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# The Study of Bio-Inspired Surfaces for Fouling Resistance

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***Abstract:*** *Fouling is an issue that causes a lot of challenges in different areas. It is essential to study the different types of solid foulants and build-up methodology to engineer anti-fouling surfaces. In this work, three types of fouling, including ice fouling, protein fouling and marine fouling, with their designed antifouling materials and two general approaches are discussed. This work could be helpful in better understanding the bio-inspired surfaces for fouling resistance.*

***Keywords:*** *Fouling, Fouling resistance, Anti-fouling materials, Bio-inspired surfaces*

## 1. Introduction

Fouling is a general designation of various sorts of solids that may accumulate on the surface and cause negative effects on the surface's properties. The presence of fouling not only leads to potential dangers but also causes economic losses. Therefore, research to classify different types of solid foulants and build-up methodology to engineer anti-fouling surfaces should be of great significance. Fouling can be classified by its hardness. This classification is very useful in modeling the contact of surface, which would further help the design of anti-fouling surfaces. However, it does not fully meet the need in reality. Based on real world applications, fouling is also classified by their sources and environments.

This paper mainly covers ice fouling, marine fouling and protein fouling, with them sorted into hard fouling and soft fouling. Based on this classification, we can get a thorough research on different types of fouling and come up with a useful conclusion on developing fouling resistance surfaces.

One of the essential factors to determine whether a surface is anti-fouling or not is the contact angle of the surface. In this case, three different models were used to analyzed: the Young's Model, the Wenzel State and the Cassie-Baxter State (Fig 1) [1].

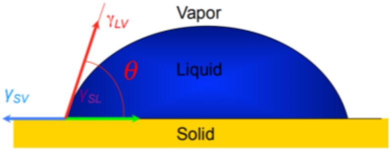

*Figure 1. Young's Model [1]*

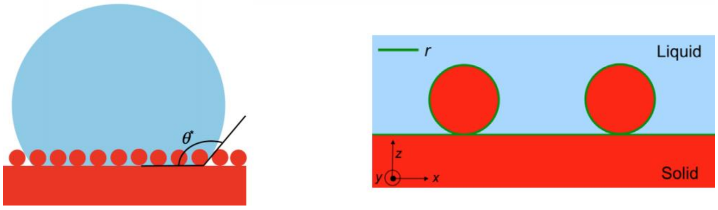

*Figure 2. Model for Wenzel State [1]*

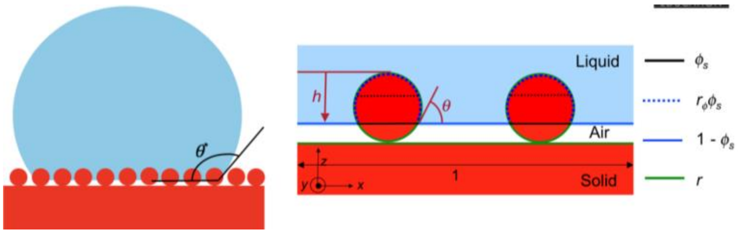

*Figure 3. Model for Cassie-Baxter State [1]*

In conclusion, the model of Cassie Baxter state can better reflect the real situation when air pockets are present underneath the contacting liquid, while the Wenzel model can better apply when air pockets are not present on a rough surface.

## 2. Ice Fouling

Ice, snow, or their mixtures, when they adhere to different electronic or transport devices, will cause significant damage to the equipment. The weight of the ice layers covered on the power lines can put a massive amount of stress on wires to overwhelm it, even cause a pole fire. Before looking into reasonable solutions, first, we need to understand the concept called the ice-adhesion strength. It can be expressed as:

$$Ice\ adhesion\ strength\ (\tau) = \frac{Maxium\ forcee\ (fx)}{Contact\ Area\ (A)} \tag{1}$$

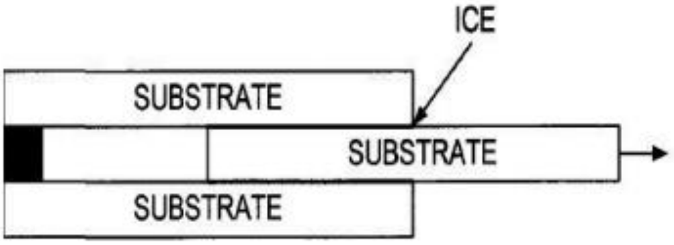

*Figure 4. Testing Modes of Ice Adhesion Strength [2]*

The ice adhesion strength for different materials is analyzed, and results show that it could vary significantly between materials. Factors that contribute to low ice-adhesion materials are examined using the equation,

$$\tau = A\sqrt{\frac{W_a G}{t}} \tag{2}$$

Where G is shear modulus, $A$ is a constant, $W_a$ is the work of adhesion, and $t$ is the thickness of the soft substrate [3].

### *2.1 Antifouling by Preventing the Ice Formation*

One reasonable approach to preventing fouling by ice is condensation prevention. The superhydrophobic material fulfills the needs in some way. One of the superhydrophobic surfaces designed by Jung can delay nucleation for 25 hours at -21 ℃. Nevertheless, the ice was eventually formed around all the surface, which indicates that this antifouling approach has limitations [4]. Superhydrophobic material usually has complex geometry surfaces. In this case, when condensation happened between those complex geometry structure, it will increase the ice adhesion strength and make the deicing process hard.

### *2.2 Antifouling by Reduction in Ice Adhesion Strength*

Thus, scientists try to implant an antifreeze protein in the surface. This organism can survive in subzero conditions [5]. The structure of this material is shown below (Fig. 5).

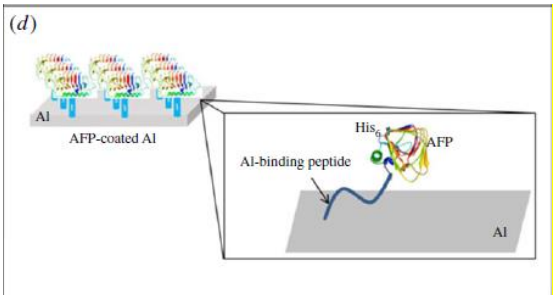

*Figure 5. Schematic diagram of AFP functionalized aluminum [6]*

Also, Wong and his research group designed a new method of frost prevention [7]. The whole process is shown in Figure 6.

The modulus of ice adhesion strength helps examining factors that lower the ice adhesion strength. Researchers use the material contained hygroscopic polymers instead of a lubricating surface. As a result, they developed a self-lubricating material with an ice adhesion strength of 0.4kPa [8], which is lower enough to prevent ice fouling. Besides, there is a way reducing the ice adhesion by electrolysis [9]. However, there are some surfaces of objects that are not electrically conductive.

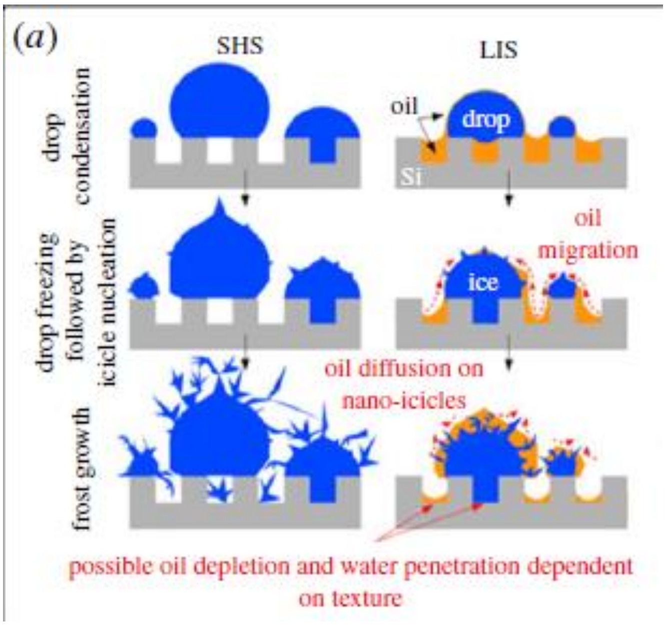

*Figure 6. The mechanism of ice nucleation [6]*

## 3. Protein Fouling

Protein fouling is one of the major components of biofouling. Nature gives different types of solutions to control protein fouling, for instance, grooming, sloughing and chemical secretions [10]. There is a wide range of industries suffering from bio-contamination, like the medical industry, food industry. Common effects of protein fouling to human activity are concluded in Tab.1 and Tab.2.

*Table 1. Protein fouling in medical industry [10]*

| Type of Fouling | Associated Challenges |
|---|---|
| Orthopedic implant | Removal owing to infection |
| Respirator | Ventilator-associated pneumonia |
| Contact lens | Eye infection |
| Catheter | Urinary tract infections |
| Hemodialysis | Infectious break-outs |
| Teeth/dental implant | Periodontal disease, gingivitis |
| Biosensor | Failure from fibrous encapsulation |

*Table 2. Protein fouling in other industries [10]*

| Type of Fouling | Associated Challenges |
|---|---|
| Membrane | Reduced flux |
| Heat exchanger | Reduced convention efficiency |
| Drink water | Pathogens in potable water |
| Food, paper and paint | Food spoilage and worker health risks |
| Metal-cutting fluid | Filter blockage and worker health risks |

### *3.1 Preventing Protein Absorption*

There are three ways to prevent protein absorption: PEG chains, SAM chains and Zwitterion [11]. They all involve forming a film to repel proteins or to strengthen protein resistance by taking advantage of the interactions between the polymers and the proteins.

The principle of PEG chains is that using physical or chemical adsorption to attach PEG to the substrate to form a PEG protein resistant film (Fig. 7) [12].

Self-assembled monolayer (SAM) is another way to increase protein resistance. The advantage of SAM is increasing the density of chains, which leads to more effective surface coverage. Zwitterions blind to water strongly to create a hydration layer, which prevents protein adsorption [14]. Phosphorylcholine (PC) is one of the commonly utilized zwitterionic surfaces. Zwitterionic PC groups and SAM oligo ethylene glycol are found to be synergistic. With a combination of them, better protein resistance is achieved [15].

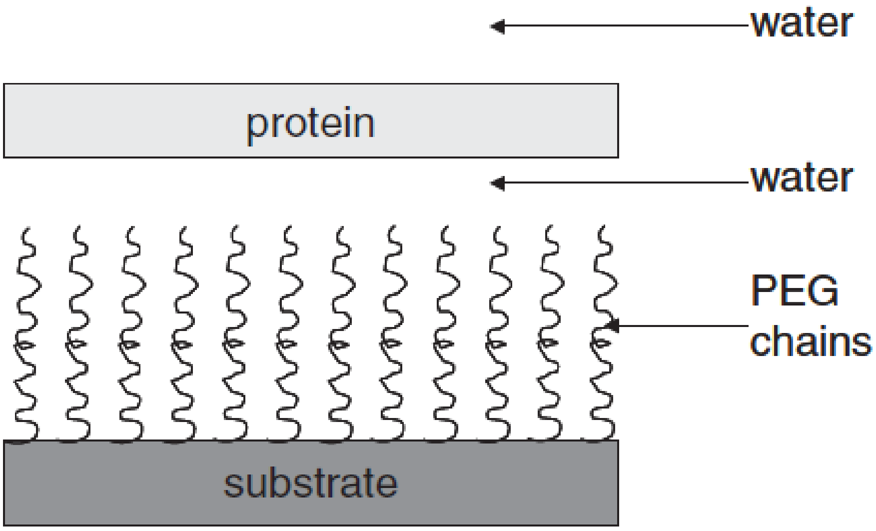

*Figure 7. PEG resist bio-fouling schematic diagram [13]*

These materials that prevent protein adsorption provide efficient antifouling strategies, but they still have limitations, which are discussed in Tab.2.

*Table 3. Limitations for materials that prevent protein adsorption [12, 13, 16, 17]*

| Type | Limitation | Reason |
|---|---|---|
| PEG | Unable to reduce protein absorption to desired limit | Less attached polymer chain density due to steric issues |
| | Cannot achieve as high protein resistance as SAM | |
| SAM | Lower protein resistance | Short chain length |
| | Selection on substrate | Different conformation will be formed on different surface. Some conformation cannot resist protein. |
| | Lack robustness compared to PEG | |

### *3.2 Protein-Degrading Films*

A protein-degrading film is designed to degrade the protein. Protease coating is used on the surface of protecting container by two methods: degrade protein and the potential of degradation will reject to adsorb protein. A common protease is called $\alpha$-chymotrypsin ($\alpha$-CT). Sol-gel entrapment is better than covalent attachment for $\alpha$-CT [18]. The leaching problem could be solved well with cylindrical nanotubes as the enzyme container [19]. Because some bacteria use protein and polysaccharides to build a connection to synthetic substrates, adding PMMA substrates can inhibit biofilm formation [20]. There are two main types of self-cleaning coatings: superhydrophobic films and photoactive films. The limitations for protein antifouling coatings are discussed in Tab.4.

*Table 4. Limitations for protein-degrading films [20, 21]*

| Type | Limitation | Reason |
|---|---|---|
| Sol-gel entrapped -CT | Less stable than covalent attachment | Leaching and autolysis of enzyme is not controlled well |
| Superhydrophobic film | Contaminant may attach to uncovered surface | Not degrade the contaminant so contaminant always exist |
| Photoactive film | Remain some contaminant | Highly reactive species may not degrade all contaminants completely. The product of contaminant may still trouble. |

## 4. Marine Fouling

Marine fouling is the colonization of organisms from diverse species in different sizes on submerged surfaces. Materials immersed in water create comfortable environment for the growth of marine organisms, which can be often seen in shipping and leisure vessels, etc.

There are generally two types of marine fouling. One is the soft fouling formed by non-calcareous fouling organisms, like algae, and the other type is hard fouling caused by calcareous species, like mussels. The surface colonization can be simplified to the “successional model” (Fig. 8) [22].

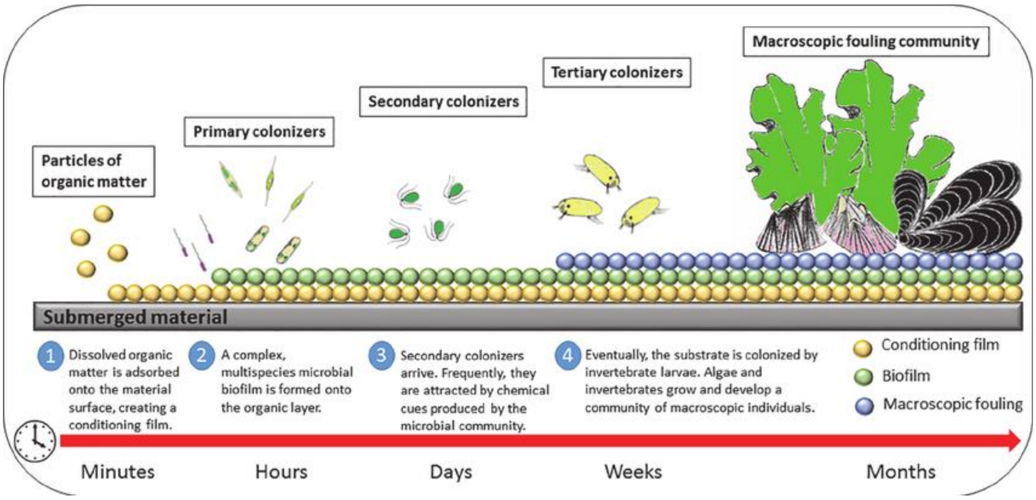

*Figure 8. The simple successional model for the marine fouling [22]*

### *4.1 Chemical antifouling methods*

Free radicals or reactive oxygen generators can cause degradation of diatomaceous soils and thereby reduce fouling. Although they are usually equipped with photosensitizer dyes to induce more efficient light absorption, their performance is limited by the intensity of the incident light [11]. Another degradation mechanism is the use of biocides. However, these fungicides often cause damage to other organisms and cause unnecessary marine pollution.

### *4.2 Physical antifouling methods*

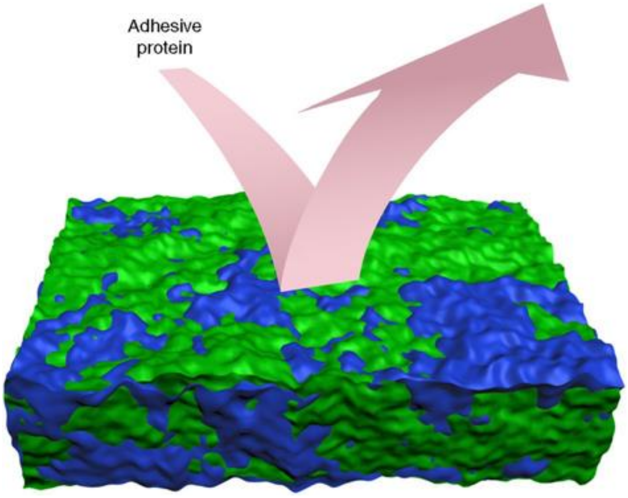

*Figure 9. The protein repelling chemical heterogeneous or 'mosaic-like' surface [24]*

Amphiphilic polymer coatings (Fig. 9) can interfere with the sedimentation of hydrophilic and hydrophobic foulant by adjusting surface chemistry [23].

Another physical method is to construct an antifouling surface with microtopography. From mollusk shells to shark skins, the biological surfaces of many marine animals have complex surface topography. Among them, shark skin and invertebrate shells have excellent performance on the surface of many marine organisms [25]. Molded topographies in PDMSe was inspired by the skin of fast-moving sharks at ~1/25th of the scale. It could reduce 85% zoospores settlement of the macroalga Ulva compared with smooth PDMSe [26].

## 5. Conclusions

Fouling is an issue that causes challenges in different areas. Although different types of fouling have their various anti-fouling materials, two general approaches were applied to solve the fouling issue. One is to prevent fouling species from attaching by making the surface fouling-unfavorable, and the other one is to make the attached foulants easily remove. Different antifouling materials were discussed in previous sections, but the current limitation is to find a method that works to prevent both soft and hard fouling. Future research on environmentally friendly antifouling materials is required under the surfaces' complicated environment.

## Acknowledgement

These authors contributed equally to this work and were listed in alphabetical order.

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