure formula of emulsifier (**a**) Stearyl trimethyl ammonium bromide (**b**) Sodium dodecyl benzene sulfonate.

The infrared spectra of the coatings cured were shown in Figure 2a. For coating 5011, the strong shoulder absorption peak of 1011–1083 cm⁻¹ is determined by the Si–O bond stretching vibration. The causes are characteristic absorption peaks generated after the Si-O-Si bond and the C-O-C bond overlap, and the bending vibration peak of the C–H bond of Si–CH₃ at 1258 cm⁻¹, all of which are characteristic peaks of silicone. At 1718 $\rm cm^{-1}$, there is a C=O vibration peak from the curing agent. Relatively weak peaks at 1470 and 730 cm⁻¹ are provided by the $-C-(CH_2)_n$ -C- bond. Thus, the emulsifier provided $-C-(CH_2)_n-C-$ of the coating surface peak. During the cross-linking and curing process of coating 5011, small molecular substances of cationic emulsifiers presented on the coating surface. For the infrared spectrum of coating 5012, there is an $-SO_3$ anti-symmetric stretching vibration peak at 1192 cm⁻¹. The stretching vibration peaks at 2852–2960 cm⁻¹ are provided by the -CH₃ and -CH₂-. Therefore, there also were anionic emulsifier small molecule substances on the surface of coating 5012 to further determine if emulsifier exists on the surface of the cured coating. The coatings were cleaned with ethanol by supersonic, and the infrared spectroscopy of the cleaned coating were shown in Figure 2b. The peaks at 730 and 1218 cm⁻¹ disappeared, and the peaks at 1470 cm⁻¹ also weakened greatly. This also represents that the small molecules emulsifier did not participate in the crosslinking reaction of the coating system.



Figure 2. Infrared spectrum curve of studied coatings (a) cured (b) cleaned.

3.2. Curing Mechanism

The water-based silicone coating prepared in this paper is a thermosetting coating. The film-forming mechanism consists of two parts: the physical film formation mechanism and the chemical film formation mechanism. The physical film formation mechanism mainly refers to the evaporation of water in the system; then, the particles were close to each other and the deformation was stacked. The chemical film formation mechanism is that between the curing agent KH-570 and the PDMS in the particles had a cross-linking curing reaction to form a three-dimensional network structure. Based on the polymer latex film formation process, summarized by Steward [18], the film

formation mechanism diagram of the silicone emulsion used in this paper was drawn, as shown in Figure 3. In the system, because water volatilized slowly, the chemical film formation of the silicone emulsion is in the process of water evaporation. The curing agent contacted the silicone resin emulsion particles, then a crosslinking curing reaction occurred in the system. Under the action of capillary pressure, the silicone resin particles are brought close to each other with the evaporation of water. Finally, the liquid solidifies into a uniform film.



Figure 3. Schematic model of film formation process of silicone emulsion. (a) the early stage of painting; (b) the early stage of cross-linking reaction; (c) after drying on surface; (d) the cross-linking reaction is completed; (e) completely cured; (f) basic structure of silicone emulsion; (g) structural formula of crosslinker.

The reaction process between the curing agent and the silicone emulsion particles is shown in Figure 4. First, the curing agent KH-570 is hydrolyzed to generate silanols in an aqueous system, as shown in Figure 4a. Then, under the action of a catalyst silanols reacted with the hydroxyl-terminated of emulsion particles to generate a three-dimensional network structure, as shown in Figure 4b. Among them, *R* is a methacryloyloxy group and does not participate in the crosslinking reaction of the system. It was proved in the coating chemical analysis that the emulsifier also did not participate in the crosslinking reaction of the system.



Figure 4. Chemical reaction principle of waterborne silicone. (**a**) The curing agent hydrolysis reaction; (**b**) Crosslinking reaction between silanol and silicone.

3.3. Crosslinking Density of Coating

The density of coating 5011 is 0.992 g/cm^3 before swelling, and the density of coating 5012 is 0.997 g/cm^3 . Their M_c values measured are shown in Table 2. The M_c value of coating 5011 is significantly lower than the M_c value of coating 5012. The smaller the M_c value, the higher the crosslink density. The reason for this is the acid-base degree of the emulsion. The pH value, measured of DY-OH5011 emulsion, is 6.8, while the pH value of DY-OH5012 emulsion is 7.9. The curing agent KH-570 is a kind of silane coupling agent, which needs to be hydrolyzed before cross-linking reaction with the silicone emulsion particles. The condensation rate of KH-570 is faster than the hydrolysis rate under alkaline environment [19], so KH-570 cannot produce a large amount of silanol in DY-OH5012 emulsion particles, silanol need to solubilize to a stern layer formed by emulsifier. The structure of the emulsifier affects the ability of the silanol to pass through the stern layer, as shown in Figure 5. As the anionic emulsifier has an unsaturated hydrocarbon chain, as shown in Figure 1, its solubilization effect is inferior to that of a cationic emulsion and the curing agent is not high in 5012 system, and the crosslinking reaction between the emulsion and the curing agent is not high in 5012 system, and the crosslinking density of coating 5011 is higher than that of coating 5012.

Sample	Density Before Swelling (g/cm ³)	$M_{\rm c}$
5011	0.992	6076 ± 128
5012	0.997	22189 ± 322



Figure 5. Schematic diagram of crosslinker entering emulsion particle (a) coating 5011 (b) coating 5012.

3.4. Morphology of Coating

The morphologies of coating 5011 and coating 5012 are respectively shown in Figure 6a,b. The surface of coating 5011 is smoother than that of coating 5012. The roughness of coating 5011 is 1.657 µm, while the roughness of coating 5012 is 6.771 µm. In the 5012 system, the crosslinking and curing of the coating is uneven and slow, so internal stress is generated inside the coating. As the stress increases, micro-cracks are generated on the surface of coating 5012. The system 5011 is suitable for the hydrolysis of the curing agent KH-570, so the curing agent generated a large amount of silanol for the crosslinking reaction. The crosslinking reaction can be carried out uniformly in the coating 5011, so there are fewer defects on the surface of the coating 5011.



Figure 6. Morphology of studied coatings (a) coating 5011 (b) coating 5012.

3.5. Surface Properties of Coating

Table 3 shows the contact angle measurement results of the two coatings. The water contact angles are higher than 105°, and they had good hydrophobic properties. The surface free energy of the coatings is very low, about 20 mJ/m². Silicone has a unique Si–O main chain structure, and the side chain methyl group is connected to the silicon atom by a sigma bond, blocking the contact of the Si–O main bond with the external environment. The methyl group not only has a barrier protection effect, but also is strongly non-polar [21].

Sample	Contact Angle (°)		Surface Free	Surface Roughness	
1	Water	Diiodomethane	Energy (mJ/m ²)	S _a (μm)	
5011	107.67 ± 1.28	85.08 ± 1.85	20.01 ± 0.51	1.657	
5012	109.25 ± 2.07	82.67 ± 1.73	20.59 ± 0.48	6.771	

Table 3. Surface interface characteristics of coating.

3.6. Tensile Properties of Coating

The tensile stress–strain curves of the two coatings are shown in Figure 7, and the tensile properties results are shown in Table 4. The elastic modulus is almost the same, but the elongation and breaking strength of coating 5011 are significantly higher than those of coating 5012, and the elongation could reach more than 230%. The breaking strength is 0.35 MPa. The mechanical properties of coating 5011 are different from coating 5012, mainly because the crosslink density of the former is higher than that of the latter. In addition, the micro-cracks and defects on the surface of coating 5011 are significantly less than those of coating 5012, which made coating 5012 easier to break during the stretching process. The tensile fracture morphology of the coatings was shown in Figure 7. Clearly, the fracture surface of coating 5011 is more fine and smooth than that of coating 5012. Figure 8 is the fracture morphology of the coating are smaller and uniformly distributed than coating 5012, reflecting that the relative molecular mass (M_c) between the adjacent cross-linking points of coating 5011 is smaller, and the coating cross-linking density is higher, than that of coating 5012.



Figure 7. Stress-strain curve of coatings.

Sample	Elastic Modulus (MPa)	Elongation (%)	Breaking Strength (MPa)
5011	1.12 ± 0.112	237 ± 12	0.35 ± 0.025
5012	1.11 ± 0.631	206 ± 5	0.26 ± 0.018

Table 4. Mechanical property parameters of coatings.



Figure 8. Fracture morphology of coatings (a) coating 5011 (b) coating 5012.

3.7. Bacterial Adhesion and Desorption Performance of Coating

The ability of the coating to resist bacterial biofilm adhesion was evaluated by using a solid-medium culture method. Figure 9 shows pictures of each medium after IMAGE PRO PLUS treatment. It can be concluded that the number of bacteria attached to the washed samples is significantly less than the rinsed samples. The number of bacteria attached to the surface of the 5011 coating is less than the solvent-based silicone coating, and the number of bacteria attached to the 5012 coating is comparable to the solvent-based silicone coating.



Figure 9. Images of bacterial colonies (**a**) rinsed coating 5011; (**b**) rinsed coating 5012; (**c**) rinsed solvent-based silicone coating; (**d**) washed coating 5011; (**e**) washed coating 5012; (**f**) washed solvent-based silicone coating.

Figure 10 shows the number of bacterial communities on the surface of each culture medium using IMAGE PRO PLUS software. It can be seen that the number of adhesive bacteria on the two coatings is less than that on the glass slide. The low surface energy characteristics of the coating and the presence of emulsifiers can inhibit the adhesion and growth of bacteria on the coating surface. The cationic emulsifier (stearyl trimethyl ammonium bromide) in coating 5011 belongs to the quaternary ammonium salt. It can destroy the cell membrane after contact with bacteria and has a certain killing effect on bacteria [22]. In 5012 system anionic emulsifier sodium dodecyl benzene sulfonate also has a certain inhibitory effect on acetylcholinesterase activity in bacteria [23], so it is difficult for bacteria to adhere to the coating surface. After being washed, the number of bacteria attached to the sample is significantly less than that of the rinsed sample, indicating that marine bacteria are easily removed from the two coating surfaces. However, because of its smooth surface, 5011 was better than 5012 in the bacteria removal performance, with a removal rate more than 50%.





3.8. Navicula Tenera Adhesion and Desorption Performance of Coating

To further characterize the antifouling properties of the coating, we performed *Navicula Tenera* attachment text. Table 5 shows the number of *Navicula Tenera* on the surface. We can see that the number of *Navicula Tenera* attached to the surface of coating 5011 is very small. The number of *Navicula Tenera* on the surface of 5012 coating is more than that of coating 5011. And the number of *Navicula Tenera* on the surface of glass slide is far more than that of the coating.

Table 5.	Chlorophyll	concentration	on the template.
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Sample	Chlorophyll Conc	Removal Rate (%)	
1	Washed	Rinsed	
5011	0.09 ± 0.002	0.43 ± 0.014	78.7
5012	1.41 ± 0.187	3.80 ± 0.098	62.8
Glass slide	27.60 ± 1.34	44.90 ± 2.85	38.5

The color changes of *Navicula Tenera* were recorded during the text. Figure 11a is the picture of *Navicula Tenera* solution, Figure 11b,c are pictures of coating 5011 soaked in *Navicula Tenera* solution. The *Navicula Tenera* changed from normal yellow-brown to yellow after 1 day. Finally, it turned white. This showed that *Navicula Tenera* is gradually inactivated and completely inactivated after two days. The pictures of *Navicula Tenera* soaked with coating 5012 are shown in Figure 11d,e. *Navicula Tenera*

did not change significantly after one day, but turned yellow-green after two days. This shows that the inhibitory effect of coating 5012 on *Navicula Tenera* is less than that of coating 5011. Therefore, both emulsifiers have an inhibitory effect on the activity of *Navicula Tenera*, and the inhibitory effect of stearyl trimethyl ammonium bromide on the activity of *Navicula Tenera* is stronger than that of sodium dodecyl benzene sulfonate.



Figure 11. Changes in *Navicula Tenera* solution during test. (**a**) at glass slide before test; (**b**) at coating 5011 for 1 day; (**c**) at coating 5011 for 2 day; (**d**) at coating 5012 for 1 day; (**e**) at coating 5012 for 2 day; (**f**) at glass slide after test.

4. Discussion

In waterborne silicone antifouling coating formulations, the silicone emulsion (Component A) is provided by supplier. In order to make it cure at room temperature into a film, a crosslinking agent (Component B) needs to be added to the emulsion. There are two reasons why KH-570 was selected as a crosslinking agent. First, KH-570 has three groups that can react with the hydroxyl groups in the silicone emulsion to form a three-dimensional network structure. Secondly, it has a strong polarity. By solubilization, a crosslinking agent easily penetrates the fence layer and enters the inside of the emulsion particles, as shown Figure 12. The catalyst is dibutyltin dilaurate (Component C), which is a toxic substance. In the original conception of the formula, in order to achieve environmental protection effects, bismuth neodecanoate was used as a catalyst. However, it was found that bismuth neodecanoate would destroy the stability of the cationic silicone aqueous emulsion. Therefore, we must first use dibutyltin dilaurate to ensure the establishment of the system, which is convenient for studying and comparing the effect of two emulsifiers on the performance of aqueous silicones' coating. In subsequent research work, dibutyltin dilaurate will be gradually replaced by tin dilaurate.

Due to the different emulsifiers used in the preparation of silicone emulsions, the pH values of the silicone emulsions were different. The pH value of the silicone emulsion affects the process of hydrolysis of the cross-linking agent to produce silanol, and the emulsifier in the emulsion affects the silanol, entering the emulison particles through the solubilization to cross-link with the silicone. The two emulsions have different pH values and different emulsifiers, resulting in different degrees of crosslinking in the coating system. The environment of the 5012 emulsion is alkaline, which makes the silanol easily undergo condensation reaction and reduces the yield of the silanol. Moreover, the emulsifier in DY-OH5012 emulsion is sodium dodecylbenzenesulfonate with an unsaturated hydrocarbon chain, and it is difficult for silanol to enter the emulsion particles through solubilization. Therefore, the crosslink density of coating 5012 is lower than that of coating 5011. The higher the

crosslink density of the coating, the better the mechanical properties of the coating. Therefore, the elongation and breaking strength of coating 5011 are higher than those of coating 5012.



Figure 12. Schematic diagram of crosslinking agent entering emulsion particle.

The mechanical properties of the water-based silicone coating determines the service life of the coating, and the antifouling performance determines the work effect of the coating. For the antifouling performance of water-based silicone coatings, the relative adhesion factor is an important parameter for evaluating and screening fouling release type antifouling coatings. $\sqrt{E} * \gamma$ is also defined as the relative adhesion factor. The amount of adhesion on the coating surface is directly proportional to the relative adhesion factor [24]. Table 6 shows the relationship between the relative adhesion factor and the number of attached colonies. The surface energy and elastic modulus of 5011 and 5012 were basically the same. According to the above theory, the number of bacteria attached to the two kinds of coating is basically the same. However, through bacterial adhesion experiments, it was found that there was a difference in the amount of bacterial adhesion between the two coatings. The number of bacterial colonies attached to the surface of coating 5011 was lower than that of coating 5012. Through the infrared curve analysis of the functional groups on the surface of the coating, it was found that an emulsifier presented on the surface of the coatings. The cationic emulsifier stearyl trimethyl ammonium bromide belongs to the quaternary ammonium salt, which has a certain inhibitory effect on the activity of bacteria. The anionic emulsifier sodium sodium dodecyl benzene sulfonate on the surface of coating 5012 also inhibits bacterial activity. The experimental results showed that the number of bacterial colonies attached to the surface of coating 5011 is less than that of coating 5012. Therefore, stearyl trimethyl ammonium bromide is more effective than sodium dodecyl benzene sulfonate at making it difficult for bacteria to adhere to the coating surface. In addition, stearyl trimethyl ammonium bromide has a strong inhibitory effect on Navicula Tenera. Therefore, coating 5011 has better antifouling performance than coating 5012.

Table 6. Relative adhesion factors and number of attached colonies.

Sample	Relative Adhesion Factor	Number of Attached Colonies (×10 ⁶ CFU)
5011	4.73 ± 0.238	190 ± 23
5012	4.78 ± 0.550	242 ± 42

The work done during fouling organism removal is equal to the adhesion energy of the fouling organism plus the deformation energy of the coating. The adhesion energy of fouling organism is proportional to the relative adhesion factor, and the deformation energy of the coating is related to the elastic modulus [25]. The smaller the elastic modulus of the coating, the smaller the energy consumed by the fouling organisms in the detachment process making the fouling organisms easier to remove. Table 7 shows the relationship between the amount of sample removal and the relative adhesion factor

and elastic modulus. Coating 5011 and 5012 have similar relative adhesion factors and elastic modulus, so the removal effect of bacteria should also be similar. However, the bacterial adhesion experiments showed that the removal rates of the two coatings are significantly different. The reason for this is their surface morphologies. The surface roughness of coating 5011 is 1.657 μ m, and the surface roughness of coating 5012 is 6.771 μ m. The surface of coating 5012 is rougher than coating 5011. Moreover, a large number of pores and undulations are observed on the surface of coating 5012. These coating defects provided a fulcrum for the adhesion of bacterial colonies. It is difficult for bacterial colonies that adhere to the surface of coating 5012 to be removed, so the removal effect is worse than that of coating 5011.

Sample	Relative Adhesion Factor	Elastic Modulus (MPa)	Fouling Removal Rate (%)	Roughness (µm)
5011	4.73 ± 0.238	1.12 ± 0.112	57.4 ± 4.95	1.657
5012	4.78 ± 0.550	1.11 ± 0.631	32.6 ± 3.87	6.771

Table 7. Influence of elastic modulus and surface roughness on the amount of fouling removal rate.

5. Conclusions

Two kinds of water-based silicone antifouling coatings using silane coupling agent KH-570 as curing agent can be cured to form a film at room temperature. The coatings have low surface energy characteristics, and the surface free energy of the coatings is about 20 mJ/m². After the coating is cured, small emulsifier molecules would present on the surface. Of the two aqueous silicone coatings studied, the crosslink density of coating 5011 is greater than that of coating 5012. The breaking strength and elongation of coating 5011 are greater than those of coating 5012, and the surface of coating 5011 is smoother than that of coating 5012. The emulsifier can reduce the adhesion of bacteria and *Navicula Tenera* on the surface of coatings, and the stearyl trimethyl ammonium bromide cationic emulsifier has a higher effect on reducing the adhesion of bacteria and *Navicula Tenera* on the coating surface.

Author Contributions: Conceptualization, S.L., Z.Z. and Y.Q.; methodology, S.L. and Z.Z.; software, Z.Z. and Y.Q.; validation, S.L., Z.Z. and Y.Q.; formal analysis, S.L., Z.Z. and Y.Q.; investigation, S.L.; resources, Z.Z. and Y.Q.; data curation, S.L.; writing—original draft preparation, S.L.; writing—review and editing, S.L., Z.Z. and Y.Q.; visualization, S.L., Z.Z. and Y.Q.; supervision, Z.Z. and Y.Q.; project administration, Z.Z. and Y.Q.; funding acquisition, Z.Z. and Y.Q. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Natural Science Foundation of China (51879021), Project of Equipment Pre-research Field Fund (61409220304).

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

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