# The antifouling performance of biomimetic fish slime-like PVA/PAAm hydrogels modified coating in marine

Xiaoting Ren, Qingyang Zeng, Jina Xu, Wenkai Zhang, Lili Xue and Kejia Li



August 17, 2018

# The antifouling performance of biomimetic fish slime-like PVA/PAAm hydrogels modified coating in marine

Xiaoting Ren[1,a], Qingyang Zeng[1,b], Jina Xu[1,c], Wenkai Zhang[1,d], Lili Xue[1,e] and Li Li[1,f]

[1]Institude of Materials Processing and Intelligent Manufacturing, College of materials science and chemical engineering, Harbin Engineering University, 145 Nantong Street, Harbin City, Heilongjiang Province, 150001, PR China

[a]renxiaoting@hrbeu.edu.cn, [b]zengqingyanghao@163.com, [c]504370090@qq.com, [d]850345913@qq.com, [e]xuelili@hrbeu.edu.cn and [f]lili_heu@hrbeu.edu.cn

**Keywords:** Hydrogel;coating; Antifouling; Adhesion

**Abstract.** In this paper, a fish slime-like coating modified by poly vinyl alcohol/polyacrylamide (PVA/PAAm) hydrogel which is the semi-interpenetrating network polymer was designed. A physical blending method loading PVA/PAAm hydrogels powder into the organic silicon resin was employed to prepare the coating. The oil-resistance of the coating was performed by time-sequence images of washing dyed beef tallow stain away. The results showed that the PVA/PAAm hydrogels modified coating had the greater ability of stain removal. The biomass of a marine microalgae species, Nitzschia closterium and f. minutissima attached on the coating were investigated using UV-Visible Spectrophotometer (UV) and Scanning electron microscopy (SEM). The results showed that the microalgaes showed a significantly lower numbers attached on PVA/PAAm hydrogels modified coating in comparison with on the organic silicon coating.

## 1. Introduction

Marine biofouling can be defined as an undesirable accumulation of bacteria, microalgae, diatoms and invertebrates grown on all kinds of submerged facilities. It has always plagued both commercial and naval fleets [1]. For instance, it increases the surface roughness and weight resulting to the reduction of the speed and maneuverability. It leads to the more frequently dry-docking cleaning [2] and higher fuel consumption [3, 4]. And it also introduces invasive species into non-native environments resulting to ecological damage [5], etc. Marine biofouling takes place on immersed surfaces as a result of several successive steps consisting of the formation of a conditioning film firstly, the following adhesion of macroalgae, fungi, protozoa and the last invertebrate larvae attachment [6]. In this complex process, it is also generally accepted that a lot of physical-chemical factors of the submerged surface influence on biofouling, such as surface tension and energy, wettability, elastic modulus, surface chemistry, surface roughness and topography etc [7] [8]. Bio-inspired self-cleaning performances from biology have recently provided new insights into designing a high-efficient and non-toxic antifouling (AF) coating. Hydrogel has been actively investigated as antifouling coating material due to its soft, high-water-content, reducing effective attached area, and low surface energy just like fish slime [9] [10]. Jian Ping Gong et al. reported that one of the key factors of hydrogel antifouling performance was the low elastic modulus. More recently, researchers successfully developed many new kinds of cross-linked polymer hydrogels for effective marine antifouling. In addition, Lei Jiang et al. prepared hydrogel with hierarchical surfaces displaying superoleophobicity, which showed the possibility for antifouling application. Obviously, hydrogel is a potential marine antifouling material.

However, developing absolute hydrogel coatings seems extremely difficult, if not totally impossible, due to its poor adhesion strength to substrates. In this paper, the coating modified by PVA/PAAm hydrogel powder was prepared. The coating microstructure was investigated by SEM. Moreover, the self-cleaning property of dyed oil stain was provided by the PVA/PAAm hydrogels. Thus, the coating modified by PVA/PAAm hydrogels is a desirable strategy to prevent marine microalgae attaching. More importantly, such a coating has an impressive antifouling performance in marine.

## 2. Experimental

### 2.1. PVA/PAAm Hydrogel synthesis

A two-step method was used to synthesize the PVA/PAAm hydrogel. First, the single network (SN) PVA hydrogel, as the first network of the PVA/PAAm hydrogel, was synthesized. PVA powers of 1.25 g were dissolved in deionized water of 15 mL through heating and stirring for 6 h at 95°C in an oil bath. The precursor mixture solution was poured into a plastic dish that served as a mold at room temperature, and sealed up in a freezer at -20°C for 18 h, and then thawed at room temperature for 6 h. Second, PVA hydrogel was immersed in an aqueous Acrylamide (AAm) solution of 1 mol% KPS for 24 h, which subsequently polymerized in a constant temperature of 50°C for 15 h to get PVA/PAAm hydrogel.

### 2.2. Coating preparation

Antifouling coatings modified by PVA/PAAm hydrogel particles of diameter of 40μm and 70μm were prepared. And the contents of the PVA/PAAm hydrogel particles were 5%, 10% and 15% respectively. Firstly, the PVA/PAAm hydrogel powder with certain weight was blended with silicon coating through stirring rapidly for 20 min. Then, the B component of the silicon coating curing agent was added into the A component by quickly stirring for 5 min. The mixed coating was sprayed on the 250×300mm low carbon steel plate to solidify for 24 h.

### 2.3 Biomass adhesion

A typical benthic marine microalgae, Nitzschia closterium f. minutissima, was originally obtained from the Marine National Key Laboratory Center for Collections of Marine Bacteria and Phytoplank to Xiamen University (CCMBP), Pearl River Estuary, China. For each algal species examined, stock culture of 10 mL was transferred under sterile conditions into each 2 L Erlenmeyer flask, each containing 1 L sterile artificial seawater with Guillard's f/2 nutrient media. Each penicillin and streptomycin antibacterial mixture of 5000 units were added to each flask prior to seeding with inoculum of a volume containing 100 cells of microalgae. The two species were maintained in growth cabinets at 20 ± 1°C, a 14:10 h light/dark (L/D) cycle of fluorescent lights at 2000 lux and gently stirred twice daily. The microalgae cells adhesion on the surface of the coatings was determined by cell concentration counting on a sample with a known dilution factor using a cell count chamber hemocytometer (Fisher USA) and an optical microscope (Fisher USA). The cell concentration was correlated to the optical densities at 680 nm (OD680) of the microalgae samples. The microalgae solution was measured using a UV-2550-Visible Spectrophotometer (SHIMADZU Corporation, Japan). The microalgae solution sample was diluted with deionized water to an OD680 range of $10^6$, $5\times10^5$, $1\times10^5$, $5\times10^4$, $1\times10^4$, $5\times10^3$ and $1\times10^3$ cells/mL. Conversions of OD680 to cell concentration were performed based on linear fitting equations.

### 2.4 Field trials

The field trials were carried out at Longkou port, the Bohai sea, China. All the samples were held on a PMMA frame. There were six samples exposed, three organic silicon coatings. They were arranged in a coated steel-square formation. The exposed area of sample was 160 ×400 mm. The rack was suspended in a vertical orientation to a depth of 1.5 m under the sea. The trial began in July 2012 and was run for a period of 12 weeks.

## 3. Result and Discussion

### 3.1 The surface morphology observation

Fig. 1 is the surface morphology of the PVA/PAAm hydrogel powder modified coating characterized by SEM photograph after 2h immersion in artificial sea water (ASW). It can be seen that the surface of the coatings had randomly located bumps-like hydrogel point which would be the water absorbed component after immersion into sea water to form an attached water film as a fish slime-like layer. Moreover, the more contents of PVA/PAAm hydrogel powders were loaded, the more damages the coatings had. The damage of the coating can depress the AF performance significantly. Thus, the contents of PVA/PAAm hydrogel powder can not be more than 15wt%. In addition, the coating with the hydrogel powder diameter of 70μm had larger size damage than that of 40μm.

Fig. 2 is the surface macroscopic morphology of the PVA/PAAm hydrogel powder modified coating, with the powder diameter of 40μm, after 2h immersion in ASW. The flexible, slippery and tightly adhering water film originated from the water molecules locked within the network of hydrogel polymer chain can be found on the surfaces of the coatings [11]. Moreover, the more contents of PVA/PAAm hydrogel powders were loaded, the denser water absorption points were found, resulting in a more homogeneous and continuous water film. The water film is biophysically similar to the hydrophilic flexible fish slime. The results showed that the coating modified by the hydrogel powder of diameter of 40μm and the content of 15wt% was the best kind of coating to provide a fish slime-like property.

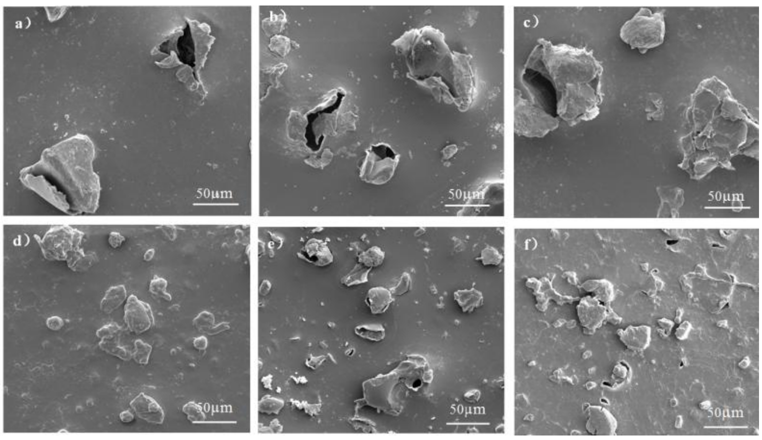


Fig 1. the surface morphology of PVA/PAAm powder modified coating SEM photograph after 2h immersion in ASW, the diameter of 70μm: (a)5wt%, (b)10%, (c)15%, and the diameter of 40μm: (d)5wt%, (e)10wt%, (f)15wt%


Fig. 2 The digital photograph of the coating modified by PVA/PAAm powder of diameter 40μm after 2h immersion in ASW, the hydrogel powder contents: (a)5 wt%, (b)10%, (c)15%.

### 3.2 The self-cleaning property

The adhesion of marine organisms begins with the adhesion of extracellular polymers. The adhesion layer changes the physical and chemical properties of the surface of the material so that the marine microorganism is easy to adhere to and is suitable for settlement. It is considered that the oily substances in the extracellular polymers play an important role in the marine bioadhesive process on the material surfaces. Therefore, the oil repellent properties of the materials contribute greatly to the anti biological fouling properties of the materials.

Self-cleaning test for the PVA/PAAm hydrogels modified coating was carried out by the oil-resistance on the coating tilted at sliding angle 30° and observed by high-speed camera imaging to determine good self-cleaning ability (Fig. 3). The water current whirled away the whole dyed oil stain in its path while washing for hydrogel coating. There is no consistent conclusion on the effect of substratum surface energy on the microorganism attachment. However, it is accepted widely that the modification of surface properties to obtain a more hydrophilic and oil-resistant surface can decrease the adhesion of microorganisms.

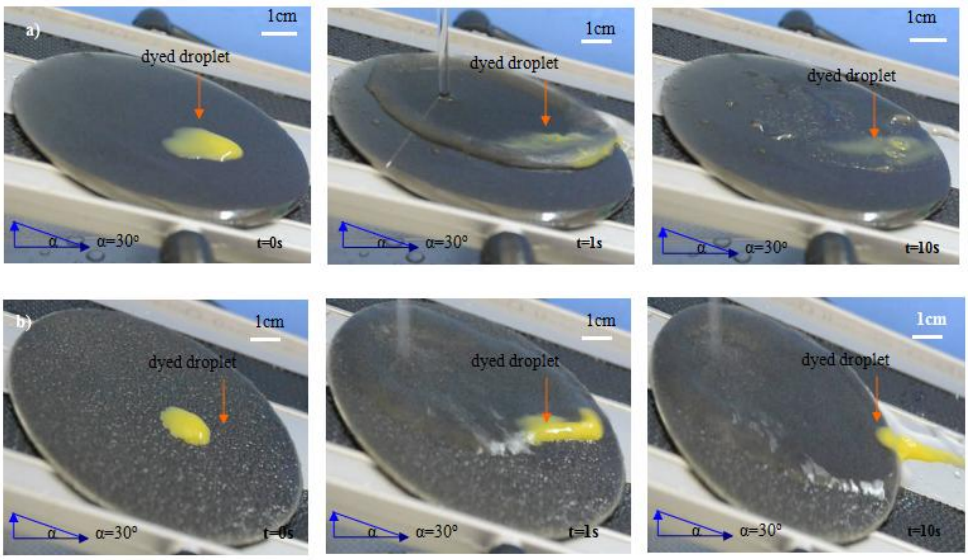


Fig. 3. Time-sequence images comparing oil-resistance of dyed beef tallow drop on a PVA/PAAm hydrogel modified coating and the silicon coating. Tallow is whirled away on the PVA/PAAm hydrogel modified coating(b), but it wets and stains the traditional silicon coating surface(a).

### 3.3 The antifouling performance

The presence of marine microalgae on the paints can be observed in the first week and a differentiation between the coating modified by PVA/PAAm hydrogel and the silicon coating can be performed. Fig. 4 presented the microalgae morphology SEM micrographs attached on the surface of the two coatings after 5 weeks immersion in marine. For the silicon coating, there were lots of the microalgas connected with their neighboring at their lateral ends, which formed integral and thick biofilm. However, the PVA/PAAm hydrogel modified coating was covered only by few and single microalgas approximates to zero. The biomass composed of microalgae on the coatings was shown in Fig. 5. More microalgas settles on surface of the silicon coating with the cell density of $2.76\times10^4$ cells/cm$^2$ of Nitzschia closterium f.minutissima. However, there were no microalgas found on the coating modified by PVA/PAAm hydrogel of diameter of 40μm and of the content of 15wt%.

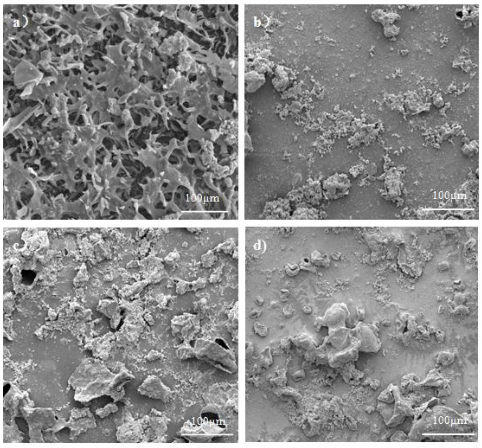

Fig. 4 Algae density of Nitzschia closterium f.minutissima on the surface of the silicon coating, and PVA/PAAm hydrogel modified coating with the hydrogel powder contents of (b)5 wt%, (c)10 wt%, (d)15 wt%.

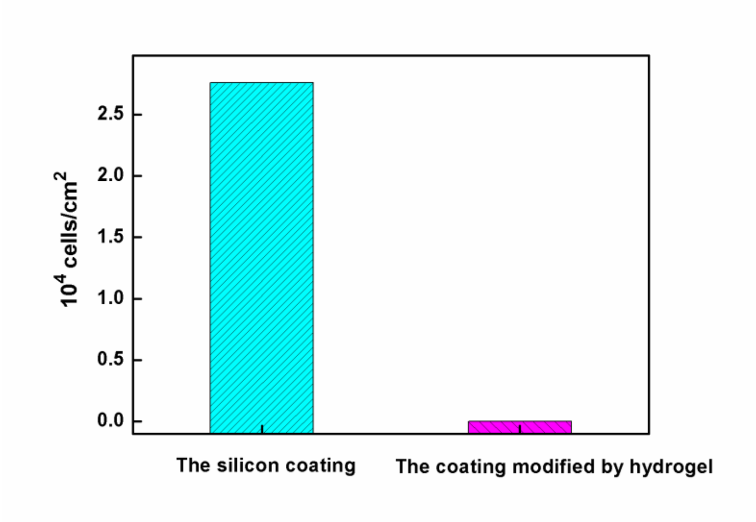


Fig. 5 The biomass of Nitzschia closterium f.minutissima on the surface of the silicon coating, and the coating modified by PVA/PAAm hydrogel with the diameter of 40μm and the content of 15wt%.

### 3.4 The Field trails

To confirm the antifouling performance of the coating modified by PVA/PAAm hydrogel of diameter of 40μm and the content of 15wt%, field trails were carried out in the marine environment for 12 weeks from August, demonstrated in Fig. 6. As can been seen, blue mussel and barnacle of the length at least 2 cm dominated the organic silicon coating accounting for more than 90% of the fouling mass, whereas no barnacle settled down on the PVA/PAAm hydrogel modified coating. It is demonstrated that the PVA/PAAm hydrogel modified coating may provide an effective attachment resistance to reduce biofouling or to increase the ease of foulants removal, which shows excellent antifouling performance.

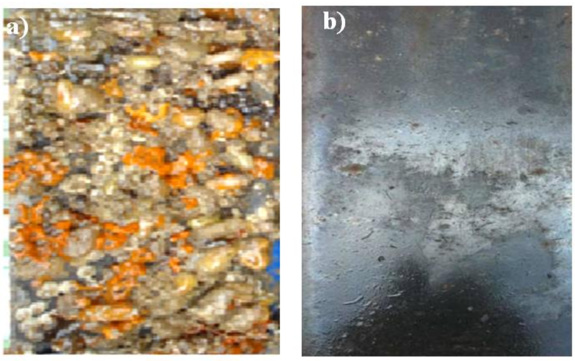


Fig. 6. Biofouling morphology on (a) the silicon resin coating, (b) the PVA/PAAm hydrogel modified coating with the hydrogel powder contents of 15wt%

## 4. Conclusion

In this study, adding PVA/PAAm hydrogel powder into the organic silicon coating is put forth as an effective method to prepare the antifouling coating, which preserves the bonding strength to substrate of the silicon matrix for application. The wet fish-mucus-like hydrogel film provided a higher self-cleaning ability of the oily stain removal. Under this premise, the comprehensive studies of the most important antifouling performance were performed. The results showed that the coating modified by PVA/PAAm hydrogel attached in significantly lower number marine organisms in comparison with the silicon coating. It can be concluded that the fish slime-like coating modified by PVA/PAAm hydrogel had an excellent antifouling performance.

## Reference


[1]R. Chapman, Protect. Coat. Eur. PCE. vol.3 (3) (1998) p.32.

[2]A. Abbott, P.D. Abel, D.W. Arnold, A. Milne, Sci. Total Environ. vol.258 (1-2) (2000) p.5-19.

[3]M.A. Champ, Sci. Total Environ. 258 (1-2) (2000) p. 21-71.

[4]D.M. Yebra, S. Kiil, K.D. Johansen, Prog. Org. Coat. 50 (2004) P.75-104.

[5]M.S. Brancato, OCEANS'99 MTS/IEEE, in: Riding the Crest into the 21st Century, vol. 2 (2), 1999, p. 676.

[6]M. Wahl, Mar. Ecol. Prog. Ser. vol.58 (1989) p.175-189.

[7]K. Becker, M. Wahl, Biofouling, vol.4 (1991) p.275-291.

[8]Chao Liu, Chunfeng Ma, Qingyi Xie and Guangzhao Zhang, Self-repairing silicone coatings for marine antibiofouling. J. Mater. Chem. A, 2017, 5, 15855.

[9]Dongmian Zang, Hui Yi, Zhandong Gu, Lie Chen, Dong Han, Xinglin Guo, Shutao Wang, Mingjie Liu, and Lei Jiang, Interfacial Engineering of Hierarchically Porous NiTi/Hydrogels Nanocomposites with Exceptional Antibiofouling Surfaces. Adv. Mater. 2017, 29, 1602869.

[10]Xin Zhao, Hao Wu, Baolin Guo, Ruonan Dong, Yusheng Qiu, Peter X. Ma,

Antibacterial anti-oxidant electroactive injectable hydrogel as self-healing wound dressing with hemostasis and adhesiveness for cutaneous wound healing. Biomaterials 122 (2017) P.34-47.

[11]Ling Lin, Mingjie Liu, Li Chen, Peipei Chen, Jie Ma, Dong Han, and Lei Jiang. Bio-Inspired Hierarchical Macromolecule-Nanoclay Hydrogels for Robust Underwater Superoleophobicity. Adv. Mater. 2010, 22, P.4826-4830.