Study on Fouling-Resistant Performance Improvement of Silicone-Based Coating with Poly(Acrylamide-Silicone)

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In this paper, an improved fouling-resistant silicone-based coating was designed and prepared with the addition of an amphiphilic additive of poly (acrylamide-silicone) (PAS) into silicone. The preparation of the amphiphilic additive and the designed coating was introduced and characterized. Test results showed that, the addition of PAS into silicone coating could significantly increased the underwater air bubble contact angles (which were measured between the coating surface and the air bubble on the bubble side) of the coating surface, and 0.5% (w/w) of PAS loading in silicone could give it the highest underwater air bubble contact angle hysteresis. The results also showed that the diatoms “random” initial contact with the surface was sensitive to the underwater air bubble contact angle, while the “intentional” bonding, such as diatoms permanent adhesion as well as mussels exploring for basal byssus deposition, was sensitive to the underwater air bubble contact angle hysteresis. When 0.5% (w/w) of PAS was loaded in silicone, the coating showed maximum effect on the inhibition of diatoms permanent adhesion and mussel basal byssus deposition, and it also could significantly lower the flow shear stress necessary to remove 50% of the settled diatoms Navicula sp. by 52% in comparison with control silicone coating. The addition of less than 1.5%(w/w) of PAS had no toxicity for diatom Navicula sp. as well as mussels Mytilus galloprovincialis. Therefore, the copolymer of PAS could be used as a promising antifouling additive to enhance the antifouling ability of silicone-based coatings.

Keywords: Antifouling coating, enhancement, silicone, poly(acrylamide-silicone), underwater contact angle.
1. INTRODUCTION

Biological fouling can bring about some unwanted and detrimental consequences to marine ship [1-3]. Firstly, it could increase hull corrosion to lose its strength, and it also could increase hydrodynamic drag leading to more fuel consumption and higher maintenance costs [4-6]. Usually, the ship hull will be painted an antifouling coating to prevent biological fouling. The best performing coatings are those containing metal based compounds like copper or tributyltin, however which can lead to serious irreversible adverse influence to the marine ecological environment, such as imposex in oysters, and death of dolphins, porpoises as well as whales [7-8], so it is necessary to develop new eco-friendly antifouling alternatives to protect marine ecological environment.

It is well known that silicone-based coatings act essentially by means of a barrier layer with a combination of properties including ultra-smooth surface, low surface energy and low elastic modulus, which are necessary to minimize chemical and mechanical locking of fouling species, and this makes silicone become a very attractive candidate in developing new eco-friendly antifouling materials[9-13]. Now, polymers based on poly(dimethyl siloxane) (PDMS) have already been applied in the formulation of some antifouling coatings [12,14-17], which are the major type of material currently marketed as non-toxic marine coatings[18]. However, it is also a matter of fact that some marine organisms still can adhere onto the silicone surface[19-20], especially diatoms, which can develop slime films and do not release from vessels operating at high speeds over 30 knots [16,21-22], and this can increase the frictional drag by as much as 5%-25%[2,21] as well as fuel costs up to 15% [5,23-24]. Because silicone based materials is promising and important in developing new eco-friendly antifouling materials, it is very significant and necessary to take some ways to further improve its antifouling ability [13, 22].

It has been reported that most hydrogels, including those originating from natural resources, such as agarose, alginate, chitosan and poly (vinyl alcohol substituted with light-sensitive stilbazolium groups) (PVA-SbQ) [25], as well as poly(ethylene glycol)[26]and some types of synthetic polymer gels[27], showed antifouling activity against marine organisms, and this ability of hydrogels is explained in terms of an “easy-release” mechanism in which the high water content and the elastic modulus of the gel are two important functional parameters[27]. Inspired by the antifouling mechanism of hydrogels, an enhanced fouling-resistant silicone-based coating with functionalized hydrogelike surface was designed and prepared in this paper. Firstly, an amphiphilic additive of poly(acrylamide-silicone)(PAS) was prepared with acrylamide and octamethylcyclotetrasiloxane (D4), since PAS can be hydrated and become microhydrogels, then its addition into silicone base could make the surface become localized microhydrogel and hydrophilic when this coating was immersed into seawater. Studies showed that diatoms was very difficult to adhere to hydrophilic surfaces [28], therefore the local hydrophilic environment was helpful to improve its antifouling ability against diatoms. Meanwhile, the mosaics of hydrophilic and hydrophobic domains also could effectively lower the adhesion strength for fouling organisms on the coating surface in comparison with only hydrophobic or hydrophilic domains on the surface[29], therefore it was also helpful to further inhibit the settlement of fouling organisms other than diatoms.
2. EXPERIMENTAL PART

2.1 Materials

Acrylamide and potassium hydroxide were purchased from China National Medicine Corporation, among which the acrylamide would firstly be polymerized into polyacrylamide (PAM) in the preparation procedure and then via the PAM and silicone that the copolymer of PAS was finally produced. Potassium peroxydisulfate came from AiBi Chemistry Inc, which and potassium hydroxide both acted as catalysts. Acrylic acid was purchased from BASF. D4 came from DaYi Chemical Inc. Hexamethyldisiloxane (MM) and vinyltriethoxysilane (A-151) were purchased from GuiBao Chemical Inc and Union Carbide Corporation, respectively. Silicone coating materials (including part A: hydroxy-terminated PDMS, part B: Dibutyltin dilaurate and ethyl silicate 40) came from YunQing Chemical Inc. Dimethyl sulfoxide (DMSO) was purchased from HengDa Chemical Inc.

2.2 Preparation of Poly (acrylamide-silicone) (PAS)

The copolymerization was carried out in a round-bottom flask under protection of nitrogen atmosphere. Prepolymer was firstly synthesized by acrylamide (0.14mol) with potassium peroxydisulfate (0.1mmol) as catalyst in water (100ml), and then after the reaction continued for 1 hour at 60 °C, the PAM would be yielded. Hereafter, potassium hydroxide (4mmol), D4 (6mmol), MM (0.5mmol), A-151 (5mmol) and DMSO (6mmol) were added into the flask and the temperature was set up to 80 °C to continue the preparation for 3 hours, then in order to remove water in the product, it should be washed by ethanol, and then after being dried, pulverized, the copolymer was obtained.

2.3 Characterization of Poly (acrylamide-silicone)(PAS)

The poly(acrylamide-silicone)(PAS) prepared as above mentioned procedure was characterized by FT-IR spectroscopy (AVATAR-380, Nicolet). Infrared spectra of neat films on KBr plate were recorded and analyzed. $^1$H-NMR spectra were performed on a NMR spectrometer (JNM-ECP600, JEOL) for solutions in D$_2$O.

2.4 Preparation of PAS incorporated silicone coating

Firstly, PAS was incorporated with silicone base part A of hydroxy-terminated PDMS respectively, then the curing agent of part B was added into the mixture, and the amount ratio of part A and part B is 97.5:2.5 (w/w), finally all of these ingredients were blended in uniform with proper solvent. Then certain volume of blends were coated onto the glass slides (7.5×2.5cm$^2$), the coating was left to cure in air for 2 days. The coating thickness was controlled at 200±10µm.
2.5 Measurement of underwater contact angles

The underwater contact angles of PAS incorporated silicone coating and control silicone coating were measured using a captive-air-bubble technique on a contact angle goniometer (KSV CAM101, Finland) at room temperature [30]. The sample was immersed upside down in Milli-Q water. An air bubble was snapped off the tip of a stainless steel syringe hooked needle (0.5-mm o.d. and 0.3-mm i.d.), and allowed to contact the coating surface. The contact angles reported were measured between the coating surface and the air bubble on the bubble side. Thus a low air bubble contact angle indicates a hydrophobic surface, while a higher contact angle indicates a more hydrophilic surface [31]. Dynamic contact angle measurements were performed through the addition and retraction of a small air bubble (Ca.5μl) on the surface. The advancing and receding contact angle behavior was digitally recorded and image analysis software was used to measure the angles.

2.6 Toxicity test

The toxicity of PAS was first evaluated with diatoms [32]. The diatoms Navicula sp. (1.0×10^6 cells/ml) were cultured in tubes at 20 °C with a light: dark cycle of 12h:12h, the photolumen was controlled at 112.5 μmol photon.m^-2.s^-1. The tubes were filled with 2 ml F/2 culture medium containing a certain concentration of PAS from 0 to 1.5%(w/w) respectively (each concentration have six replicates), and the diatoms growth in tubes without PAS were used as controls. All the tubes were incubated for 72h. Inhibition of the diatoms growth compared with controls was determined by measurements of optical density in a spectrophotometer (Fluorax, HORIBA JY). The 72h toxicity end-point (LC50) in this test was calculated as the concentration of PAS which caused a 50% reduction in diatoms growth relative to the control.

The toxicity of PAS was also evaluated with mussels Mytilus galloprovincialis. Firstly, adult mussels (10mm~20mm in shell length) were collected from the Taipingjiao beach of Qingdao and maintained in an aquarium filled with seawater for 24h, and then those showing exploratory behavior ones were selected for further test. Secondly, four selected mussels were cultured 24h further in each dish that respectively filled with 20ml of 1.5%(w/w) PAS seawater solutions as well as seawater only as control. Hereafter, all of the selected mussels were transferred into new dishes filled with fresh seawater without PAS and cultured another 24h for observation. The test was run in six replicates.

2.7 Diatoms settlement test

Firstly, PAS incorporated silicone and control silicone were coated onto the glass slides (7.5×2.5cm²) respectively, and the coating were left to cure in air for 2 days (coating thickness: 200±10μm). After that, the coated glass slides were placed in culture dishes respectively, each dish contained 200 ml F/2 culture medium of diatoms Navicula sp. (1×10^6 cells/L). The dishes were placed in a climatic cabinet (JC2000A, Powereach Inc) at 20°C with a light: dark cycle of 12h:12h, the photolumen was controlled at 112.5 μmol photon.m^-2.s^-1.
Six replicates of each coatings were observed after 7 days. When observed, coating slides were firstly removed and dipped gently in seawater up and down several times to remove those loosely attached diatoms, and then they were immediately subjected to optical microscope observation (KH-3000, Kostar). The cells were counted in average of 30 fields of view on each of replicate slides to provide cell settlement data[33].

2.8 Mussel byssus deposition test

Firstly, PAS-incorporated silicone and control silicone were coated onto glass plates respectively as before mentioned. The test organisms of 4 mussels were fixed onto a polystyrene rod with putting cyanoacrylate adhesive on one valve of each mussel, and then the rod was attached sharply onto the coated plates using silicone sealant, this could give no influence on the selection behavior of coating surfaces of foot while the mussels were immobilized[34]. Hereafter, the prepared assay plates were set to the bottom of an experimental aquarium filled with seawater for 24h respectively to observe the number of mussel basal byssus secreted on different coatings and the time of initial byssus appeared. To settle, mussels will reach out their foot to touch the surface to find if it is suitable, if which is identified as good enough to settle, then they will secrete basal byssus to fix onto the surface as quickly as possible. Therefore, the deposition of basal byssus produced by mussel and the time taken for initial basal byssus deposition occurred on different coating surface can strongly show their various inhibition effect on mussels. The test was run in six replicates.

2.9 Determination of removal percentage of diatoms with water shear stress

The PAS incorporated silicone and control silicone coated glass slides (7.5×2.5cm²) were respectively prepared as described previously. To evaluate the attachment strength of diatoms on the coating surface, the settled slides were exposed to shear in specially designed flow channel apparatus[35], modified by fitting a higher capacity pump(4kW), and the designed velocity range in the test section was 0.4-6.1 m s⁻¹ (Reynolds number based on channel height and bulk mean velocity of 7,600 to 66,000), the resulting wall shear stress could be varied from approximately 5.4-40.5 Pa. After the coated slides were placed in culture dishes contained 200 ml F/2 culture medium of diatoms Navicula sp.(1×10⁶ cells/L) for certain time as mentioned before, they were taken out and subjected to water shear stress in flow channel. The percentage of removal was calculated from the difference of counted diatoms between samples before and after exposure to the flow channel, and exposure duration of slides to the flow was set at 2min, each set of samples was run in six replicates. The critical impact pressure to remove 50% of the diatoms was determined from plots of percentage removal versus impact pressure.
3. RESULTS AND DISCUSSION

3.1 Characterization of poly (acrylamide-silicone) (PAS)

The poly (acrylamide-silicone)(PAS) was characterized by FT-IR spectroscopy. The spectra of PAS, PAM and the mixture of PAM and D4 were presented in Figure 1. For the PAM as shown, the stretching vibration absorption band of N-H (amido) groups appeared at 3414 cm\(^{-1}\), and that of -CH\(_2\) (methylene) groups appeared at 2926 cm\(^{-1}\), the characteristic absorption band of -C=O (carbonyl) groups appeared at 1652 cm\(^{-1}\) and the flexural vibration absorption band of -CH\(_2\) (methylene) groups appeared at 1459 cm\(^{-1}\). Compared with PAM spectra, the spectra of mixture of PAM and D4 not only kept all the characteristic absorption bands of PAM, but also it had characteristics absorption bands of Si–O–Si groups at 1080 cm\(^{-1}\). For the PAS, its’ spectra was nearly the same as that of the mixture of PAM and D4, but at 1080 cm\(^{-1}\), the characteristics absorption bands of Si–O–Si groups split into two bands, this indicated that D4 circle had opened and bonded to PAM, so it could be concluded that PAS had been successfully prepared.

![Figure 1. FT-IR spectra of PAM, PAS as well as mixture of PAM and D4](image)

From the NMR spectrum of PAS(Figure 2), it could be seen that \(^1\)H-NMR (in D\(_2\)O) peaks appeared at 2.0 ppm, 1.5 ppm and 0 ppm, and this strongly showed that \(-\text{CH}_2-\text{CH}_1-\text{C}=\text{O}\) (2.0ppm, 1H; 1.5ppm, 2H) of AM and \(-\text{Si(}\text{CH}_3)_2-\text{O}-\) of D4 (0ppm,6H) did become parts of PAS.

![Figure 2. \(^1\)H-NMR spectrum of PAS](image)
3.2 Toxicity of PAS for diatoms *Navicula sp.* and mussels *Mytilus galloprovincialis*

The toxicity of PAS was evaluated with diatoms in accordance with the toxicity test [32]. The diatoms growth in test tubes, including the controls and those tubes containing PAS of 0.05% (w/w), 0.1% (w/w), 0.2% (w/w), 0.5% (w/w), 1.0% (w/w) and 1.5% (w/w), were measured after 72h, and the results were shown in Figure 3. The statistical analysis of data revealed that the variation of amount of PAS had no significant different influence on the diatoms growth even it reach 1.5% (w/w)(ANOVA at 6 concentrations as well as controls, \(p>0.05\)), therefore the LC\(_{50}\) of PAS is surely much more than 1.5% (w/w). This indicated that the amount of PAS lower than 1.5% (w/w) in the coating had no toxicity for diatom *Navicula sp.*

![Figure 3](image1.png)

**Figure 3.** Diatoms density in test tubes containing various concentration of PAS after 72h(ANOVA at 6 concentrations as well as controls, \(p>0.05\)). The diatoms density were presented as the mean±SD of six replicates.

![Figure 4](image2.png)

**Figure 4.** Mussel byssus deposition number in seawater solution of 1.5%(w/w) PAS as well as in seawater in first 24h(t-test, \(p<0.05\)); and mussel byssus deposition number in fresh seawater without PAS after they were moved out and transferred to new dishes respectively for another 24h(t-test, \(p>0.05\)). The mussel byssus number were presented as the mean±SD of six replicates.
The toxicity of PAS was further evaluated with mussels. Test results showed that in the first 24h, the number of byssus secreted by mussels in seawater solution of 1.5% (w/w) PAS was 25.5% lower than that secreted by mussels in control dishes filled with seawater only (t-test, \( p<0.05 \)). However, when they were transferred into fresh seawater without PAS and cultured for another 24h, all the mussels, including both of those subjected culturing in seawater solution of 1.5% (w/w) PAS and those cultured in seawater only as controls, secreted byssus and settled onto the bottom as normal. The results were shown in Figure 4. The statistical analysis showed that there was no significant differences of byssus number between mussels moved out from seawater solution of 1.5% (w/w) PAS and those from seawater (t-test, \( p>0.05 \)). From above analysis it could be seen that 1.5% (w/w) of PAS was effective on inhibiting the mussel byssus deposition behavior and had no toxicity on its bioactivity as well as life.

### 3.3 Effect of PAS loadings on diatoms settlement and mussel byssus deposition

The PAS-incorporated silicone coatings were prepared with PAS loadings of 0, 0.25% (w/w), 0.50% (w/w), 0.75% (w/w), 1.00% (w/w), 1.25% (w/w), and 1.50% (w/w), respectively onto the glass slides (7.5x2.5 cm\(^2\)). 7-day diatoms settlement and 24h mussel byssus deposition were tested as before mentioned, and the results were shown in Figure 5. From which it could be seen that, compared with silicone control, the addition of PAS in silicone could significantly lower the number of diatoms settlement as well as mussel byssus deposition. The diatoms settlement decreases with the increasing of PAS loadings in PAS-incorporated silicone coatings, and this indicated that the addition of PAS was helpful to inhibit the diatoms to settle onto silicone coating surface. It also showed that PAS could lower mussel byssus deposition with the increasing of PAS loadings when it was not more than 0.5% (w/w), while the number of mussel byssus deposition increased with the increasing of PAS loadings when it was more than 0.5% (w/w).

![Figure 5. 7-day diatoms settlement and 24h mussel byssus deposition on the surface of PAS-loaded silicone coating with various PAS loadings as well as silicone controls. All the tests were run in six replicates, and there were 4 mussels on each surface.](image-url)
3.4 Measurement of underwater contact angles for PAS-loaded silicone

The underwater contact angle on the surface of PAS-loaded silicone coatings with various PAS loadings were measured, and the results were shown in Figure 6. From which it could be seen that the underwater contact angle on the air bubble side increased significantly on the surface of PAS-loaded silicone coatings in comparison with silicone controls, and this clearly indicated that the surface was reconstructed after immersion in water[33]. From the figure, it also could be seen that the underwater contact angle on the surface of PAS-loaded silicone coatings changed over time with PAS loadings in silicone, the higher the PAS loadings in silicone, the more rapid the contact angle reach a nearly constant higher value. All the PAS-loaded silicone coatings reached the constant condition within 24 hours. In comparison, the contact angles on the surface of silicone controls increased very slowly to reach a final value of 78±1 degrees. This suggested that it was PAS, not PDMS, that lead the reconstruction behavior after the surface of PAS-incorporated silicone was immersed in water.

Figure 6. Underwater captive air bubble contact angle on the surface of PAS-loaded silicone coating with various PAS loadings as well as silicone controls. The coating composition details were shown in the figure. The contact angle was presented as the mean±SD of six replicates, and underwater captive air bubble contact angles of 3 points were measured on each slide.

The advancing contact angles and receding contact angles of PAS-loaded silicone as well as silicone control were also measured using underwater captive air bubble as before mentioned and shown in Table 1. From Table 1, it could be seen that there was a significant hysteresis between the advancing and receding contact angles of underwater captive air bubble on all the PAS-loaded silicone coating surfaces as well as silicone controls, among which the underwater air bubble contact angle hysteresis on the surface of 0.50% PAS loaded silicone was 23 degrees and more than that on other surfaces with various PAS loadings as well as on silicone controls. Since the contact angle hysteresis means that if the underwater air bubble was easy to move off the surface or not. The higher the contact angle hysteresis, the more difficult for the air bubble to move off the surface, thus the more attractive for hydrophobic substances to adhere. However, there was few hydrophobic substances in mussel byssus, therefore with the increasing of air bubble contact angle hysteresis on the surface, which will become less and less possible for mussel byssus to adhere.
Table 1. Advancing and receding captive air bubble underwater contact angle (degree)

<table>
<thead>
<tr>
<th></th>
<th>Advancing angles</th>
<th>Receding angles</th>
<th>Contact angle hysteresis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicone control</td>
<td>86 ±2</td>
<td>80 ±2</td>
<td>6</td>
</tr>
<tr>
<td>PAS-incorporated</td>
<td>115 ±2</td>
<td>103 ±2</td>
<td>12</td>
</tr>
<tr>
<td>silicone(0.25%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAS-incorporated</td>
<td>121 ±2</td>
<td>98 ±2</td>
<td>23</td>
</tr>
<tr>
<td>silicone(0.50%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAS-incorporated</td>
<td>124 ±2</td>
<td>104 ±2</td>
<td>20</td>
</tr>
<tr>
<td>silicone(0.75%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAS-incorporated</td>
<td>125 ±1</td>
<td>107 ±1</td>
<td>18</td>
</tr>
<tr>
<td>silicone(1.0%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAS-incorporated</td>
<td>127 ±2</td>
<td>111 ±2</td>
<td>16</td>
</tr>
<tr>
<td>silicone(1.25%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAS-incorporated</td>
<td>128 ±1</td>
<td>113 ±1</td>
<td>15</td>
</tr>
<tr>
<td>silicone(1.5%)</td>
<td></td>
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</table>

This was also in agreement with that the number of mussel byssus deposition on the surface of 0.50%(w/w) of PAS-loaded silicone was fewer than those on all other PAS-loaded silicones. Considering all the results of mussel byssus deposition on the surface of silicone with various PAS loadings, it would further conclude that the variation of the number of mussel byssus deposition was in reverse with that of underwater air bubble contact angle hysteresis. When it went up, the mussel byssus deposition would go down, and then this made the underwater air bubble contact angle hysteresis the leading factor that influence the mussel byssus deposition behavior on the surface of PAS-loaded silicone.

3.5 Effect of PAS loadings on initial mussel basal byssus deposition and diatom permanent adhesion

It was well known that mussel would first explore the surface to find if it was suitable for settlement before the mussel basal byssus deposited onto the surface. The more difficult the surface for mussel to settle, the longer the explore time before the initial mussel basal byssus deposition appeared. The results of mussels explore time on the surface of PAS-incorporated silicone varied with PAS loadings as well as silicone controls was shown in Figure 7. From which it could be seen that the hours taken for initial mussel basal byssus deposition occurred on PAS-incorporated silicone coating surface was much longer than that on the control silicone coating surface, and it took the most time for mussels basal byssus deposition on to the surface of 0.50%(w/w) of PAS-loaded silicone coatings. This was the same with the above underwater air bubble contact angle hysteresis analysis. The results also indicated that the PAS-incorporated silicone coating had remarkable inhibition enhancement for mussel byssus deposition in comparison with control silicone coating.
Figure 7. Mussels explore time before initial byssus deposition occurred on the surface of PAS-loaded silicone coating with various PAS loadings as well as silicone controls. All the tests were run in six replicates, and there were 4 mussels on each surface.

To evaluate the influence of PAS loadings on the diatom adhesion behavior, the PAS-incorporated silicone coatings with various PAS loadings as well as silicone controls were exposed to water pressure at 27Pa, and the percentage of diatoms removal changed with the diatoms post-settlement time were determined. It was well known that, diatoms would firstly glide onto the surface and got initial adhesion, and this would be reversible, the adhesion strength was low, therefore the percentage of removal would be high for diatoms in this stage, however when diatoms got enough adhesion strength, they would adhere onto the surface permanently, and the percentage of removal would decrease significantly in comparison with that at initial adhesion.

Table 2. Lasting time for diatom initial adhesion on various coating surface

<table>
<thead>
<tr>
<th></th>
<th>Lasting time for initial adhesion, hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicone control</td>
<td>3.00 ±0.25</td>
</tr>
<tr>
<td>PAS-incorporated silicone(0.25%, w/w)</td>
<td>5.25 ±0.25</td>
</tr>
<tr>
<td>PAS-incorporated silicone(0.50%, w/w)</td>
<td>7.67 ±0.22</td>
</tr>
<tr>
<td>PAS-incorporated silicone(0.75%, w/w)</td>
<td>7.17 ±0.23</td>
</tr>
<tr>
<td>PAS-incorporated silicone(1.00%, w/w)</td>
<td>6.50 ±0.25</td>
</tr>
<tr>
<td>PAS-incorporated silicone(1.25%, w/w)</td>
<td>6.09 ±0.20</td>
</tr>
<tr>
<td>PAS-incorporated silicone(1.50%, w/w)</td>
<td>5.83 ±0.20</td>
</tr>
</tbody>
</table>

Therefore, the sudden significant decrease of removal percentage should be an indication of the transition from initial adhesion to permanent adhesion for diatoms [35-36], and the lasting time for initial adhesion before this transition occurred showed that the surface was easy or not for diatoms to get enough adhesion strength to adhere permanently, the longer the time, the more difficult the surface for diatoms to adhere permanently, and the better the surface to inhibit the diatoms adhesion. The
results showed that on the surface of silicone controls, the percentage removal of diatoms decreased greatly from 3h to 6h, while on PAS-incorporated silicone coating surface, which decreased greatly from 5.25h to 7h for 0.25%(w/w) of PAS loaded as well as from 7.67h to 9h for 0.50%(w/w) of PAS loaded, as to other coatings with PAS loadings of 1.00%(w/w) and 1.50%(w/w), the percentage removal of diatoms decreased greatly respectively in range of 6.5-8h, 5.83-7.5h. The lasting time for initial adhesion should be that before the above significant removal percentage drop occurred[35-36], and which were summarized in Table 2.From Table 2, it could be seen that all the lasting time for initial adhesion on PAS-loaded silicone were much longer than that on silicone controls, and this means that the addition of PAS into silicones significantly improved the inhibition for diatom permanent adhesion. The longest lasting time for initial adhesion of 7.67h on PAS loaded silicone surface with 0.50%(w/w) PAS loadings also indicated that which had the maximum inhibition effect on diatom permanent adhesion among all the test samples.

3.6 Relationship of underwater air bubble contact angle, diatom settlement and mussel basal byssus deposition

From the above analysis, it could be seen that the results of diatoms settlement after 7 days included those just in initial adhesion and those already in permanent adhesion. Since the diatoms in permanent adhesion actually transited from initial adhesion, thus the final counted diatoms indicated were those could form initial bonding-“the first kiss” on the surface, however whether this initial bonding could occur or not was determined by the diatom-substratum “chemistry”, which was a transitory chemical attraction resulted from the initial contact for diatoms and substratum[36]. According to the above test results, the underwater air bubble contact angles of coating surface increased with the increasing of PAS loadings in silicone, and the higher the PAS loading, the higher the PAS loading, the higher the balanced underwater air bubble contact angle, in other words, the more hydrophilic the surface. Since diatom Navicula sp. had a stronger attachment to hydrophobic surfaces than to hydrophilic surfaces[33], thus this trend of hydrophilization was in agreement with the variation of diatoms settlement number with PAS loadings in silicone coating, the diatoms settlement decreased with the increasing of PAS loadings in PAS-loaded silicone coatings, therefore it was supposed that the diatoms initial bonding-“the first kiss” was sensitive to the underwater air bubble contact angle of the surface, and which perhaps was an important factor that influenced the diatom-substratum “chemistry”.

After the initial bonding, whether diatoms could get enough attachment strength and finally transited into permanent adhesion, according to our above results, was sensitive to the underwater air bubble contact angle hysteresis on the surface, perhaps this was related with that diatoms could have “intentionally” actions in this stage, like adjusting their position. If they got a sense that the surface was easy for them to get enough attachment strength, they would finally transited into permanent adhesion, and this was quite different from “the first kiss”, there was no positive action for diatoms in that transitory procedure and reached a surface “randomly” either by gravity or in water currents[33,36]. As to mussels, the above results also showed that their basal byssus deposition was sensitive to the underwater air bubble contact angle hysteresis on the surface. Considering that mussel
basal byssus deposition was a true “intentionally” surface exploring behavior, therefore the underwater air bubble contact angle hysteresis perhaps could act as an important factor to influence the bonding behavior for those species which could “intentionally” take positive action to get enough attachment strength.

3.7 Determination of critical surface pressures for 50% removal of diatoms on coating surface

After the coated slides of PAS-loaded silicone coatings with various PAS loadings as well as silicone controls were prepared as mentioned above and placed in culture dishes contained 200 ml F/2 culture medium of diatoms Navicula sp.(1×10^6 cells/L) for 24h, they were taken out and exposed to water shear stress in range of 5.5-40.5Pa to determine the removal percentage of diatoms on each coating surface. Then the relationship of diatoms removal percentage with the variation of water shear stress on each coating surface could be drawn and from which the critical surface pressure for 50% removal of diatoms shall be determined[35]. The results were summarized in Table 3. From which, it could be seen that critical surface pressure for 50% removal of diatoms on 0.5%(w/w)PAS-loaded silicone surface was 12±2.0Pa, and this was 52% lower than that of 25±1.5Pa on the surface of silicone controls. All the results of variation of critical surface pressure for 50% removal of diatoms were in agreement with the above analysis of the lasting time for initial adhesion on various coating surface, the more difficult the surface for diatoms to get permanent adhesion, the lower the critical surface pressure for 50% removal of diatoms in the same condition.

Table 3. Critical surface pressure for 50% removal of diatoms on various coating surface

<table>
<thead>
<tr>
<th></th>
<th>Critical surface water pressure, Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicone control</td>
<td>25 ±1.5</td>
</tr>
<tr>
<td>PAS-incorporated silicone(0.25%, w/w)</td>
<td>21 ±1.0</td>
</tr>
<tr>
<td>PAS-incorporated silicone(0.50%, w/w)</td>
<td>12 ±2.0</td>
</tr>
<tr>
<td>PAS-incorporated silicone(0.75%, w/w)</td>
<td>16 ±0.5</td>
</tr>
<tr>
<td>PAS-incorporated silicone(1.00%, w/w)</td>
<td>17 ±0.5</td>
</tr>
<tr>
<td>PAS-incorporated silicone(1.25%, w/w)</td>
<td>19 ±1.0</td>
</tr>
<tr>
<td>PAS-incorporated silicone(1.50%, w/w)</td>
<td>20 ±1.0</td>
</tr>
</tbody>
</table>

4. CONCLUSION

This paper proposed a new channel to improve the fouling resistant ability of silicone-based coating with a new copolymer, poly (acrylamide-silicone) (PAS). Results showed that its addition could enable the silicone-based coating surface effectively lower the diatom settlement, and also the addition of 0.5%(w/w) of PAS into silicone could gave the coating surface maximum inhibition effect on the mussel basal byssus deposition as well as diatoms permanent adhesion. Compared with the silicone control coating, the 0.5%(w/w) of PAS-loaded silicone could lower 52% of the critical water
shear stress for 50% removal of diatoms on the coating surface. Therefore, the copolymer of PAS offers a very promising additive to further improve the antifouling ability of silicone-based coating, which can be combined with other approaches together to further develop silicone-based high efficiency antifouling materials.

The results also showed that the addition of PAS into silicone could gave some significant change for the coating surface features, such as the underwater air bubble contact angles and their hysteresis, and it seems that the diatom settlement was sensitive to the underwater air bubble contact angles while diatom permanent adhesion and mussel basal byssus deposition were sensitive to the underwater air bubble contact angle hysteresis. This could be helpful in developing new eco-friendly silicone-based coatings as well as other antifouling materials.

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References

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